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METAMATERIALS : NOVEL RELAXOR AND MAGNETOELECTRIC

NANOCOMPOSITE

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by

Tanmoy Maiti

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The thesis of Tanmoy Maiti was reviewed and approved* by the following:

Amar S. Bhalla  
Professor of Materials and Electrical Engineering  
Thesis Co-Advisor  
Co-Chair of Committee

Ruyan Guo  
Professor of Electrical Engineering and Materials Research  
Thesis Co–Advisor  
Co-Chair of Committee

L. Eric Cross  
Evan Pugh Professor Emeritus of Electrical Engineering

Dinesh K. Agrawal  
Professor of Materials

Jiping Cheng  
Senior Research Associate  
Special Member

James P. Runt  
Professor of Polymer Science  
Associate Head of Graduate Studies, Materials Science and Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The aim of this thesis work is to design both scientifically and technologically important two different classes of novel materials: (i) an environmental friendly lead free relaxor system constituting two different kinds of materials neither of which exhibits the relaxor behavior in pure form (ii) a unique diphasic nanocomposite in combination of ferroelectric and magnetostrictive materials resulting magnetoelectric response which is not observed in either of the phases.

Although Extensive research has been carried out on the ferroelectric relaxor behavior ever since the discovery of exceptional dielectric properties of the lead based disordered perovskites like PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3} (PMN), PbZn\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3} (PZN), the origin of the physical phenomena of relaxor ferroelectrics is still not understood completely. Recently, research emphasis is leaning towards barium-based relaxors, as these are environmental friendly lead free oxide. Among the doped BaTiO\textsubscript{3} systems, BaZr\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} (BZT) solid solution has attracted considerable attention in both bulk and thin film due to its potentiality for various device applications. Although BaTiO\textsubscript{3}-BaZrO\textsubscript{3} system was identified as a solid solution as in early 1950s most studies were focused on the temperature dependence of the dielectric constant, the nature of the phase transitions and the ferroelectric relaxor behavior of this materials in lower concentration (x< 0.40) of Zr in Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} system over the years. In this thesis, we have studied structure-property correlation of the various Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} compositions and a new complete phase diagram of Barium Zirconate Titanate, Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} has been developed in the
composition range $0 \leq x \leq 1.00$. Barium Zirconate Titanate, $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ system depending on the composition, successively depicts the properties extending from simple dielectric (pure $\text{BaZrO}_3$) to polar cluster dielectric, relaxor ferroelectric, 2\textsuperscript{nd} order like diffuse phase transition, ferroelectric with pinched phase transitions and then to a proper ferroelectric (pure $\text{BaTiO}_3$). So far there has been no other single solid solution system that demonstrates all complex aspects of ferroelectricity.

$\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (BZT) ceramics of the several compositions have been prepared by convention solid state synthesis route. All the BZT compositions were verified to be single phase perovskite by studying the room temperature XRD behavior of these compositions. Dielectric behavior of the BZT ceramics has been studied with and without bias in the temperature range from 300 K to 15 K. The dielectric properties of the material show typical relaxor-like behavior for the $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ compositions with $0.25 < x < 0.75$. However, in the $\text{Zr}^{4+}$ rich $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ solid solution compositions ($0.80 \leq x \leq 1.00$) polar cluster like behavior has been observed.

In contrary to the classic relaxor ferroelectrics like PMN, PZN etc where intrinsic disorder prevails, in our present investigation we have introduced the disorder gradually through breaking the long range translational symmetry of $\text{BaZrO}_3$ by the incorporation of $\text{Ti}^{4+}$ ion in $\text{BaZrO}_3$ lattice to observe the relaxor behavior in a non-ferroelectric material like $\text{BaZrO}_3$ with low dielectric constant ($<40$). From the thermal hysteresis in dielectric behavior and d.c. field dependent dielectric studies it has been concluded that with the incorporation of $\text{Ti}^{4+}$ ion in the $\text{BaZrO}_3$ matrix $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ compositions ($x \geq 0.80$) start showing polar-cluster like behavior. Beyond an optimum content of polar $\text{BaTiO}_3$ in the non polar matrix of $\text{BaZrO}_3$ probably a critical size and distribution density...
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To enhance our understanding the relaxor behavior in BaZr$_x$Ti$_{1-x}$O$_3$ ceramics pyroelectric, thermal strain measurements have been carried out from the cryogenic temperature to very high temperature (~650 K). Powder neutron diffraction measurements have been carried out to determine the structure of the BZT relaxor compositions. Structural analysis of the powder neutron diffraction by Rietveld refinement reveals the global structure of the BZT relaxors as cubic. High q-resolution neutron scattering data has been collected on the BZT relaxor compositions by triple axis spectrometer. However, no such splitting in the Bragg peaks of BZT ceramics has been observed even at 4 K and mirror the results obtained from the powder neutron diffraction data predicting the global structure of BZT relaxors as cubic. The local structure of the BZT ceramics has been investigated by Raman spectra. It is seen from the Raman investigation that local polar regions exist in the BZT ceramics even at 550 K at which temperature both end members of the phase diagram BaZrO$_3$ and BaTiO$_3$ are cubic in pure form. From the detailed investigation on the structure and properties of BaZr$_x$Ti$_{1-x}$O$_3$ compositions it can be said that BZT is an engineered material designed by self-assembled polar nano-regions resulting some unusual properties, which can not be predicted from its constituents BaTiO$_3$ and BaZrO$_3$. Hence BaZr$_x$Ti$_{1-x}$O$_3$ is qualified as meta-materials.

Further we have shown that one can engineer a meta-material, which can show dielectric relaxation behavior even none of the constituents of the materials does not
show such properties. We have shown a potential approach to fabricate the relaxor materials by making the ceramic composite of environmental friendly Ba-based diffuse ferroelectric BaZrxTi1−xO3 (x= 0.20 and 0.25) with non-ferroelectric MgO.

Magnetoelectric composites were prepared using both conventional sintering and single mode microwave sintering techniques in the environment of the E-field. In thesis work PbMg1/3Nb2/3O3-31% PbTiO3 (PMN-PT) has been used as the ferroic material and ferrites like CoFe2O4 and Mn0.1Zn0.9Fe2O4 are used as the magnetostrictive materials to make the magnetoelectric metamaterial composites. The magneto-electric coefficients on these samples were calculated by applying the magnetic field and observing the changes in the electric polarization in the composites.
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Chapter 1
INTRODUCTION

1.1 Introduction
The purpose of this thesis is to design two technologically important different classes of
novel materials: (i) an environmental friendly lead free relaxor system constituting two
different kinds of materials neither of which exhibits the relaxor behavior in pure form
(ii) a unique diphase nanocomposite in combination of ferroelectric and magnetostrictive
materials resulting magnetoelectric response which is not observed in either of the phases.

The common feature of both of these different sets of materials is that their
compositional architecture is designed in such a way so that they exhibit some new or
superior properties, which can not be predicted by the constituent materials. Hence these
two sets of materials are termed as “meta-materials”. It seems appropriate to start by
briefly describing about the meta-materials.

1.2 Meta-materials
Metamaterials are the special class of engineered diphase (or multiphase) composites
having a product of the dissimilar properties of the two components. The two material
phases/ components should have the necessary ingredient property elements to build or
generate the resultant new property of a ‘metamaterial’ not present in the two individual
phases. The design length scale can be micro/nano and the composite can be assembled
or self-assembled but is useful for the particular interrogating wavelength.
Meta-materials are broadly defined as the artificial structures with its electromagnetic properties defined from its structure rather than from the constituent materials it is composed of. The most common meta-materials are the left-handed materials, which are characterized by negative constitutive parameters like permittivity, permeability, and refractive index. Figure 1.1 shows the example of negative refractive index in meta-materials. Pendry (2000) and Smith et al. (2000) showed the applications and possibility of negative refractive index in a material.

Figure 1.1. Negative refractive index in a left-handed material

The aim of this thesis work is to develop two different kinds of meta-materials:
(a) The environmental friendly lead free relaxor ferroelectrics, which show some unusual properties by controlling the nano-polar clusters and (b) A unique nanocomposite “meta materials” which exhibit superior magnetoelectric properties not observed in the constituent materials.
1.2.1 Unusual properties of relaxor system:

This approach has been taken in order to understand and design the metamaterials. With this perspective the system, which is selected has some well studied property parameters of the end members. The two end members are well known dielectrics BaZrO$_3$ and BaTiO$_3$. Among them, BaTiO$_3$ is a well-known proper ferroelectric material and BaZrO$_3$ is a non-ferroelectric material. Also we have selected these candidates as being non-lead compounds. By proper synthesis and processing approach, compounds of BaZrO$_3$:BaTiO$_3$ have been fabricated which have the BaTiO$_3$ clusters in the BaZrO$_3$ matrix.

In this thesis the whole phase diagram of the Barium Zirconate Titanate or BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) solid solution system has been investigated and we have observed how the relaxor behavior has gradually been evolved with the increasing substitution of Ti$^{4+}$ ions for the Zr$^{4+}$ in the matrix of BaZrO$_3$ which has very low dielectric constant (~27). Unlike the classical relaxors like PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN), PbZn$_{1/3}$Nb$_{2/3}$O$_3$ (PZN) this BZT system shows relaxor ferroelectric behavior in the wide range of compositions by controlling the polar BaTiO$_3$ clusters in the non-polar matrix of BaZrO$_3$. These BZT ceramic compositions show very high dielectric constant on the order of $10^4$ whereas neither of the two end members of BZT phase diagram shows so high dielectric values. Infact BaTiO$_3$ ceramic shows the dielectric constant of a few thousands (~2000) and BaZrO$_3$ has the dielectric constant <40. Also some of these BZT compositions show very strong response to the electric field. After studying the whole BZT phase diagram it is seen that the dielectric, ferroelectric properties do not follow any scaling law in this system. Since the BaZr$_x$Ti$_{1-x}$O$_3$ system, has unique capabilities of resulting materials with
properties different than the conventional solid solution and those do not follow the simple mixing rules considering the properties of the constituents, BaTiO$_3$ and BaZrO$_3$; the BaZr$_x$Ti$_{1-x}$O$_3$ relaxor compositions can be classified as a unique example of metamaterials where the polar clusters result in the relaxor materials with the unusually large dielectric properties not present in either of the end member compositions.

1.2.2 Magnetoelectric Nanocomposite

In composite meta-materials, the product property defines meta-material. These are engineered nano-composites, which exhibit superior properties, which are not exhibited in the individual phases in a composite. For reasons that have yet to be understood completely, a homogeneous coexistence of magnetism and ferroelectricity (in a wide temperature range) is a very rare occurrence. In more common instances, the two characteristics belong to two different materials, which make up a fine scale solid mixture. Figure 1.2 shows the example of a composite meta-material in magneto-electric

![Diagram showing the magneto-electric effect in a meta-material](image-url)

Figure 1.2: Magneto-electric effect in a meta-material

Figure 1.2 shows the example of a composite meta-material in magneto-electric
composites. In diphasic composites, combination of ferroelectric and magnetostrictive materials results in magneto-electric response, which is not observed in either of the phases, which result in meta-material.

The major objective of this part of the thesis is to search, develop, and characterize unique composite “meta material” which exhibits superior magnetoelectric properties not observed in the constituent materials. Also it is a challenge to maintain the chemical, crystalline, and ferroic properties of the individual phases in such a “meta material”. To achieve the desired magnetoelectric properties, the nanocomposite of ferroic and ferrites/magnetic materials have been fabricated using both conventional and microwave sintering techniques with the aim of achieving minimum or no chemical reactivity between the two individual components.

1.3 Organization of the Thesis

The work carried out in this dissertation is presented in eight chapters. Chapter two presents literature survey and background information relevant to this thesis work that can guide the reader to specific details to access a state–of–art understanding of relaxor and magnetoelectric materials and the structure–property trends associated with relaxor behavior. Furthermore, a brief introduction to the basic concepts like ferroelectricity, relaxor ferroelectric, composite, magnetoelectric behavior is given to aid the reader.

Chapter three acquaints the reader with the experimental procedures utilized within this study. It is the hope that technical aspects learned in the characterization of the materials
within this study may be employed by other researchers in the field to further a general understanding of relaxor ferroelectrics and magnetoelectric materials.

Chapter four discusses the structure of the relaxor ferroelectric compositions by X-ray diffraction and Neutron diffraction. Further the structural analysis of the relaxor compositions is discussed both qualitatively and quantitatively by Rietveld analysis of powder neutron diffraction data.

Chapter five, a comprehensive one, presents the results of physical properties measurements of the relaxor ferroelectrics. Dielectric, pyroelectric and thermal expansion behavior of the $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT) relaxor ferroelectrics are studied and they have been correlated with the Raman spectra investigations along with structural analysis discussed in chapter three. Electric field response to the dielectric behavior of relaxor ferroelectrics is also discussed in this chapter. The key relaxor parameters are identified and discussed in relation to all the $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ compositions. Further the $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ relaxor system is compared with classical relaxor ferroelectric materials.

Chapter six presents the relaxor ferroelectric behavior of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3\cdot\text{MgO}$ composites. In this chapter, we have shown a potential approach to fabricate the relaxor materials by making the ceramic composite of environmental friendly Ba-based diffuse ferroelectric $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x=0.20$ and $0.25$) with non-ferroelectric MgO.

Chapter seven presents the magnetoelectric behavior of the nanocomposite metamaterials. Finally, chapter eight is a summary of the major conclusions that result from the performed work. There are also suggestions for future work on relaxor ferroelectric and magnetoelectric behavior.
The BaZrxTi1-xO3 relaxor system has been explored for the potential applications in tunable microwave devices like tunable filters, phase shifters, antennas etc. as a part of this thesis work [Maiti, Guo, and Bhalla (2006, 2007)]. To further enhance the suitability of BZT compositions and tailoring their dielectric properties, MgO has been introduced to fabricate the Ba(ZrxTi1-x)O3 : MgO composites for optimum device applications [Maiti, Guo, and Bhalla (2007)]. To maintain the coherence of this thesis, these works are not included here. However, the cross-reference of these papers are given in the Appendix A, B and C.
Chapter 2

BACKGROUND

2.1 Introduction

This thesis work deals with the environmental friendly lead free relaxor ferroelectrics and magnetoelectric nanocomposites. Extensive research on the ferroelectric relaxor behavior has been carried out from basic experimental measurement to first principle theoretical calculations to device applications (e.g. piezoelectric transducers, actuators, capacitors etc.) ever since the discovery of exceptional dielectric properties of the lead based disordered perovskites like PbMg1/3Nb2/3O3 (PMN), PbZn1/3Nb2/3O3 (PZN). Although numerous relaxor materials have been extensively studied over a long period the mechanism, which leads to the relaxor behavior always opens up new questions about the unusual ferroelectric properties of this family of materials. Recently, research emphasis is leaning towards barium based relaxors, as these are environmental friendly lead free oxide. On the other hand the coexistence of magnetic and ferroelectric behavior is hard to achieve. In this thesis novel magnetoelectric materials have been designed and characterized by making nanocomposite. It is the intent of this chapter to sort through some of these information and provide the reader with a brief background of information pertaining to the current investigation such that a qualitative and semi–quantitative description of a relaxor ferroelectrics and magnetoelectric nanocomposite can be appreciated.

2.2 Proper Ferroelectric

The term ‘ferroelectric’ was first used by Valsek [1921] to describe the similarities between the nonlinear electrical properties of Rochelle salt and the magnetic
properties of the ferromagnetic materials. The crystallographic symmetries of the paraelectric and ferroelectric phases are important factors in the ferroelectric behavior of the material. All crystalline materials are divided into 32 different crystal classes or point groups. Out of 32 crystal classes, 11 have a center of symmetry and in one a combination of symmetries effectively provides such a center, leaving 20 classes, which are non-centrosymmetric. All the materials of these 20 classes are piezoelectric. In 10 of these 20 classes, a unique polar axis exists; none of the symmetry operations of the crystal point group can turn this axis around. The existence of a polar axis in a crystal allows the appearance of a spontaneous electrical polarization. Such materials are known as pyroelectrics. A restricted group of pyroelectrics has the further property of being ferroelectric where the direction of polarization can be reversed or reoriented on application of an electric field. Thus all ferroelectrics are pyroelectric and piezoelectric but all piezoelectrics are not pyroelectric and all pyroelectrics are not ferroelectric.

Ferroelectricity is the presence of spontaneous electric dipole moment in crystals, whose direction can be switched between two or more equivalent crystallographic directions by applying an external electric field. The ferroelectric materials retain new orientation of the polarization even after removal of the external electric field. Under an alternating field, one observes hysteresis loop between polarization (P) and electric field (E) in a ferroelectric material. Initial application of electric field to a virgin ferroelectric sample leads to the growth of domains with favorable polarization direction with respect to the electric field direction. For sufficiently high electric fields the polarization reaches saturation (P_s). Reducing the field to zero leaves the material with remnant polarization (P_r). As the direction of field is reversed, polarization is first reversed to zero and then
changes its direction as the field produces saturation polarization in the opposite direction. This whole cycle of operation gives rise to a hysteresis loop between polarization and applied electric field. The field at which polarization becomes zero is called the coercive field \((E_c)\).

Dielectric constant \((\varepsilon')\) of a ferroelectric material obeys Curie-Weiss law (eq. 2.1)

\[
\frac{1}{\varepsilon} = \frac{T - T_0}{C}
\]  

in the non-polar (paraelectric) phase which appears above a characteristic temperature called as Curie point \((T_c)\). \(C\) and \(T_0\) in the equation 2.1 are called Curie constant and Curie temperature, respectively. The Curie temperature is a formula constant obtained by extrapolation, while Curie point is the actual temperature of the transition from polar to nonpolar state or vice-versa. For a first order phase transition \(T_c\) is greater than \(T_0\) while in a second order phase transition the two are equal (i.e. \(T_c = T_0\)). Actually, the ferroelectric phase change occurs due to a structural phase transition involving change in the relative position of ions at \(T_c\).

Curie-Weiss law behavior is one of the key features of ferroelectricity. Many scientists have used this to demonstrate the presence of ferroelectricity in a material. In summary, the Curie-Weiss law is a characteristic of ferroelectrics, while the ability to reorient the spontaneous polarization is a necessary condition for ferroelectricity.

2.3 Relaxor Ferroelectric

2.3.1 Introduction

\(A^{\text{III}}B^{\text{VI}}O_3\) perovskite oxides constitute a fascinating and technologically important family of materials. Ferroelectricity is a common property found in perovskites.
In contrast to ferromagnetism, the ferroelectric state is associated with an underlying lattice distortion because of chemical and/or physical disorderness, at nanoscale to microscale dimensions that strongly influences the behavior of these systems. One of the consequences of disorder is so-called “relaxor” behavior [Cross, 1987]. Unlike proper ferroelectrics, relaxor ferroelectrics exhibit a broad and frequency dispersive permittivity maximum. This broadening of the Curie temperature due to the broad peak observed in the temperature dependent dielectric behavior, was first observed by Smolenskii and Isupov [1954] in the solid solution of Ba(Ti1-xSnx)O3. Relaxor ferroelectric behavior is generally observed in the complex perovskite and tungsten bronze families. Some common examples of relaxor ferroelectrics are PbMg1/3Nb2/3O3 (PMN), PbZn1/3Nb2/3O3 (PZN), (Pb1-xLa_x)(Zr1-yTi_y)O3 (PLZT), (Pb,Ba)Nb2O6 (PBN) etc. Fig. 2.1 shows a typical dielectric behavior for a Pb(In0.5Nb0.5)O3 relaxor ferroelectric [Bokov et.al. (1999)].

![Graph](image-url)

**Fig. 2.1.** Scaling of (a) the real and (b) imaginary part of dielectric constant of relaxor ferroelectric (PbIn0.5Nb0.5O3) with frequency and temperature. Data is taken from the same sample over seven orders of magnitude in frequency. [Bokov et. al. (1999)].
Table 2.1. Applications and examples of relaxor ferroelectric materials

<table>
<thead>
<tr>
<th>Application Area</th>
<th>Relaxor Candidate Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitors</td>
<td>PbMg_{1/3}Nb_{2/3}O_3 and Related Composition</td>
</tr>
<tr>
<td>Actuators</td>
<td>PbMg_{1/3}Nb_{2/3}O_3, PbZn_{1/3}Nb_{2/3}O_3, Pb[(Mg_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3</td>
</tr>
<tr>
<td>Transducers</td>
<td>PbMg_{1/3}Nb_{2/3}O_3, PbZn_{1/3}Nb_{2/3}O_3, Pb[(Sc_{1/2}Nb_{1/2})_{1-x}Ti_x]O_3</td>
</tr>
<tr>
<td>Smart Structure</td>
<td>PbMg_{1/3}Nb_{2/3}O_3, (Pb_{1-x}La_x)(Zr_{1-y}Ti_y)O_3</td>
</tr>
<tr>
<td>Pyroelectric</td>
<td>Pb(Sc_{1/2}Ta_{1/2})O_3, (Ba_xSr_{1-x})TiO_3</td>
</tr>
<tr>
<td>Electro-optic</td>
<td>(Pb_{x}Ba_{1-x})Nb_{2}O_6, (Pb_{1-x}La_x)(Zr_{1-y}Ti_y)O_3</td>
</tr>
<tr>
<td>Photorefractive</td>
<td>(Sr_xBa_{1-x})Nb_{2}O_6, PbMg_{1/3}Nb_{2/3}O_3</td>
</tr>
<tr>
<td>Tunable Dielectrics</td>
<td>BaZr_xTi_{1-x}O_3 and Composite materials</td>
</tr>
</tbody>
</table>

Relaxor ferroelectric materials, due to its unusual properties, have attracted considerable attentions from the scientific community [Bell et.al. (1993), Blinc et.al. (2001), Bokov et.al. (2006), Burns and Dacol (1983, 1990), Cross (1987, 1994), Glinchuk (2004), Glazounov et.al. (1998, 1999, 2000), Kleemann et.al. (1993, 2001, 2005), Pandey (1995), Pirc et.al. (1999), Randall and Bhalla et.al. (1990), Samara (2003), Smolenskii (1960, 1969), Thomas (1990), Uchino (1994), Viehland et.al. (1990, 1991), Westphal et.al. (1992), Xu et.al. (2006), Ye (1998)]. Relaxor ferroelectrics have found a vast range of applications in electronics, electro-mechanics, optoelectronics and others, because of its large dielectric, pyroelectric, piezoelectric and electro-optic properties. Some of the important areas of applications and the prime candidate materials for each that are currently in use are listed in Table 2.1.
2.3.2 Relaxor Ferroelectric Behavior

The macroscopic properties of relaxor ferroelectrics are quantitatively different from proper ferroelectrics. Relaxor ferroelectrics differ from ordinary ferroelectrics in terms of their frequency and temperature dependent dielectric response. Some important differences between relaxor and proper ferroelectrics are shown in Table 2.2 and Figure 2.2.

Table 2.2. Property comparison between proper and relaxor ferroelectrics

<table>
<thead>
<tr>
<th>Property</th>
<th>Proper Ferroelectric</th>
<th>Relaxor Ferroelectric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature dependence of permittivity ( \varepsilon = \varepsilon(T) )</td>
<td>Sharp 1st or 2nd order transition about Curie temperature ( T_C )</td>
<td>Broad/ diffuse phase transition about Curie maximum ( T_{\text{max}} )</td>
</tr>
<tr>
<td>Frequency dependence of Permittivity</td>
<td>Weak</td>
<td>Strong</td>
</tr>
</tbody>
</table>
| Dielectric behavior in paraelectric regime | Obeys Curie-Weiss law: \[
\frac{1}{\varepsilon} = \frac{T - T_0}{C}
\] | Obeys modified Curie-Weiss law equation: \[
\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_{m})^\gamma}{C_1}
\] |
| Remnant polarization                  | Large                 | Small                 |
| Scattering of light                   | Strong anisotropy (birefringence) | Very weak anisotropy (pseudo-cubic) |
| Diffraction of X-rays                 | Line splitting below the structural phase transition | No X-ray line splitting due to pseudo cubic structure |
Fig. 2.2: Comparison in selected properties between proper ferroelectrics and relaxor ferroelectrics for (a) polarization hysteresis behavior, (b) temperature dependent polarization and (c) inverse of dielectric constant as a function of temperature [Kleemann et.al., 2005 ].
Several features that distinguish relaxor ferroelectrics from proper ferroelectric materials are:

(i) The sharp well-defined phase transition temperature (Curie temperature) which is found in proper ferroelectrics is absent in case of relaxors. In contrast, relaxor ferroelectrics exhibit strong dielectric dispersion over distribution time scales that span as many as twelve orders of magnitude, depending on the temperature. The temperature at which the dielectric permittivity is maximum ($T_m'$), increases with increasing frequency, unlike the proper ferroelectrics, while magnitude of the peak decreases. In the same manner the temperature of the loss maxima ($T_m''$) in relaxors increases with increase in frequency whereas peak value increases unlike the dielectric permittivity. The value of $T_m''$ is much lower than that of $T_m'$ at the same frequency.

(ii) Ordinary ferroelectrics exhibit Curie-Weiss behavior above a transition temperature $T_C$ and Debye-type dielectric relaxation below $T_C$. In relaxor ferroelectrics, the dielectric constant does not follow the Curie-Weiss law behavior (Equation 2.1) in the paraelectric region. Instead it follows what is sometimes called the quadratic Curie-Weiss law:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T - T_m)^2}{2\delta^2 \varepsilon_m}$$

(2.2)

where $\varepsilon$ is the real part of the dielectric permittivity, $\varepsilon_m$ is the dielectric constant at $T_m$, and $\delta$ is the diffuseness parameter. The quadratic relation is valid
for the materials which show the diffuse phase transition like the classical relaxor ferroelectric PMN. However, many materials show immediate behavior between the linear and the quadratic limits. Uchino [1982] addressed this issue by introducing a variable power law and the modified Curie-Weiss law:

\[
\frac{1}{\varepsilon - \varepsilon_m} = \frac{(T - T_m)^\gamma}{C_1}
\]  
(2.3)

\[
C_1 = 2 \varepsilon_m \delta'
\]  
(2.4)

Where \( C_1 \) is the modified Curie-Weiss constant, \( \delta \) is the diffuseness parameter and \( \gamma \) is called as degree of relaxation. The equation (2.3) can be solved graphically using log-log plot. The slope of this curve represents the value of the degree of relaxation, \( \gamma \), and the intercept of this curve gives the diffuseness parameter, \( \delta \), by solving the following equation:

\[
\delta = \left( \frac{e^{-\text{int except}}}{2 \varepsilon_m} \right)^{1/\gamma}
\]  
(2.5)

The value of the degree of relaxation can vary like \( 1 < \gamma < 2 \). The limiting values \( \gamma = 1 \) and \( \gamma = 2 \) reduce the expression to Curie-Weiss law valid for the case of normal ferroelectric and to the quadratic dependence valid for an ideal relaxor ferroelectric, respectively.

(iii) In proper ferroelectrics, the polarization (P) versus electric field (E) hysteresis loop is nearly of square shape and shows the large remnant polarization, \( P_R \), due to the switching of macroscopic long-range ordered domains. The remnant and saturation polarization in proper ferroelectrics decrease with increasing temperature and vanish at the phase transition temperature \( T_C \). No polar domains
exist above $T_C$. In contrast, relaxor ferroelectrics show typical P-E hysteresis loop at the temperature well below $T_m$; however, the loops decay slowly into simple non-linearity as the temperature increases through the Curie range. Relaxor ferroelectrics show the gradual decrease in polarization, which extends to the temperature well above $T_m$ before reaching zero due to the fact that the nanopolar domains persist to well above $T_m$.

(iv) In a proper ferroelectric the existence of a macroscopic symmetry change at $T_C$ gives rise to the usual phase transition features with changes of the refractive properties (occurrence or drastic change of birefringence). While in the absence of macroscopic symmetry breaking no such phenomena are observed in a relaxor ferroelectric at $T_m$. Because of the scale of the nanodomains, optical birefringence and x-ray diffraction measurements do not show anisotropy or line splitting even far below $T_m$. The global symmetry of relaxors is generally reported as pseudo-cubic, even in the polar state due to this ambiguity.

The interesting properties of relaxors are attributed to nano-structural features. Thermal annealing in some relaxors may change the size of the nano-regions. The successive increase in the degree of ordering and hence the increase in size of the nano-regions from nano-to macro-scale affect the electronic, optoelectronic and electromechanical properties.

The local symmetry of relaxor ferroelectrics is typically lower than the global symmetry. When quantities such as local strain or refractive index, which depend on $(P^2)$ instead of $(P)$ are probed over a wide range of temperature $(P^2)$ is found to persist several hundred degrees of above $T_{\text{max}}$ [Bhalla et.al. (1987) and Burns et.al. (1990)]. That is,
local polar nano regions are known to exist at temperatures well above the range for corresponding solid solution systems. These polar nano regions grow into more conventional domain-like structure under high electric fields [Harmer et.al. (1989)].

2.3.3 Models of Relaxor:

Relaxor behavior has attracted fascination in the materials science and physics communities due to their rich phenomena and potential for a wide spectrum of applications. A number of competing models have been proposed that address some of the unique signatures of relaxor behavior. The first was the compositional heterogeneity model by Smolenskii [1959, 1960, and 1969]. According to Smolenskii’s compositional fluctuation model, the ions on the B-site of the Pb(B'B'')O₃ structure are randomly distributed in three dimensions. This distribution causes the inhomogeneous chemical micro-regions with different compositions, hence different Curie temperatures. Summing the contributions of each micro-region gives rise to broaden the phase transition between the paraelectric and ferroelectric states. This model, however, was not able to account for other compounds and solid solutions with mixed cation sites that did not exhibit relaxor characteristics and did not explicitly account for the interactions between individual dipoles.

Cross [1987] expanded Smolenskii’s theory and proposed the superparaelectric model by making analogy between the polar micro-regions and the spin clusters in superparamagnets. This model proposes the existence of the polar clusters of different sizes. Local structure inside the clusters is lower than cubic and local polarization directions are present. In superparamagnets, small ordered spin clusters occur only
because they do not have enough magnetocrystalline anisotropy energy to overcome thermal motion. In relaxors, the polar micro-regions have different polarization state, $+P$ and $-P$. The permittivity relaxation in relaxor ferroelectrics is due to thermally activated polarization reversals between the equivalent polar variants. The energy barrier of the

\[ \Delta H \sim K_B T \]

$\Delta H \sim$ volume of polar region

Figure 2.3. Schematic diagram of the thermal activation energy barrier for a non-interacting polar region as described by the superparaelectric model of relaxor ferroelectrics [Cross, 1987].

thermally activated flips of polarization is low and depends on the size of the clusters. Figure 2.3 shows the elastic Gibbs free energy in one of the non-interacting polar regions. Here the height of the energy barrier, $\Delta H$, is proportional to the volume of the polar region and is comparable to the thermal energy, $k_B T$; where, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature (K). Therefore, the polarization can fluctuate between the stable polarization states due to thermal excitation. The frequency of the fluctuations decreases with decreasing temperature leading the observed dispersion in the permittivity response. Eventually at the low temperature, for low thermal energies and at finite
frequencies, a subset of the relaxation times become too slow to respond to the applied measurement field and effectively become “frozen” into one of the polarization states. The superparaelectric model successfully explains many of the features associated with relaxor ferroelectric behavior.

From both composition fluctuation model and superparaelectric theory, it becomes clear that nano-scale ordered micro-regions or clusters have a major role to play behind the relaxor ferroelectric behavior. Randall and Bhalla [1990] recognized this and were able to classify he lead based complex perovskites, Pb(B′xB′′1−x)O3, according to their B-site cation order as shown in figure 2.4. They have shown that, when B-site cation ordering is absent, normal ferroelectric or antiferroelectric behavior is observed e.g. PbFe1/2Nb1/2O3 (PFN) and PbZrₓTi1−ₓO3 (PZT). When ordering of B-site cation exists, it can have either long coherence length or short coherence length. When long coherence length is present normal ferroelectric or antiferroelectric behavior is observed e.g. PbMg1/2W1/2O3 (PMW) and PbCo1/2W1/2O3 (PCW). In contrast, when only short range ordering is present relaxor behavior occurs. The complex perovskites of this class are again divided into two subgroups as stoichiometric and non-stoichiometric. The stoichiometric subgroups are the complex perovskites with x= ½ [e.g. PbIn1/2Nb1/2O3 (PIN) and PbSc1/2Ta1/2O3 (PST)] where the average B-site valence of the ordered phase is the stoichiometric 4⁺ value. On the other hand, non-stoichiometric subgroups are Pb(B′xB′′1−x)O3 perovskites with x= 1/3 [e.g. PbMg1/3Nb2/3O3 (PMN) and PbZn1/3Nb2/3O3 (PZN)] where the average B-site valence is lower than the stoichiometric 4⁺.
Figure 2.4. Classification of complex lead perovskites with respect to the B-site cation order. [Randall and Bhalla (1990)].
It has also been reported [Setter et al. (1980) and Stenger et al. (1980)] that the degree of ordering can be varied in certain relaxor ferroelectric e.g. PbSc\textsubscript{1/2}Ta\textsubscript{1/2}O\textsubscript{3} (PST) by thermal annealing and the dielectric behavior is highly correlated with the ordering of the B-site cations. This ordering process increases the coherence length from short to long range and changes the behavior from that of a typical relaxor to that of a proper ferroelectric.

Application of the superparaelectric model to the experimental data leads to the conclusion that interactions among the polar-clusters are crucial to explain the relaxor behavior and must be included in the model. Later, Viehland et al. [1990, 1991, and 1992], proposed dipolar glass model to include the cluster interactions in analogy with magnetic spin glasses and related dipolar glasses. According to this model, individual clusters interact with each other by means of dipolar interactions. As the temperature decreases, the strength of the interactions increases and at sufficiently low temperature, \( T_f \), the originally dynamically disordered polar regions will “freeze” into metastable or frustrated polar states such that clusters may not change their polarization anymore due to the presence of the random fields produced by the structural disorder. The temperature dependence of the permittivity maximum was successfully modeled by the Vögel–Fulcher relationship.

The Vögel-Fulcher [Vogel (1921) and Fulcher (1925)] law originally derived for the magnetic spin-glass systems is described as follows:

\[
\tau = \tau_0 \exp \left[ \frac{E_a}{K_B (T_m - T_{VF})} \right]
\]  

(2.6)
where $\tau_0$ is the pre-exponential factor, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant, $T_m$ is the temperature corresponding to dielectric maxima and $T_{VF}$ is the characteristic Vogel-Fulcher freezing temperature. Viehland et.al. proposed a qualitative representation of the temperature dependent relaxation time spectrum, shown in figure 2.5. Broad spectrum of relaxation time with the longest time approaching infinity is observed near freezing temperature $T_f$. At the temperature above $T_f$, the average relaxation time shortens and the width if the spectrum becomes sharpen with increasing temperature.

Fig. 2.5. A model illustrating the temperature dependence of the relaxation time spectrum. $G(\tau, T)$ is the number of polar regions having a relaxation time of $\tau$, and $T_f$ is the freezing temperature.

Viehland et.al. further argued that polarization fluctuations do not dynamically appear and disappear via intermediate return into paraelectric phase. Instead, above the freezing temperature, $T_f$, the polarization fluctuations can be visualized as the
consequences of rotation of the polarization between equivalent orientations since electro-crystalline energy is normally smaller than the paraelectric energy.

Bhalla et.al. (1987) and Burns et.al. (1990) have shown that Polar cluster embryos originate at the temperature much higher than T_f and T_m. Burns and Dacol [1990] have shown that local polarization starts to nucleate in PMN below 625K. According to dipolar glass model, these polar clusters start interacting among each another as the temperature decreases versus superparaelectric model [Cross, 1987] which does not take these interactions into account. At very high temperature, thermal fluctuations are so large that there are no well-defined dipole moments. However, on cooling, these dipolar entities grow into small polar clusters below the so-called Burns temperature, T_d [Burns and Dacol (1990)]. The volume fraction of these polar clusters increases with decreasing temperature, while the temperature activated disorder decreases. Difference between spin-glass freezing and thermal flipping of the isolated superparaelectric clusters is in the cooperative freezing phenomenon. Support for the dipolar glass model is observed from the splitting of the field–cooled (FC) permittivity and zero–field–cooled (ZFC) permittivity [Binder et.al. (1986) and Levstik et.al. (1998)]. Levstik et al. studied the glassy nature of a PMN single crystal and obtained results that represent strong evidence of spin–glass–like behavior in low external electric fields. Colla et.al. (1995) have shown that relaxor can be transformed into a proper ferroelectric upon field cooling under the applied d.c. bias with a magnitude above critical, which is about 1.8 kV/cm for PMN. Although dipolar-glass model was developed in analogous to the spin-glass, similarity can not be considered as exact analogs due to the fundamental difference between the electric dipoles, magnetic spin and their surroundings.
Bell [1993] proposed a method to calculate the dielectric properties of a superparaelectric material using the Landau–Ginzburg–Devonshire (LGD) theory of ferroelectrics assuming volume of the polar clusters as a variable parameter and that the individual polar clusters have a single phase transition temperature. The volume of the polar clusters was allowed to change with respect to temperature and when coupling between the polar clusters was incorporated into the calculation good agreement with relaxor character was observed. Thus, the relaxor ferroelectric behavior is characterized by disorder with some clustering and freezing due the frustrated interactions between the clusters in the dipolar glass model.

Tagantsev [1994] has argued that Vogel-Fulcher relationship in relaxor ferroelectrics does not necessarily imply a “freezing” in the system. Instead Vogel-Fulcher relationship can be observed in any system where the distribution of relaxation times has some regular temperature dependence and does not necessarily require manifesting a freezing at the freezing temperature. Later, Glazounov and Tagantsev [1998] characterized the freezing hypothesis by calculating the parameters in Vögel–Fulcher law, taking the position of the onset of the dispersion in the $\varepsilon(\omega,T)$ data or at the maximum relaxation time. Within experimental error, this evaluation predicted similar parameters from the Vögel–Fulcher law as those calculated from the temperature of the maximum in the permittivity response.

Recently, Glazunov et.al. [1996, 1999 and 2000] proposed “breathing model” to explain the key characteristics of the relaxor ferroelectrics. In this model, oscillation of an interphase (polar/nonpolar) boundary is introduced to describe both the temperature and frequency dependence of relaxors. Unlike the reorientation of a dipole under thermal
excitation, the breathing wall model considers the polar cluster to already be stabilized in orientation. The observed relaxor behavior of a single polar region is associated with the oscillation or movement of domain walls in the presence of an ac electric field.

Westphal, Kleemann and Glinchuk in 1992 proposed a “random field model.” They argued that the features exhibited by PMN at low temperature might not exclusively be the result of a glassy material, but could also be characterized by a system in which the structural phase transition into a ferroelectric state “is destroyed by virtue of local random fields”. According to them, compositional fluctuations with 1:1 Nb\(^{5+}\) and Mg\(^{2+}\) ordering in the perovskite B-site are the sources of quenched random field, which results in slowdown of the dynamics in PMN leading to the freezing into a ferroelectric domain state on a nanometer scale. According to this model the polar nanodomains have definite polarization contrarily to the polarization degeneracy of polar cluster fluctuations proposed by dipolar-glass model. It is thought that the random fields are the result of quenched high temperature states such as lattice defects or unavoidable impurities and these random fields and random interactions among the defects and the polar nano-domains leads to the freezing transition into a glassy state, predicting the frequency dependence of the permittivity. To support the random-field model they provided the experimental evidence of (i) observed Barkhausen jumps of polar nanodomains from optical linear birefringence studies on PMN crystals under the applied electric field and (ii) a ferroelectric anomaly of the dielectric permittivity appearing slightly above \(T_0\) under a moderate poling field. They observed that temperature dependence of the linear birefringence under applied electric field (3.3 kV/cm) in PMN single crystal showed the splitting of field cooled (FC) and zero field cooled (ZFC) regimes. This splitting usually
happens in glassy systems, such as spin, dipolar or structural glasses. From the splitting of FC and ZFC temperature dependence authors concluded that induced polar phase was stable after FC and could be sustained after subsequent removal of the E-field. They made the conclusions that their experimental evidences are not compatible with the dipolar glass model. However, they have shown that dipole glass can be transformed into a ferroelectric state under the applied electric field above a critical value, $E_C$. Linear birefringence experiments were performed at the applied voltage exceeding $E_C$ and therefore it is argued in the literature [Bobnar et.al. (2000), Colla et.al. (1996)] that Burkhausen jumps may not be used against dipolar glass model, since glassy state may have a crossover to a ferroelectric state under applied electric field over $E_C$. Crossover to ferroelectric state is further explained by spherical random-bond random-field model proposed by Pirc and Blinc [1999].

It is generally difficult to model and understand these dynamic relaxation mechanisms in solid state materials. It is usually agreed that microscopic compositional inhomogeneity is an essential feature of relaxor ferroelectrics. These inhomogeneities produce a complex energy landscape where polar nano regions must exist. It is also reported [Bonneau et.al. (1989)] that the presence of lone pair electron in Pb$^{2+}$ cation in lead based relaxors contributes large displacement leading the order-disorder mechanism. Toulouse et.al. [1994] has also shown that charge disorder is not an essential feature of relaxor behavior by demonstrating $(K_{1-x}Li_x)TaO_3$ that exhibits relaxor behavior. In one of the few experiments to probe simultaneously both spatial and temporal features of relaxor, Shur et.al. [1999] employed a time-resolved light scattering technique to deduce a fractal distribution of nanodomain growth that occurs under pulsed fields. These and other
experiments indicate that the bottom-up modeling may capture only some of the generic features of relaxors and can not be considered a complete theory. Given the number of competing model it is important to introduce new experimental results that can address the relevant length scales and time scales implicit in such models.

The work in this thesis is not aimed to answer this problem, but more to develop new environmental friendly lead free relaxor materials for potential device applications. For these materials, the structure–property relationships will be investigated. It is hopeful that, with the new type of lead-free relaxor ferroelectrics, new insights will be gained that ultimately may lead to an overall understanding of the relaxor behavior, but this is for the theoretical community.

2.4. Exploration of environmental-friendly lead-free relaxor compositions:

Extensive research on the ferroelectric relaxor behavior has been carried out from basic experimental measurement to first principle theoretical calculations to industrial application ever since the discovery of exceptional dielectric properties of the lead based disordered perovskites like PbMg_{1/3}Nb_{2/3}O_{3} (PMN) [Smolenskii et.al. (1960)], PbZn_{1/3}Nb_{2/3}O_{3} (PZN) [Yokomizo et.al. (1970)]. Although numerous relaxor materials have been extensively studied over a long period, the mechanism leads to the relaxor behavior always opens up new questions about the unusual ferroelectric properties of this family of materials. As discussed earlier in this chapter, most of the relaxor materials usually used are lead-based materials. Recently, research emphasis is leaning towards lead-free relaxor compositions for the environmental friendly application because of the disadvantage of lead-based materials due to the volatility and toxicity of PbO.
In the search of environmental-friendly lead free relaxor materials efforts have been made currently to introduce relaxor behavior by doping A or B site ions in ABO\(_3\) perovskites like quantum para-electric SrTiO\(_3\), KTaO\(_3\) and in typical ferroelectric BaTiO\(_3\). In the earlier studies relaxor behavior has been introduced by substituting the impurities in the quantum para-electric matrix e.g. Bi [Ang chen et.al. (2002)], Ca [Bednorz et.al. (1984) and Bianchi et.al. (1995)], La [Iguchi et.al. (1993) and Yu et.al. (1999)] doped SrTiO\(_3\) and Li [Toulouse et.al. (1994)], Nb [Samara et.al. (1984) and Trepakov et.al. (2001)] doped KTaO\(_3\) or in the normal ferroelectric matrix like Hf[Payne et.al. (1965)], Ce [Zhi et.al. (1997)], Sn [Novosil'tsev et.al. (1956)] doped BaTiO\(_3\).

From the literature review on all the environmental-friendly lead free relaxor ferroelectric system developed by various scientists, the crux of the problem we got that the relaxor ferroelectric behavior can be produced by two ways.

(i) **Quantum paraelectric→ Ferroelectric→ Relaxor**

The quantum paraelectric state is a highly symmetric, well understood ground state into which controlled degrees of disorder can be introduced chemically. There are qualitative differences between the routes to relaxor ferroelectricity that involves classical vs quantum paraelectricity. The mostly best studied parent systems for producing relaxors are the so-called quantum paraelectrics SrTiO\(_3\) and KTaO\(_3\). The common features of these quantum paraelectrics are that the dielectric constant initially increases with decreasing temperature in a Curie–Weiss manner but shows a departure from this behavior at intermediate temperatures followed by saturation of the dielectric permittivity at very low temperatures. This low temperature saturation of the
dielectric permittivity in quantum paraelectrics like SrTiO$_3$ and KTaO$_3$ has been attributed to the zero-point fluctuations of the lattice which precludes condensation of the soft TO mode at $q = 0$. A small concentration of dopants (e.g. SrTiO$_3$: Bi or Ca, KTaO$_3$: Li or Nb) suppress the quantum fluctuations in these quantum paraelectrics. The suppression of the quantum fluctuations eventually stabilizes a ferroelectric phase in both SrTiO$_3$ and KTaO$_3$ and on increasing the concentration of dopants it transforms into relaxor ferroelectrics.

(ii) Proper Ferroelectric $\rightarrow$ Relaxor

Another method of producing relaxors is through controlled introduction of impurities in a proper ferroelectric. BaTiO$_3$ is one of the most important ferroelectric materials and has been widely studied and used for wide range of device applications. For the homovalent substitution in the B-site, proper ferroelectric BaTiO$_3$ manifests relaxor behavior (e.g. BaTi$_{1-x}$B$_x$O$_3$; B = Sn, Ce). The interesting common feature of both Sn and Ce doped BaTiO$_3$ compositions is the pinched phase transition behavior of the system i.e. only one broad peak is found in the temperature dependence dielectric behavior at a specific dopant concentration.

In our efforts to find new lead-free ferroelectric materials, we have investigated the system BaZrO$_3$:BaTiO$_3$ or the solid solution system, Ba(Ti$_{1-x}$Zr$_x$)O$_3$. 
2.5. Barium Zirconate Titanate or Ba(Zr_xTi_{1-x})O_3 System

2.5.1. Introduction

Barium Zirconate Titanate, BaZr_xTi_{1-x}O_3 or BZT is the solid solution of barium titanate (BaTiO_3) and barium Zirconate (BaZrO_3). In this section the typical characteristics or features (related to our work) of the two end members of BaZr_xTi_{1-x}O_3 phase diagram, BaTiO_3 and BaZrO_3 are discussed.

Barium titanate is one of the most important ferroelectric materials. Above 130°C it exhibits non polar phase with cubic perovskite structure (ABO_3) as shown on Fig. 2.6.

![Figure 2.6. Unit cell of cubic BaTiO_3 perovskite.](image)

This structure may be described as simple cubic units cell with large cation A (barium) on corners, a smaller cation B (titanium) at the Body centre position, and O (oxygen) at the centers of the faces. Upon cooling down BaTiO_3 undergoes 3 phase transitions, cubic to tetragonal at ~130°C, tetragonal to orthorhombic at 5°C and orthorhombic to rhombohedral at -90°C. In the temperature range from 130°C to 5°C, the structure of
BaTiO$_3$ is tetragonal (4mm) which is ferroelectric. The tetragonal unit cell results from the distortion of the original cubic cell. Ferroelectricity arises due to the off-centre displacement of the oxygen (at face centers) and titanium (at body centers) in opposite directions along <100>. As a result one of the cube edges is elongated to become polar c-axis of the tetragonal phase. Since there are six equivalent <100> directions in the cubic phase, the polar axis can be parallel to any one of these directions. This leads to the formation of 90 degree and 180 degree domain walls in the tetragonal phase. In the temperature range of 50°C to −90°C, the structure of BaTiO$_3$ is orthorhombic which a ferroelectric phase is also having the polar axis along one of <110> direction of the original cubic unit cell. There are 12 equivalent <110> directions. The displacement of titanium and oxygen ions along one of the <110> cubic direction leads to an elongation of the face diagonals of the original cubic unit cell, producing shear of the original cube. Below -90°C, a new ferroelectric phase of BaTiO$_3$ appears with a rhombohedral structure (3m). The polar axis for this phase lies along one of the 8 equivalent original cubic <111> directions. The rhombohedral distortions can be visualized as the stretching of the original cubic cell along one of the body diagonals. Variation of dielectric constant and lattice parameter in different phases of BaTiO$_3$ is shown in the figure 2.7. The tetragonal phase of BaTiO$_3$ has been the object of most investigations as this phase is stable at and above room temperature. Due to the presence of 90° and 180° domains, macroscopic spontaneous polarization is not observed even for a single crystal of tetragonal phase, in the absence of the DC electric field. Application of a DC field may result in merging of these domains to give monodomain crystal with measurable spontaneous polarization. The orientation of all the domains along applied external DC field is not possible for
ceramic BaTiO$_3$. This results in low value of saturation and remnant polarization for ceramic samples in comparison to single crystals.

![Diagram of dielectric constant and lattice parameter variation in different phases of BaTiO$_3$.](image)

**Fig. 2.7** Variation of dielectric constant (Top) and lattice parameter (Down) in different phases of BaTiO$_3$ [Jaffe et. al. (1971)].

The other end member of the BaZr$_x$Ti$_{1-x}$O$_3$ phase diagram is barium Zirconate or BaZrO$_3$. BaZrO$_3$ has the simple perovskite structure with relatively large lattice constant, higher melting point, smaller thermal expansion coefficient, lower thermal conductivity, lower dielectric constant, and loss than that of BaTiO$_3$. Because of these refractory
properties BaZrO$_3$ is considered to be (i) a very good candidate to be used as an inert crucible in crystal growth techniques (ii) an excellent material for wireless communications and (iii) a very good substrate in thin film deposition or high temperature superconductor [Celik et.al. (2002), Chai et.al. (1997), Azad et.al. (2002), Dobal et.al. (2001), Robertz et.al. (2001), Dierickx et.al. (1996), and Erb et.al. (1996)]. BaZrO$_3$ does not show any phase transition up to 1375 K [Cordfunke et.al (1989)]. There is no strong evidence of the existence of any ferroelectric phase transition in this compound. Recently Akbarzadeh et.al. [2005] investigated a combined theoretical and experimental study on BaZrO$_3$. They observed that the real part of the dielectric permittivity saturates in overall at low temperature (below \sim 40 K) which is caused by zero-point vibration generally observed in quantum paraelectric like SrTiO$_3$, KTaO$_3$ etc. They also observed two peaks or fine structures in the temperature dependent dielectric studies around 50-65 K and 15 K, respectively. Microscopic origins like unavoidable defects and oxygen octahedral rotation occurring at a local scale are suggested for those anomalies. Although they reported several unusual features in the real and imaginary part of the dielectric permittivity, no long-range ferroelectric, antiferroelectric or antiferrodistortive structural phase transition was observed in BaZrO$_3$ down to 2 K.

### 2.5.2. Characteristics of Barium Zirconate Titanate or Ba(Zr$_x$Ti$_{1-x}$)O$_3$

Recently BaTiO$_3$ based ferroelectric compositions has received a great deal of attentions from the scientific community in searching for environmental friendly lead free ferroelectric materials. BaTiO$_3$ in its pure form does not have ideal properties for
Fig. 2.8. Temperature dependence of (a) dielectric constant $\varepsilon$ and (b) dielectric loss ($\tan\delta$) for the Ba(Ti$_{1-x}$Zr$_x$)O$_3$ ceramics with $x = 0.03, 0.05, 0.08, 0.15, 0.2, 0.25$ and $0.3$ at 0.1, 1, 10, and 100 kHz [Zhi Yu et.al. (2007)].
industrial applications. Chemical substitutions at the \( \text{Ba}^{2+} \) and \( \text{Ti}^{4+} \) sites are made to tailor the properties to meet a variety of device and performance requirements. Among the doped \( \text{BaTiO}_3 \) systems, \( \text{BaZr}_x\text{Ti}_{1-x}\text{O}_3 \) (BZT) solid solution has attracted considerable attention in both bulk and thin film due to its potentiality for various device applications [Hennings et.al. (1982), Wu et.al. (1996), Hoffman et.al. (1997) Ravez et.al. (1997 and 2000), Rehrig et.al. (1999), Dixit et.al. (2002, 2004, and 2006), Yu et.al. (2000, 2002)]. Substitution of \( \text{Ti}^{4+} \) with \( \text{Zr}^{4+} \) in \( \text{BaTiO}_3 \) exhibits several interesting behavior in the dielectric study. Temperature dependence of dielectric constant (\( \varepsilon \)) and dielectric loss.

![Phase diagram for \( \text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3 \) ceramics with \( 0 \leq x \leq 0.3 \).](image)

Fig. 2.9. Phase diagram for \( \text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3 \) ceramics with \( 0 \leq x \leq 0.3 \). (For various compositions, data were taken at 1 kHz. (Symbols are experimental data: up-triangles: data for ceramics; open circles: single crystal data; Dash curves: guide to the eyes)](Zhi Yu et.al. (2002)).
(tanδ) at various frequencies for the Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics with $x = 0.03, 0.05, 0.08, 0.15, 0.2, 0.25$ and 0.3 is shown in figure 2.8 [Yu et.al. (2007)]. It has been reported that with the incorporation of Zr$^{4+}$ in BaTiO$_3$, the rhombohedral to orthorhombic ($T_1$) and orthorhombic to tetragonal ($T_2$) phase transition temperature corresponding to pure BaTiO$_3$ increase. In contrast, the tetragonal to cubic ($T_C$) phase transition temperature decreases. Thus when Zr concentration is ~ 15 at.%, the system (BaZr$_x$Ti$_{1-x}$O$_3$) exhibits a pinched phase transition, i.e. all the above three phase transition temperatures ($T_1$, $T_2$ and $T_C$) correspond to pure BaTiO$_3$ are merged or pinched into single diffuse phase transition as shown in figure 2.9 [Zhi Yu et.al. (2002)]. With further increase in Zr contents beyond 15 at.%, a diffuse dielectric anomaly has been observed with decrease in the transition temperature and above 25 at.% Zr contents Ba(Zr$_x$Ti$_{1-x}$)O$_3$ system showed typical relaxor-like behavior both in bulk and thin film.

Ba(Ti$_{1-x}$Zr$_x$)O$_3$ system with low Zr concentration showed very high strain behavior. By using templated grain growth (TGG) method, Rherig et.al. (1999) showed that some Ba(Ti$_{1-x}$Zr$_x$)O$_3$ ($x = 0.045$ and 0.085) crystals in millimeter size grown exhibit as high as ~0.5% strain at 50 kV/cm and piezoelectric strain coefficient, $d_{33}$, of 355 pC/N at room temperature. However they observed large hysteresis in the strain. Later Zhi Yu et.al. [2000 and 2002] observed almost hysteresis free very high strain (~0.25%) and high piezoelectric strain coefficient $d_{33}$ (~850 pC/N) in the Ba(Ti$_{1-x}$Zr$_x$)O$_3$ ($x = 0.05$ and 0.08) single crystals grown by laser heated pedestal growth (LHPG) technique. Ba(Ti$_{1-x}$Zr$_x$)O$_3$ compositions with 0.20 $\leq x \leq$ 0.35 have shown the great potentials for the applications as DRAM and tunable microwave devices like tunable filters, phase shifters, antennas etc [Wu et.al. (1996), Hoffman et.al. (1997), Yu et.al. (2002), Xu et.al. (2004), Tang et.al.
(2004), Lee et.al. (2005) and Jiang et.al. (2006)]. A lot of research work has been done by various workers on the Ba(Ti$_{1-x}$Zr$_x$)O$_3$ thin film developed by various method like sol-gel process [Dixit et.al. (2002, 2004, and 2006), Dobal et.al. (2001), Zhai et.al. (2004)], pulse laser deposition (PLD) technique [Tang et.al. (2006) and Miao et.al. (2007)], soft chemical spin coating technique [Pontes et.al. (2004)], RF magnetron sputtering [Wu et.al. (1996)] etc. Recently Ohno et.al. [2006] studied the effect of particle size Ba(Zr$_{0.05}$Ti$_{0.95}$)O$_3$ composition prepared by sol-gel process. They observed that the Curie temperature of this material shifted to the lower temperature by size effect and in case of nano-particle size of 13.4 nm, the crystal structure was identified as a cubic phase at room temperature.

Although BaTiO$_3$-BaZrO$_3$ system was identified as a solid solution as in early 1950s [McQuarrie et.al. (1954)] most studies were focused on the temperature dependence of the dielectric constant, the nature of the phase transitions and the ferroelectric relaxor behavior of this materials in lower concentration ($x< 0.40$) of Zr in Ba(Ti$_{1-x}$Zr$_x$)O$_3$ system over the years. Recently, Dixit et.al. [2006] studied the Ba(Ti$_{1-x}$Zr$_x$)O$_3$ system in the composition range 0.30$\leq x \leq$0.70 in the form of thin-film. Till today many research workers [Kell et.al. (1956), Hennings et.al. (1982), Farhi et.al. (1999), Simon et.al. (2004) and Yu et.al. (2002)] have developed the phase diagram of Ba(Ti$_{1-x}$Zr$_x$)O$_3$ system in lower concentration of Zr i.e. BaTiO$_3$ rich side of the phase diagram similar to the figure 2.9. To the best of our knowledge there are no reports on the dielectric behavior in the higher BaZrO$_3$ concentration of this solid solution system. In this thesis, we have studied structure-property correlation of the whole phase diagram of Ba(Ti$_{1-x}$Zr$_x$)O$_3$ system.
2.6 Composite Materials

The two important material systems used in the current investigation are related to the ferroelectric:MgO composites and ferroelectric: ferrite diphasic composites. The following sections dealt with the subject contents related to this field.

2.6.1 Introduction:

Over the years single phase electro-ceramic materials have been used in several electric and magnetic applications. However, there are limitations to use the single phase materials in many high frequency applications due to their high losses and inflexibility of properties associated with them. In addition, magnitude of the various property coefficients is limited in single phase materials.

To meet these challenges, the properties of materials have been tailored and enhanced by making various composites by a proper selection of constituent materials for extensive applications in the electronic and magnetic components. Ferroelectric/Ferromagnetic materials, which have field dependent dielectric and electromagnetic properties, are the primary constituent materials in the electronic and magnetoelectric composites. The composite materials are prepared with the mixing of two or more materials with different properties to achieve an intermediate/desired property or result. Van Suchtelen (1972) first discussed the basic idea of synthesized composite materials. He described about the sum and product properties of the resulted composite materials depending on the property of interest. Newnham et.al. (1978, 1986) introduced the concept of connectivity pattern in the composites and described that the resulted properties can be changed by few orders of magnitude by achieving desired connectivity
pattern in the composite. Figure 2.10 shows the connectivity pattern in di-phasic composite materials developed by Newnham et al. [1978]. The importance of periodicity in composites is a major factor for the reproducibility of properties in the composite. Thus, many researchers have achieved connectivity pattern using the matrix of polymer and ceramic composites or with multi-layer laminate ceramic composite setup.

Fig. 2.10 The connectivity pattern in di-phasic composite materials [Newnham et al. (1978)].
Figure 2.11 shows a multi-layer connectivity pattern in a composite with piezoelectric and magnetostrictive phase connected in a 2-2 connectivity. When an electric field is applied to the composite, the piezoelectric expands or contracts. This expansion or contraction generates stresses in the sandwiched magnetostrictive disk. Hence, magnetic signals can be obtained when the composite is subjected to electric field.

![Figure 2.11: 2-2 connectivity pattern in magneto electric composites](image)

Although composites have better resulted properties than single phase materials, the fabrication is expensive as it involves synthesis of two different constituent materials separately and later bonding them together. Secondly, the current use of these composite materials is relatively limited in industrial applications as it is difficult to achieve long term stability of these materials.
2.6.2 Sum, Product and Combination Properties

The properties of composites can be classified into three categories namely sum properties, product properties and combination properties. The appropriate properties of

(a) **Sum**

Phase 1 : $X \rightarrow Y_1$
Phase 2 : $X \rightarrow Y_2$
\[ X \rightarrow Y^* \]

(b) **Product**

Phase 1 : $X \rightarrow Y_1/Z_1$
Phase 2 : $X \rightarrow Y_2/Z_2$
\[ X \rightarrow (Y/Z)^* \]

(c) **Combination**

Phase 1 : $X \rightarrow Y$
Phase 2 : $Y \rightarrow Z$
\[ X \rightarrow Z \quad \text{New Function} \]

Fig 2.12 Schematic diagram of Sum, Combination and Product effects of composites

[Uchino (2000)]
the phases can be invoked to design a composite depending on the application. The schematic representation of the properties is described by Uchino (2000) as shown in figure 2.12.

A sum property of the composite is defined as a weighted sum of the contributions of the individual component phases, proportional to the weight/volume fractions of the phases in a composite. The sum properties can be visualized in simple physical quantities like density and resistivity.

Combination property is obtained when the average value of output exceed the magnitude of the end components. As shown in figure, the output refers to an effect B/C which depend on two different parameters B and C. The combination value B/C exhibit a maximum at an intermediate ratios of the two phases. Thus, it is called combination property. Depending on the application, these properties can be exploited to obtain a desired effect.

A product property is a resulted property achieved in a composite but not observed in individual phases. As seen in figure, in a two component phases if one phase exhibits a property \( A \rightarrow B \) ( \( B \) is an effect resulted from application of an independent variable \( A \) ) with a proportionality tensor \( dB/dA = X \) (can be constant or value dependent on \( A \) or \( B \) ) and the second phase exhibiting \( B \rightarrow C \) with a proportionality tensor \( dC/dB = Y \), then the resulted composite will exhibit \( A \rightarrow C \) which is not present in either of the individual phases. Thus, \( A \rightarrow C \) is called a product property of composite. The proportionality tensor \( dC/dA = (dC/dB)(dB/dA) = Y.X \) is the product of the proportionality tensors of the phases, hence called product property.
Magnetolectric effect in the composites is an example of product property. For example, a composite prepared from ferroelectric BaTiO$_3$ and ferromagnetic CoFe$_2$O$_4$ has magnetoelectric effect, but this effect is not present in either BaTiO$_3$ or CoFe$_2$O$_4$. The magnetic field applied to the composite produces strain in CoFe$_2$O$_4$, which consequently transduces a strain in the ferroelectric phase resulting in electrical polarization through the piezoelectric effect. Magnetolectric effects of a few orders of magnitudes higher than single phase materials can be obtained this way. In this thesis, similar studies have been done to produce magnetoelectric effect in the composites of PMN-PT with ferrites.

2.7 Magneto-electric Composites

The magneto-electric effect can be described as an induced magnetization in a material proportional to an applied electric field or an induced electric polarization to an applied magnetic field.

Hornreich (1972) used the magnetoelectric effect for the measurement of Neel temperature. In antiferroelectric materials it is difficult to measure the Neel temperature ($T_N$) because of the absence of net magnetization below $T_N$, but using magneto-electric effect $T_N$ can be measured in these materials. Magnetoelectric effect can also be used to study the crystal structure of different materials as it reduced the number of point groups (Rado, 1970). O’Dell (1965) proposed the magneto-electric materials for the application in memory devices. As magneto-electric effect has either positive or negative sign depending upon the annealing conditions in the case of polycrystalline material. This showed that the material can be used to store information in two different states of “0” and “1”. The magneto-electric compositions can be used as transducers in recording.
heads and electromagnetic pick ups. They can also be used as a magnetic-probe for detecting ac as well as dc fields.

The magneto-electric effect can be either electrically induced magneto-electric effect or magnetically induced magneto-electric effect. The theory of magneto-electric effect was first proposed by Pierre Curie in 1894. He described that the application of symmetry conditions denotes that a body with asymmetric molecules gets electrically polarized when placed in a magnetic field and magnetically charged when placed in an electric field. However, no work was further carried out on magneto-electric materials until 1950s.

Landau and Lifshitz (1960) showed the feasibility of the magneto-electric effect on the basis of crystal symmetry. They described that if a crystal is magnetically ordered then the time reversal symmetry operation for a given crystalline geometry is not independent, thus allowing the possibility of magneto-electric effect in magnetically ordered crystal materials.

Dzyaloshinskii (1959) described further the similar work carried out by Landau and Lifshitz on the basis of detailed thermodynamics and symmetry arguments and proposed antiferromagnetic Cr$_2$O$_3$ to show magneto-electric effect. The first experimental measurement of magneto-electric effect on single crystal Cr$_2$O$_3$ was carried out by Astrov (1960, 1961). Foner and Hanbusa [1963] carried out research on polycrystalline Cr$_2$O$_3$. Later, many researchers [Martin et. al. (1964), O'Dell et. al. (1966), Hornreich et. al. (1970)] studied Cr$_2$O$_3$ and reported their work on magneto-electric effect in both single crystals and polycrystalline ceramics. Hornreith [1970] predicted a few other single phase magneto-electric materials including Cr$_2$WO$_6$, V$_2$WO$_6$, Fe$_2$TeO$_6$. However, most of the
single phase materials can not be used in device applications because of the low magnitude of magneto-electric coefficient.

Many single phase magneto-electric materials have been discovered but due to their limitations (low magneto-electric coefficients or low temperature effects) they can not be used in the real applications. On the other hand, the developments in the technology of composite materials allowed researchers to design various ceramics of magneto-electric composite materials. The composite materials can be designed to overcome the difficulties inherent in single phase materials.

A composite materials consists of a piezoelectric and a magnetic/ magnetostrictive material can be prepared to show the product property of magneto-electric effect . It can be explained as follows: the strain effect in the piezomagnetic/magnetostrictive phase due to applied magnetic field would result in stress on the piezoelectric phase of the composite. The stress produced result in electrical polarization. The converse effect is also possible in which strain produced due to electric field applied in piezoelectric phase would be transferred as stress in piezomagnetic / magnetostrictive phase, which results in induced magnetic field. Thus by definition of magneto-electric effect an applied magnetic field induces an electric polarization or applied magnetic field induces magnetic polarization in a magnetic material.

The first work on magneto-electric composites was reported at Philips Laboratories, Netherlands. Boomgaard et al. (1974) showed magneto-electric effect in Fe-Co-Ti-Ba-O composite system. Boomgaard et al. (1976, 1978) made an assumption in the calculation of magneto-electric coefficients in the composite as (i) the dielectric constant of piezoelectric phase is very large compared to the dielectric constant of the
ferrite phase; (ii) Young’s moduli for both phases are equal and (iii) there is perfect coupling between piezoelectric phase and ferrite phase.

By making above assumptions, the magneto-electric coefficients can be calculated using the following equation

\[
(dE/dH)_{comp} = m_v (dl/dH)_{ferrite} (dE/dl)_{piezoelectric}
\]  \hspace{1cm} (2.6)

where, \((dl/dH)\) is the change in dimension per unit magnetic field and \(dE/dl\) is the change in dimension per unit electric field, \(m_v\) is the volume fraction of ferrite in the composite.

Boomgaard used these assumptions to calculate magneto-electric coefficients in BaTiO\textsubscript{3}-CoFe\textsubscript{2}O\textsubscript{4} composites. They reported magneto-lectric coefficient value of 130 mV/come. Later, they also carried out similar work with BaTiO\textsubscript{3}-NiFe\textsubscript{2}O\textsubscript{4} doped with Co and Mn but found smaller values of magneto-electric coefficients.

Lupeiko et.al. (1994) reported magneto-electric coefficient in PZT-NiFe\textsubscript{2}O\textsubscript{4} based composites. They also carried out measurements with the addition of Bi\textsubscript{2}O\textsubscript{3} with dopants of manganese and copper oxides in the composites. The observed values of magneto-electric coefficients were \(151 \times 10^3\) V/A. The work was extended with the first laminated structure based magneto-electric composites (Lupeiko et al.,1995). They showed their work on the basis of connectivity pattern in the composites and observed higher values of magneto-electric coefficients. The corresponding work was carried out in various places and reported with connectivity schemes including 3-0 and 2-0 with composite materials such as BaTiO\textsubscript{3}-NiFe\textsubscript{2}O\textsubscript{4}, BaTiO\textsubscript{3}-LiFe\textsubscript{5}O\textsubscript{8}, Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12}-CoFe\textsubscript{2}O\textsubscript{4}.

Ryu et.al. (2002) reported giant magneto-electric coefficient in the laminated structure composites of piezoelectric PMN-PT single crystal and magnetostrictive
tefernol-D single crystal. They observed magneto-electric coefficient of 10.3 V/CmOe, almost 80 times higher than any previously reported work. Even though they reported such high values but there is a fundamental limitation on the magnitude of the magneto-electric coefficient of this structure. Due to the laminated structure and bonding layer the long term stability of these composite materials is still difficult to achieve. Also, the structure is difficult to miniaturize which limits their use in small device applications.

Table below shows the various magnetic units described to analyze the properties of a material.

Table 2.3: Conversion of Magnetic units (Source – Semiconductor group Siemens)

<table>
<thead>
<tr>
<th>Unit System</th>
<th>Magnetic Induction, $B$</th>
<th>Magnetic Field, $H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI units</td>
<td>Tesla: $1T = 1Vs/Am^2$</td>
<td>A/m</td>
</tr>
<tr>
<td>Older units</td>
<td>Gauss: $1G = 10^{-4}T$</td>
<td>Oersted: $1Oe = 10^7/4\pi A/m$</td>
</tr>
</tbody>
</table>

Conversion Table for Common Magnetic Units

<table>
<thead>
<tr>
<th></th>
<th>mT (Tesla)</th>
<th>G (Gauss)</th>
<th>kA/m</th>
<th>Oe (Oersted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mT</td>
<td>= 1.0000</td>
<td>= 10.000</td>
<td>= 0.7960*</td>
<td>= 10.000*</td>
</tr>
<tr>
<td>1G</td>
<td>= 0.1000</td>
<td>= 1.0000</td>
<td>= 0.7960*</td>
<td>= 10.000*</td>
</tr>
<tr>
<td>1 kA/m</td>
<td>= 1.2560*</td>
<td>= 12.560*</td>
<td>= 1.0000</td>
<td>= 12.560</td>
</tr>
<tr>
<td>1 Oe</td>
<td>= 0.1000*</td>
<td>= 1.0000*</td>
<td>= 0.0796</td>
<td>= 1.0000</td>
</tr>
</tbody>
</table>

* in free air
Chapter 3
EXPERIMENTAL PROCEDURE

3.1 Introduction

It is the intent of this chapter to describe the experimental procedures used to synthesize and characterize of various ceramic samples in our research works on relaxor ferroelectrics and magnetoelectric composites. Compositions are prepared by means of conventional mixed oxide solid state reactions among oxide powders to form desired phases and then later consolidated into highly dense polycrystalline materials. Electrical measurements are performed on dense samples to explore the dielectric pyroelectric response in the presence of an electrical stimulus. Thermal strain measurement has been carried out by dilatometry experiments. Structural information and phase purity are determined using room temperature X–ray diffraction techniques. Temperature dependent powder neutron diffraction technique, high q-resolution neutron diffraction by triple axis spectrometer and Raman spectra are used in wide range of temperatures to explore the micro/macro structure of the relaxor materials and are correlated to the macroscopic electrical properties. Magnetoelectric set up is also described for the magnetoelectric coefficients measured for the composites.

3.2 Ceramic Processing

The following sections describe the synthesis of ceramics materials and composite for developing the environmental friendly lead free relaxor ferroelectrics and
magnetoelectric meta-materials. Research on the relaxor ferroelectricity has been carried out on the environmental friend lead free BaZr$_x$Ti$_{1-x}$O$_3$ ceramics and its composite with dielectric MgO. Magnetoelectric materials have been prepared by making composite of ferroelectric and magnetostrictive materials. In this thesis work PbMg$_{1/3}$Nb$_{2/3}$O$_3$-31% PbTiO$_3$ (PMN-PT) has been used as the ferroic material and ferrites like CoFe$_2$O$_4$ and Mn$_{0.1}$Zn$_{0.9}$Fe$_2$O$_4$ are used as the magnetostrictive materials.

3.2.1 Processing of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics and its composite with MgO

Conventional mixed oxide ceramic processing was used to synthesize the compositions of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics. Samples were fabricated with reagent grade oxide powders, barium carbonate (BaCO$_3$, 99.997%, Alfa Aesar), titanium oxide (TiO$_2$, 99.995%, Alfa Aesar) and Zirconia (ZrO$_2$, 99.978%, Alfa Aesar). The starting powders were all tested for loss on ignition (accounting for hydroxyl and carbonates that evolve during firing) to reduce the driving force of secondary phase formation.

To prepare the stoichiometric compositions of Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics with $x=1.00$, 0.95, 0.90, 0.85, 0.80, 0.75, 0.70, 0.60, 0.50, 0.45, 0.40 and 0.35, powders were stoichiometrically weighed and mixed in ball-mill for 30 h with stabilized zirconia media (TOSOH Ceramics) using alcohol as the milling media. These mixtures were then dried at 353 K. Calcination of the mixed powder was carried out at 1473K for 2 hrs. Before pelletization, the calcined powders were ball-milled for breaking the agglomerates with stabilized zirconia media and dried as detailed above. To improve the green strength of the powder compacts, acrylic binder was added to the powder at 3–5 wt% and crushed to pass through an 80–mesh sieve before pressing pellets of 10 mm diameter. Pellets were
Fig. 3.1 Schematic flow–chart of the mixed oxide ceramic processing route.

1. **BaCO$_3$ (99.997%)**, **ZrO$_2$ (99.998%)**, **TiO$_3$ (99.995%)**

2. Mixing in Ball-mill for 30 hrs. using Alcohol

3. Drying at 80$^\circ$C

4. Calcination at 1200$^\circ$C for 2 hrs.

5. Ball-milling for breaking the agglomerates

6. Drying at 80$^\circ$C

7. 3–5 wt% acrylic binder added and powder crushed to pass 80–mesh sieve

8. Pressing-Green Pellet

9. Binder burnout 550$^\circ$C (1.5$^\circ$/min heating rate)

10. Sintering at 1500 – 1600$^\circ$C for 15 hrs.

11. XRD for phase determination
pressed under a uniaxial pressure of 300 MPa and underwent binder burnout at 823 K. After the binder burn-out, samples were sintered in closed crucibles at temperatures between 1773 K and 1873K for 15 hrs. Weight losses were maintained below 0.1%, indicating no major changes in stoichiometry. Figure 3.1 depicts a flowchart of the mixed oxide processing route used in this study.

To prepare the stoichiometric composites of $v$Ba(Zr$_x$Ti$_{1-x}$)O$_3$:MgO with $x=0.20$ and 0.25, the conventional solid state route has been followed as described above. Powders of BaCO$_3$ (99.997%), TiO$_2$ (99.995%) and ZrO$_2$ (99.978%) in appropriate ratios were mixed in ball-mill and calcined at 1473K for 2 h and milled again the same process as shown in figure 3.1 for preparing BZT ceramics. Then, high purity grade magnesium oxide (MgO, Alfa Aesar) was added to the Ba(Zr,Ti)O$_3$ powder, in the weight ratio of 50:50 (BZT:MgO) and the mixture was ball milled again. After adding the binder the composite powder was pressed into pellets. Then binder burn out was carried out at 823K. Sintering of the pellets was carried out at 1773K for 10 h.

3.2.2 Processing of Magnetoelectric Composites

Magnetoelectric composites were prepared with PMN-PT as piezoelectric phase. Figure 3.2 shows the phase diagram of PMN-PT. Its is believed [Randall et.al. (1990)] that the morphotropic phase boundary (MPB) region lies with PbTiO$_3$ percentage between 30-35%. PMN-PT composition with 31% PbTiO$_3$ has been chosen for the current research work to shift the cubic phase to temperature higher than room temperature as shown in the figure 3.3. Also the purpose for choosing this composition is to use the advantage of MPB to achieve high electrostrictive coefficients.
Fig. 3.2 Phase diagram of PMN-PT as a function of mole percentage of PbTiO₃ [Randall et.al. (1990)].

Fig. 3.3 Temperature dependence of dielectric constant of PMN-31%PT crystal [Randall et.al. (1990)].
Materials chosen for magnetic phase were ferrites such as CoFe$_2$O$_4$ and Mn$_{0.1}$Zn$_{0.9}$Fe$_2$O$_4$. These materials have high magnetostrictive coefficients and high reproducible properties.

Magnetoelectric composites were prepared by mixed oxide ceramic processing route with sintering in both conventional furnace and microwave furnace with E-field. The starting chemical powders used in this research are PMN-31%PT (TRS Technologies Inc.), CoFe$_2$O$_4$ (MRI, PSU) and Mn$_{0.1}$Zn$_{0.9}$Fe$_2$O$_4$ (MRI, PSU). All the pre-calcined powders were weighed and mixed in appropriate ratios to prepare the stoichiometric composites of PMN-31%PT : CoFe$_2$O$_4$ and PMN-31%PT : Mn$_{0.1}$Zn$_{0.9}$Fe$_2$O$_4$ with both (60:40) and (80:20) weight ratios. After adding the binder the composite powder was pressed into pellets. Then binder burn out was carried out at 823K. After binder burn-out, samples were pressed in Cold Isostatic Press (CIP) at 30000 Pa to achieve high green density and close the open pores appeared during the binder burn-out process. After pressing, samples were ready for sintering. Sintering of the pellets was carried out at 1473K for 2 hrs. in conventional furnace E-field microwave sintering has been carried out at 1273 K for 10 mins.

Microwave sintering is fundamentally different from conventional sintering in its heating mechanism [Roy et.al. (1985, 1997, 1999, 2002), Fang (1994), Fukushima et.al. (1994), Lee et.al. (1997), Agrawal (1998), Peelamedu et.al. (2001), Cheng et.al. (2001, 2002)]. Figure 3.4 shows the comparison mechanism in conventional and microwave sintering. Due to microwaves direct interaction with the matter and absorption, it results into volumetric heating of a material during microwave processing. In microwave heating, heat is generated by material interaction with microwaves within material instead of
Fig. 3.4 Comparison of heating mechanism in conventional and microwave sintering.

being transferred from the surrounding through external heating sources as in conventional heating. Due to volumetric heating, the microwave sintering is quite uniform. Due to heat loss at the surface the thermal gradients in the material being microwave sintered are reversed that those of the conventional heating. Therefore, if a good insulation package is not applied around the sample, the core of the work piece will be hotter than the surface. The penetrating nature of the microwave energy also means a quick response between the input power and the heating of a material. In other words, microwave heating has no thermal lag, which makes it possible to reach high temperatures very rapidly. The rapid sintering in microwave also limits the grain growth and leads to fine microstructure, consequently improving the mechanical, dielectric, and magnetoelectric properties of the material.
Fig. 3.5 Schematic diagram of the single mode microwave set-up.

- Microwave generator power source
- Magnetron head
- Circulator
- Dummy Load (with water cooling)
- E-H Tuner
- TE103 single mode microwave cavity
- Plunger
- Infrared pyrometer

Sample in H-field maximum
Sample in E-field maximum
The absorption of microwaves by a material depend on the material’s complex permittivity (ε*) and complex permeability (μ*) which are composed of real and imaginary parts as shown in equation 3.1 and equation 3.2 below:

\[ \varepsilon^* = \varepsilon' - \varepsilon'' = \varepsilon_0 (\varepsilon'_r - j \varepsilon''_r) \]  

(3.1)

\[ \mu^* = \mu' - \mu'' = \mu_0 (\mu'_r - j \mu''_r) \]  

(3.2)

where, \( \varepsilon_0, \mu_0 \) are permittivity and permeability of free space and \( \varepsilon'_r, \mu'_r \) are the effective relative dielectric and magnetic loss factors respectively.

When microwaves penetrate through a material, the internal electric fields generated within the affected volume induce translational motions of free or bound charges and rotate the charge complexes such as dipoles. The resistance of these induced motions, which are frequency dependent, causes losses which results in volumetric heating of a material.

The microwave power, \( P \), absorbed by a material inside a microwave cavity is expressed by equation 3.3 as shown below:

\[ P = 2\pi f_0 (\varepsilon_0 \varepsilon_r \tan \delta |E|^2 + \mu_0 \mu_r \tan \varphi |H|^2) \]  

(3.3)

Where, \( E \) – electric field component

\( H \) – magnetic field component

\( \tan \delta \) and \( \tan \varphi \) are the dielectric and magnetic loss components.

Both electric (E-field) and magnetic (H-field) field components participate in the absorption mechanism of microwave energy in a material. In the multi mode microwave cavity, both E-field and H-field components are used for sintering, where as, in single-
mode microwave cavity, E-field and H-field can be separated and the sample can be sintered in either field depending on the selection of field component and materials.

In our current research work single mode E-field microwave sintering is used. Figure 3.5 shows the schematic diagram of the single mode microwave set-up.

### 3.3 Density measurements

The density of the samples was measured based on buoyancy principle. In this technique weight of the sample was measured in air and followed by weight in liquid. Then, the sample weight was measured again in air. Using these three measurements density of the sample can be calculated by the following equation:

\[
Density = \frac{W_{air}}{W_{liquid} - W''_{air}} \times Density_{liquid}
\]  \hspace{1cm} (3.4)

where \( W_{air} \) is the weight of the sample measured in air after immersing in liquid. The liquid used in for calculation of density was water and xylene. The density values of water at room temperature 1g/cc and of xylene 0.861075 g/cc were used for the calculations.

### 3.4 X-ray Diffraction Study

Phase determination and room temperature structural analysis were carried out by x-ray diffraction (XRD) (Scintag PADV diffractometer) technique using DSMNT (Scintag) data acquisition and analysis software. Scans were normally obtained at room temperature in the 20 range from 10 to 120 degrees with a step size of 0.02 degrees, a count time of 0.5 seconds and a step scan rate of 0.04 degrees per minute. Calcined
powders and sintered pellets were crushed and annealed \((T > T_c)\) to form powder mounts in a zero background single crystal quartz holder for XRD analysis.

3.5 Scanning Electron Microscope (SEM) / Energy Dispersive Spectrum (EDS) Characterization

SEM and EDS studies were carried out to examine the microstructure evolution, grain size distribution and uniformity of grains and chemical reactivity. Scanning electron microscopy (SEM, Hitachi S–3500N) was used to study the microstructure of polished pellet surfaces. The pellet surfaces were polished to a 0.3 \(\mu\)m finish and thermally etched at about \(3/4\) the sintering temperature, typically \(\sim 1100^\circ\)C for 15 minutes. The software package UTHSCSA Image Tool was used to measure the average grain size. The final average grain size was calculated by adjusting for the two dimensional cross section of three dimensional grains by multiplying by a factor of 1.56 according to Fullman [1953]. Energy dispersive spectroscopy (EDS, Princeton Gamma Tech) was used in conjunction with the SEM analysis to identify and quantify local elemental compositions of selected samples.

3.6 Neutron diffraction measurements

Neutron powder diffraction data were collected using the BT-1 high-resolution powder diffractometer at the NIST Center for Neutron Research. Photograph of BT-1 and schematic diagram of the instrument are shown in figure 3.6. A monochromatic neutron beam \((1.5403 \text{ A}^0)\) was produced by a Cu \((3 1 1)\) monochromator, with \(90^\circ\) take off angle. Collimators with horizontal divergences of 15, 20, and 7 arcmin were used before and
Fig. 3.6 Photograph of BT-1 (Top) and schematic diagram of the instrument as viewed from above (below).
Fig. 3.7 Photograph of BT-9 triple axis spectrometer (Top) and schematic diagram of the top-view of the instrument (below).
after the monochromator, and after the sample, respectively. About 10 g of sample was sealed under inert atmosphere inside a vanadium can about 5 cm high and 0.9 cm in diameter. The diffraction intensities were measured in steps of 0.05° in the 2θ range from 3° and 168°. The sample was cooled with a He- cryostat under vacuum. Data was collected in the temperature range from 300 K to 4 K.

High q-resolution neutron scattering data were collected on the BT-9 triple axis spectrometer located at the NIST Center for Neutron Research. Photograph of BT-9 and schematic diagram of the top-view of the instrument are shown in figure 3.7. The diffuse scattering near the Bragg peaks was measured at fixed incident and final neutron energies $E_i = E_f = 14.7$ meV ($\lambda = 2.359$ Å) using the (002) reflection of highly oriented prolytic graphite (HOPG) crystals as monochromator and analyzer. To maximize the instrumental sensitivity to subtle structural distortions and changes in lattice spacing of the ceramic samples, the BT9 spectrometer was operated in a special non-standard configuration in which no analyzer was placed. The horizontal beam collimations were 15'-47'-10'-10' when analyzer was used and 15'-47'-open-10' when no analyzer was used.

3.7 Rietveld Refinement of Powder Neutron diffraction Data

The powder neutron diffraction data obtained on BZT samples were analyzed using Rietveld technique. Powder neutron diffraction has been widely used for many decades to identify and characterize the crystal structure. The disadvantages of powder neutron diffraction data for structural analysis are the effects of peak overlapping which is severe at high scattering angles, difficulty of measuring accurate Bragg intensities, merging of weak intensity reflections into background. Other factors affecting the powder
neutron diffraction data are preferred orientation, fluorescence profile broadening and instrumental effects. Due to all these limitations, it is very difficult to extract the detailed structural information from powder diffraction data. However many of these factors can be taken care of by the introduction of suitable corrections. Conventional method of profile fitting is used to obtain positions and intensities of individual Bragg reflections from step-scanned diffraction data. The integrated intensities of individual reflections are used for obtaining structure factors. The hkl indices and the corresponding structure factors are used to solve the structure. However this profile fitting technique works well for relatively simple, high symmetry structures, which have diffraction patterns with minimal peak overlap. For complex structure with low symmetry, diffraction pattern might consist of hundreds of Bragg reflections with severe peak overlapping which makes it difficult and often impossible to decompose the pattern into its constituent reflections.

The application of the Rietveld method to powder neutron diffraction data yield maximum amount of information from the patterns in contrast to the convention profile fitting procedure, as it does not use integrated intensities of reflections but employs the entire powder diffraction pattern, thereby overcome the problem of peak overlap. In the Rietveld method, each data point in the digitized intensity versus 2\theta curve is an independent observation and during refinement procedure, structural parameters, background coefficients and profile parameters are varied in a least squares procedure until the simulated pattern based on the structural model matches well with the observed pattern. In the least squares refinement process, the quantity minimized is called residue (s). It is weighted sum of the squares of difference between the observed and calculated
values of the intensities, i.e. \( s = \sum w_i (y_i^{\text{obs}} - y_i^{\text{cal}})^2 \) where the weight \( w_i = \text{reciprocal of variance} \), \( y_i^{\text{obs}} \) = observed intensity at the \( i^{\text{th}} \) step and \( y_i^{\text{cal}} \) = calculated intensity at the \( i^{\text{th}} \) step. The calculated counts \( y_i^{\text{cal}} \) are determined by summing the contributions from neighboring Bragg reflections and the background.

In the Rietveld refinement of structure, at least one should have (a) a set of data of intensities with respect to angles and (b) appropriate value of the refinable (instrumental and structural) parameters, so that we could be able to refine the structure. Rietveld refinement process will adjust the refinable parameters until the residue is minimized. The different variables refinable in the Rietveld method are scale factor(s), zero angle of \( 2\theta (2\theta^0) \), cell parameters (a,b,c, \( \alpha, \beta, \gamma \)), atomic coordinates (x,y,z), thermal parameters\( (B_{ij}) \), occupancies\( (N) \), background parameters\( (B_i) \) and full width at half maximum parameters\[u, v, w\]. In the Rietveld refinement, the parameters are adjusted until the ‘best fit’ between the calculated and observed pattern is obtained. The best fit depends on whether a global minimum rather a false minimum has been reached. One needs various criteria of fit in order to make these judgments. To see the progress of refinement, some conventional fitting criteria have been used. They are generally called R-factors and are defined as under.

(a) \( R_p \) =profile agreement factor provides the summed over all profile points and is given by,
\[
R_p = \frac{\sum |y_i^{\text{obs}} - y_i^{\text{cal}}|}{\sum y_i^{\text{obs}}} \quad (3.5)
\]

(b) \( R_{wp} \) = weighted profile agreement factor. For precise and accurate fitting \( R_{wp} \) should be close to the expected R-factor.
\[
R_{wp} = \left[ \frac{\sum w_i (y_i^{\text{obs}} - y_i^{\text{cal}})^2}{\sum w_i (y_i^{\text{obs}})^2} \right]^{1/2} \quad (3.6)
\]
(c) $R_{\text{EXP}}$ = expected R-factor which is based on counting statistics only and is an estimation of minimum Rwp observable for a given. It will be high when data signal is weak and is given by,

$$R_{\text{EXP}} = \frac{[(N-P+C)/\sum w_i(y_i^{\text{obs}})^2]^{1/2}}{\sum w_i(y_i^{\text{obs}})^2}$$

(3.7)

Where $N$, $P$, and $C$ are number of observations, variables and constraints respectively.

(d) $R_B$ = R-Bragg factor.

$R_B$ is a useful quantity measuring the quality of structural fit, which relates to the peak area and not the peak shape.

$$R_B = \frac{\sum |I_k^{\text{obs}} - I_k^{\text{cal}}|}{\sum I_k^{\text{obs}}}$$

(3.8)

Where $I_k$ is the intensity assigned to the kth Bragg reflection at the end of the refinement cycles.

(c) The goodness of fit of the system is also represented by an indicator called chi-squared and expressed as

$$\chi^2 = S^2 = \frac{R_{\text{wp}}/R_\text{E}}{\sum} = \frac{S}{(N-P+C)}$$

(3.9)

3.8 Sample preparation for electrical measurements

Disk shaped samples were used whenever possible (or appropriate). The disks were ground until the faces were flat and parallel. Then the major faces were polished to a 12 $\mu$m finish using a silicon nitride polishing compound. 10 mm diameter disks were thinned to approximately $\leq 0.5$ mm during polishing. When other shapes were required, they were cut using an x-y saw with a diamond impregnated blade.

The polished ceramic samples were cleaned in an ultrasonic bath for 15 mins. After cleaning, the samples were annealed at 923 K to remove the strain developed during polishing. Gold electrodes were deposited using magnetron sputtering (SCD 050,
Bal-Tec Inc.) Any excess electrode on the sides of the samples was gently sanded off with fine sand-paper. The samples were tested with a digital multimeter to check the quality of the electrodes. To facilitate good electrical contact, a dot of air-dry silver was painted on the gold electrodes. Fine gauge silver wires was also attached when necessary.

3.9 Dielectric Measurements

Dielectric and the related electrical properties were measured in order to understand the dielectric constant vs temperature behavior, transition temperature and to observe the desirable dielectric constant in the materials. D.C. field dependent dielectric behavior was studied out to observe the E-field response of the samples.

The dielectric measurements were made in the temperature range of 15 K to 300 K using a multi frequency LCR meter. Multi- frequency LCR meter is a microprocessor controlled Impedance Bridge, which measures impedance of the specimen by supplying voltage signal (rms) of 1V under unbiased condition. LCR meter used in this experiment was HP-4284A. The impedance obtained by LCR meter is converted to capacitance and subsequently to dielectric permittivity and loss tangent in a computer assisted set up. The temperature controller (Lakeshore model 330) and a closed cycle helium cooled cryostat (Displex DS-202 and HC-2, APD Cryogenics Inc.) were used to vary the temperature of the system. Field dependent dielectric measurements were conducted with the addition of voltage source (TREK 610, TREK Inc.) and a 2 kV blocking circuit that isolated the LCR meter from the high voltages applied to sample. These instruments were interfaced with a
Fig. 3.8 Schematic diagram of the dielectric measurement set-up.
controlling computer for monitoring and collecting data. The sample holder of this system is capable of one sample per run.

A sample was placed in the vacuum chamber on thermally conductive grease to prevent undesired movement and shorts from occurring. The silver wires were attached to the electrodes in the vacuum chamber and a vacuum was created. Once the vacuum was established, the dielectric measurement can be started. Figure 3.8 shows a schematic diagram of the dielectric measurement set-up.

3.10 Pyroelectric Measurements

In the current work pyroelectric properties were measured in order to study the phase transition and polarization of the ceramic samples. The pyroelectric measurements were carried out in the same system as used for low temperature dielectric measurements. The pyroelectric measurements are conducted by using the Byre-Roundy [1972] technique in which the charge or current is measured as a function of temperature on a sample of known dimensions. For a crystal of area $A$, the collected current density $I$ can be related to the pyroelectric coefficient using the equation:

$$\rho = \frac{d\rho}{dT} = \frac{q}{AdT} = \frac{i}{AdT} = \frac{i}{A} \frac{dT}{dt}$$  \hspace{1cm} (3.10)

For pyroelectric measurements an electric field is applied to the sample through the high voltage source to electrically pole the sample while cooling the sample from 300 K to 15 K using an APD Cryogenics HC-2 unit controlled by a LakeShore 330 Autotuning Temperature Controller. After poling the voltage source is disconnected and the sample was shorted and grounded to remove any excess surface charge built up during poling.
Then it is hooked up to a pyroelectric measurement box that amplified input signal (and which was attached to a multimeter). A computer program was run which controlled the heating/cooling setup and data was collected by interfacing between the computer and the assisted measurement setup.

3.11 Thermal Strain Measurement

When a solid material is subjected to a change of temperature, there is a small change in the dimension of that solid i.e. a thermally induced strain is generated. For a homogeneous isotropic solid, this thermal strain is often proportional to the temperature change.

\[
\frac{\Delta L}{L} = \alpha [\Delta T]
\]

(3.11)

\[
\Delta L = \text{Change in Length} \\
\Delta T = \text{Change in Temperature} \\
\alpha = \text{Coefficient of Thermal Expansion (CTE)}
\]

Dilatometric thermal expansion measurements are generally employed to determine the thermal strain generated during the course of heating. The use of this technique has mainly been confined for the study of monophasic materials, alloys and composites. The information about phase transitions in materials, sintering behavior, thermal expansion coefficients and their anisotropies have been obtained from this technique.

In our current research thermal strain has been measured by this dilatometric method in the BZT relaxor compositions to determine the Burns temperature \(T_d\) i.e. the temperature where the relaxor ferroelectric starts deviating from the linear behavior of the thermal strain. Figure 3.9 shows the photograph of our dilatometric instrument used for
thermal strain measurement. Thermal strain was measured with reference to a standard sample like fused silica of the similar dimension.

![Image](image_url)

**Fig. 3.9** Photograph of the dilatometer used for the thermal strain measurements.

### 3.12 Raman Spectra

Raman spectra of the ceramic samples were recorded using an ISA T 64000 triple monochromator. An optical microscope with 80 X objective was used to focus the 514.5 nm radiation from a Coherent Innova 99 Ar+ laser on the sample. The same microscope objective was used to collect the backscattered radiation. The scattered light collected by the microscope and dispersed by the spectrometer was detected by a charge-coupled
device (CCD) detection system. With 1-inch CCD and 1800 grooves/mm grating, the spectral resolution was typically less than 1 cm \(^{-1}\).

### 3.13 Magneto-electric measurements

The magneto-electric measurements were carried out from the voltage output vs magnetic field measurements and were assisted by the help of University of Texas, Arlington. The basic feature of the magneto-electric measurements setup that was used for the measurements is shown in figure 3.10. In magnetoelectric composites, the electric polarization generated as a function of the applied magnetic field. Thus, applying magnetic field and measuring polarization provided magnetoelectric coefficient of the composite. The measurements of the non-linear magnetoelectric effect in composites require a DC bias along with an AC measuring magnetic field. A permanent magnet or a DC electromagnet provided the DC magnetic field bias. Thus, samples were placed between two electromagnets, which provided the bias field. A signal generator was required to drive the electromagnet coils and generated the AC magnetic field. The electric charge generated was measured through a charge amplifier and the output voltage from the amplifier measured through the oscilloscope. The output voltage and the AC magnetic field data was computed and the resulted magnetoelectric coefficient of the composites were calculated.

The results reported in this thesis were obtained using the Lock-in amplifier method. The magnetoelectric property was measured in the terms of the variation of the coefficient \(dE/dH\) as a function of d.c. magnetic bias field. An electromagnet (GMW 5403 Magnet, Power and Buckley Inc., New Zealand) was used for the bias field up to
0.25 T (2.5 kOe). The coefficient was measured directly as response of the sample to an a.c. magnetic input signal at 1 kHz and 1 Oe amplitude superimposed on the dc bias field, both parallel to the sample axis. A lock-in amplifier (Stanford Research Systems) was used to drive the Helmholtz coils and generate the a.c. magnetic field. The electric charge (Q) generated from the piezoelectric layer was measured through a charge amplifier (5010B Dual Mode Amplifier, Kistler Instrument Co. NY). The electric field generated in response to applied magnetic field was computed using the following equation, where $Q = C.V.$

$$E = \frac{Q}{A.\varepsilon_0.\varepsilon}$$

(3.12)

Fig. 3.10 Schematic diagram of the magnetoelectric measurement system
Chapter 4

Phase and Structural Characterization of BaZr$_x$Ti$_{1-x}$O$_3$ Ceramics

4.1 Introduction

In this chapter we have reported the room temperature XRD studies of all the BaZr$_x$Ti$_{1-x}$O$_3$ ceramics for structural analysis and phase purity checking. The structure of the BaZr$_x$Ti$_{1-x}$O$_3$ relaxor compositions have been investigated by powder neutron diffraction study and high q-resolution neutron diffraction by triple-axis spectrometer in the temperature range from 300 K to 4 K.

As discussed in previous chapter, all the BaZr$_x$Ti$_{1-x}$O$_3$ ceramics has been prepared by conventional solid state route. Prior to the measurement of the various physical properties of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics with $0.35 \leq x \leq 1.00$, all the compositions were verified to be single phase perovskite solid solution by room temperature x-ray diffraction measurements. As discussed in chapter 2 the global symmetry of the relaxor ferroelectrics are generally cubic. To investigate the structure of the BaZr$_x$Ti$_{1-x}$O$_3$ relaxor compositions powder neutron diffraction study has been carried out on the categorically chosen two BZT relaxor compositions, BaZr$_{0.30}$Ti$_{0.70}$O$_3$ (BZT-30) and BaZr$_{0.60}$Ti$_{0.40}$O$_3$ (BZT-60) in the temperature range from 300 K to 4 K. BaZr$_{0.30}$Ti$_{0.70}$O$_3$ is believed to be relaxor as discussed in the chapter 2.5.2 and the relaxor properties of the BaZr$_{0.60}$Ti$_{0.40}$O$_3$ ceramics are discussed in the next chapter. The global structure of the BZT relaxors shows the cubic symmetry down to 4 K. To further verify the structure of the BZT relaxor compositions high q-resolution neutron scattering study has been carried out using triple-axis spectrometer.
Fig. 4.1. XRD pattern of sintered Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} ceramics with 0.35 \leq x \leq 1.00.
4.2 Room temperature x-ray diffraction study

Figure 4.1 depicts the X-ray diffraction patterns of the sintered BaZrₓTi₁₋ₓO₃ ceramics with 0.35≤ₓ≤1.00. All the reflections in the XRD patterns can be indexed with respect to the perovskite structure as shown in figure 4.2 for Ba(Zr₀.₆₀Ti₀.₄₀)O₃ ceramic, as an example.

![XRD pattern of sintered Ba(Zr₀.₆₀Ti₀.₄₀)O₃ ceramic.](image)

It is evident from these diffraction patterns that single phase BaZrₓTi₁₋ₓO₃ ceramics are obtained for all the compositions as no extra peak of any secondary phase has been found in the diffraction patterns. This implicates that BaZrₓTi₁₋ₓO₃ exhibit as the solid solution system in the whole composition range 0≤ₓ≤1.00. As no splitting has been observed in any of the pseudocubic profiles of the diffraction pattern, the room temperature structure of the BaZrₓTi₁₋ₓO₃ ceramics with 0.35≤ₓ≤1.00 can be regarded as cubic.
Fig. 4.3. Powder neutron diffraction patterns of sintered BaZr$_{0.30}$Ti$_{0.70}$O$_3$ and Ba(Zr$_{0.6}$Ti$_{0.4}$)O$_3$ ceramics at various temperatures.
4.3 Neutron diffraction study of the BaZrxTi1-xO3 relaxor compositions

Figure 4.3 shows the powder neutron diffraction patterns of sintered BaZr0.3Ti0.7O3 and Ba(Zr0.6Ti0.4)O3 ceramics at various temperatures. The powder neutron diffraction data for the ceramic samples has been collected using BT-1 powder diffractometer in NIST. Data were collected at different temperatures viz. room temp, the temperature just below the Tm in dielectric constant peak and the temperature much below the Tm, as shown in the figure 4.3. It is to be noted that the Tm for BZT30 and BZT60 from the temperature dependence studies of dielectric behavior are ~230K and ~145K respectively at 100 kHz. It is evident from the figure that there is almost no change in pseudocubic profiles in the diffraction patterns with the decrease in temperature.

4.3.1 Rietveld Analysis of the BaZr1-xTi1-xO3 Structure

In order to understand the structure of the BZT ceramics, we carried out Rietveld analysis of the powder neutron diffraction data in the 2θ range 3 to 165 degrees for both the BZT compositions at various temperatures with the help of Full Prof Program [Rodriguez-Carvajal (2001)]. The background was fitted with sixth order polynomial, while the peak shapes were described by pseudo-Voigt function. In all the refinements, scale factor, zero correction, background, and half width parameters, lattice parameters, positional coordinates (x, y, z) and thermal parameters were varied. Occupancy parameters of all the ions were fixed to nominal composition during refinement. For all the ions, the isotropic thermal parameters (Biso) were also refined. No correlation between the positional and thermal parameters was observed during refinement and as such it was
Fig. 4.4. Observed (open circles), calculated (continuous lines) and difference (bottom of the figure) profiles obtained after Rietveld refinement of neutron powder diffraction data for Ba(Zr$_{0.30}$Ti$_{0.70}$)O$_3$ at 300 K and 230 K using the Cubic symmetry of space group Pm3m. The bars represent cubic peak positions.
Fig. 4.5. Observed (open circles), calculated (continuous lines) and difference (bottom of the figure) profiles obtained after Rietveld refinement of neutron powder diffraction data for Ba(Zr$_{0.30}$Ti$_{0.70}$)O$_3$ at 180 K and 4 K using the Cubic symmetry of space group Pm3m. The bars represent cubic peak positions.
Fig. 4.6. Observed (open circles), calculated (continuous lines) and difference (bottom of the figure) profiles obtained after Rietveld refinement of neutron powder diffraction data for Ba(Zr_{0.60}Ti_{0.40})O_3 at 300 K and 145 K using the Cubic symmetry of space group Pm3m. The bars represent cubic peak positions.
Fig. 4.7. Observed (open circles), calculated (continuous lines) and difference (bottom of the figure) profiles obtained after Rietveld refinement of neutron powder diffraction data for Ba(Zr_{0.60}Ti_{0.40})O_3 at 90 K using the Cubic symmetry of space group Pm3m. The bars represent cubic peak positions.

possible to refine all the parameters together. As no such splitting has been found in the Bragg peaks of the diffraction patterns the structure of the BZT ceramics were assumed to be cubic with Pm3m space group. In the cubic phase with the Pm3m space group, Ba occupies 1(a) sites at (0, 0, 0), Ti/Zr occupy 1(b) sites at (½, ½, ½) and oxygen occupies 3(c) sites at (½, ½, 0).

Figures 4.4 to 4.7 depict observed, calculated and difference profiles obtained after Rietveld refinement of neutron powder diffraction data for Ba(Zr_{0.30}Ti_{0.70})O_3 and Ba(Zr_{0.60}Ti_{0.40})O_3 ceramics at various temperatures in the 2θ range 3^0-165^0 using the
cubic symmetry of space group Pm3m. It is evident from the difference profiles that the fits are quite good. Refined structural parameters are listed in Tables 4.1 for both the BZT compositions at different temperatures. It is seen from the table that the lattice parameter for BZT-60 is higher than BZT-30 i.e. lattice parameter increases with increase in Zr\(^{4+}\) content. This is expected, as the lattice parameter of pure BaZrO\(_3\) is higher than that of pure BaTiO\(_3\). It is also evident that the small decrease in lattice parameter occurs with the decrease in temperature for both the compositions as shown in figure 4.8. From the Rietveld analysis of the powder diffraction data it can be concluded that the structure of BZT ceramics is cubic down to 4 K.

![Graph showing the evolution of lattice parameter with temperature for BZT-30 and BZT-60](image)

Fig. 4.8 Evolution of the lattice parameter with the temperature for BaZr\(_{0.30}\)Ti\(_{0.70}\)O\(_3\) (BZT-30) and BaZr\(_{0.60}\)Ti\(_{0.40}\)O\(_3\) (BZT-60) ceramics obtained after Rietveld analysis of the neutron powder diffraction data at various temperatures. The error bar for each data point is smaller than the size of the symbols.
Table 4.1: Refined structural parameters for Ba(Zr$_{0.30}$Ti$_{0.70}$)O$_3$ (BZT-30) and Ba(Zr$_{0.60}$Ti$_{0.40}$)O$_3$ (BZT-60) ceramics at various temperatures

<table>
<thead>
<tr>
<th>compo</th>
<th>coordinates</th>
<th>lattice parameter</th>
<th>Rwp</th>
<th>Rexp</th>
<th>R_p</th>
<th>R_B</th>
<th>$\chi^2$</th>
</tr>
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<td>x</td>
<td>y</td>
<td>z</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BZT30 at 300K</td>
<td>Ba 0 0 0</td>
<td>Zr/Ti 0.5 0.5 0.5</td>
<td>O 0.5 0.5 0</td>
<td>4.082759</td>
<td>19.3</td>
<td>8.72</td>
<td>22.4</td>
</tr>
<tr>
<td>BZT30 at 230K</td>
<td>0 0.5 0</td>
<td>Zr/Ti 0.5 0.5 0.5</td>
<td>O 0.5 0.5 0</td>
<td>4.080826</td>
<td>19.4</td>
<td>8.45</td>
<td>22.3</td>
</tr>
<tr>
<td>BZT30 at 180K</td>
<td>0 0.5 0</td>
<td>Zr/Ti 0.5 0.5 0.5</td>
<td>O 0.5 0.5 0</td>
<td>4.079673</td>
<td>19.3</td>
<td>8.30</td>
<td>22.0</td>
</tr>
<tr>
<td>BZT30 at 4 K</td>
<td>0 0.5 0</td>
<td>Zr/Ti 0.5 0.5 0.5</td>
<td>O 0.5 0.5 0</td>
<td>4.077271</td>
<td>18.3</td>
<td>8.96</td>
<td>19.2</td>
</tr>
<tr>
<td>BZT60 at 300K</td>
<td>0 0.5 0</td>
<td>Zr/Ti 0.5 0.5 0.5</td>
<td>O 0.5 0.5 0</td>
<td>4.131104</td>
<td>17.7</td>
<td>8.60</td>
<td>18.7</td>
</tr>
<tr>
<td>BZT60 at 145K</td>
<td>0 0.5 0</td>
<td>Zr/Ti 0.5 0.5 0.5</td>
<td>O 0.5 0.5 0</td>
<td>4.126984</td>
<td>18.1</td>
<td>8.07</td>
<td>18.6</td>
</tr>
<tr>
<td>BZT60 at 90 K</td>
<td>0 0.5 0</td>
<td>Zr/Ti 0.5 0.5 0.5</td>
<td>O 0.5 0.5 0</td>
<td>4.126512</td>
<td>17.6</td>
<td>7.92</td>
<td>17.9</td>
</tr>
</tbody>
</table>
Fig. 4.9 Evolution of the (111) Bragg peak with temperature in the high q-resolution neutron scattering study of BaZr$_{0.30}$Ti$_{0.70}$O$_3$ (BZT-30) ceramics
Fig. 4.10 Evolution of the (111) and (200) Bragg peaks with temperature in the high q-resolution neutron scattering study of BaZr_{0.60}Ti_{0.40}O_{3} (BZT-60) ceramics.

### 4.3.2 High q-resolution neutron diffraction of the BaZr_{x}Ti_{1-x}O_{3} ceramics

High q-resolution neutron scattering data has been collected on BaZr_{0.30}Ti_{0.70}O_{3} (BZT-30) and BaZr_{0.60}Ti_{0.40}O_{3} (BZT-60) ceramics samples using BT-9 triple axis spectrometer. Figure 4.9 shows the evolution of the (111) Bragg peak with temperature in the high q-resolution neutron scattering study of BaZr_{0.30}Ti_{0.70}O_{3} (BZT-30) ceramics. As shown in the figure we observe no splitting of the (111) Bragg peak at any temperature. Subsequent neutron measurements of the (200) Bragg peak, taken with even higher q-resolution, also exhibit no splitting. In case of BaZr_{0.60}Ti_{0.40}O_{3} (BZT-60) ceramics,
evolution of the (111) and (200) Bragg peaks with temperature has been studied using the high q-resolution neutron scattering as shown in figure 4.10. No splitting has been observed for BZT-60 even at 4 K and mirror the results obtained for BZT-30. Although no such splitting was observed in the neutron diffraction studies, the structure of the BZT compositions can’t be cubic as it shows very high dielectric peak and high tunability in the field dependent dielectric behavior of these two compositions as shown in the next chapter. It is to be noted that global structure of the relaxor is cubic but the local symmetry deviates from its global structure.

In conclusion we have studied the room temperature XRD and temperature dependent neutron diffraction study in BaZr$_x$Ti$_{1-x}$O$_3$ ceramics. All the BZT compositions were verified to be single phase perovskite solid solution. The BZT relaxor compositions retain its average cubic structure down to 4 K like the classical relaxor ferroelectric PMN [Bonneau et.al. (1989), de Mathan et.al. (1991)].
Chapter 5
BaZr$_x$Ti$_{1-x}$O$_3$ Relaxor Ferroelectrics

5.1 Introduction

In the search of environmental-friendly lead free relaxor materials efforts have been made currently to introduce relaxor behavior by doping A or B site ions in ABO$_3$ perovskites like quantum para-electric SrTiO$_3$, KTaO$_3$ and in typical ferroelectric BaTiO$_3$. Recently BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) solid solution has received renewal attention due to its high-strain level, high piezoelectric properties and its potentiality as high Q materials for various microwave device applications [Rherig et.al. (1999), Yu et.al. (2000 and 2002) and Davies (1994)]. As discussed in chapter 2.5.2 various scientists have worked on BaZr$_x$Ti$_{1-x}$O$_3$ system with low Zr concentration. The system (BaZr$_x$Ti$_{1-x}$O$_3$) exhibits a pinched phase transition at x~ 0.15, i.e. all the three phase transitions correspond to pure BaTiO$_3$ are merged or pinched into one broad peak. Further increase in Zr concentration a typical ferroelectric relaxor behavior has been observed in BaZr$_x$Ti$_{1-x}$O$_3$ compositions with x>0.25. In contrast to the earlier studies on the BZT system, in our present work we have taken a “bottom-up” approach (i.e. starting the studies from the host non-ferroelectric, BaZrO$_3$) of the BaZr$_x$Ti$_{1-x}$O$_3$ phase diagram to understand at various stages, the dielectric properties, and their relative significance to the ferroelectric phenomena across the whole phase diagram. There are earlier studies where the relaxor behavior has been observed when the smaller amount of impurities of Bi, Ca, La etc. were introduced in the incipient ferroelectric matrix like SrTiO$_3$ [Bednorz et. al. (1984), Iguchi et. al. (1993), Bianchi et. al. (1995), Yu et. al. (1999) and Ang et. al. (2000)] and
Li, Nb etc in KTaO₃ [Samara et. al. (1984), Toulouse et. al. (1994) and Trepakov et. al. (2001)] or dopant like Hf, Ce, Sn etc were introduced in the proper ferroelectric, BaTiO₃ [Novosi'tsev et. al. (1956), Payne et. al. (1965) and Zhi et. al. (1997)]. In our present approach we have studied the successive changes of the dielectric behavior with the gradual addition of Ti⁴⁺ ion for the Zr⁴⁺ in a non-ferroelectric matrix of BaZrO₃ and finally the evolution of the relaxor ferroelectric behavior in the BZT system. It is worthy to note that BaZrO₃ as a host perovskite matrix has very low dielectric constant (~ 27) in comparison to the other incipient perovskite host matrix (with dielectric constants of several thousands) like SrTiO₃, KTaO₃ or BaTiO₃ used in the studies. To the best of our knowledge there are no reports on the dielectric behavior in the higher BaZrO₃ concentration of this solid solution system.

In this chapter, we report the dielectric behavior of BaZrₓTi₁₋ₓO₃ compositions with 0.35<x<1.00. In the Zr⁴⁺ rich BaZrₓTi₁₋ₓO₃ solid solution compositions (0.80≤x≤1.00) polar cluster like behavior has been observed. However, in the composition range 0.35<x<0.75 BaZrₓTi₁₋ₓO₃ ceramics show the relaxor ferroelectric behavior. Further analysis of the dielectric relaxation in all the BaZrₓTi₁₋ₓO₃ ceramics has been done by Curie-Weiss behavior, calculating the degree of relaxation, γ, and Vogel-Fulcher relation. Electric field response of all the BZT ceramics in dielectric properties has also been studied. To study the order-disorder phenomena in BZT relaxor ferroelectrics pyroelectric and thermal expansion behavior are also discussed in this chapter. Finally to understand the role of polar clusters in the BZT relaxors a comprehensive structure-property correlation has been elucidated by Raman spectroscopy.
in relation to the dielectric, pyroelectric behavior in addition with the structural analysis given in Chapter 4.

5.2. The polar cluster like behavior in Ti$^{4+}$ substituted BaZrO$_3$ ceramics

In this section we report the polar cluster like behavior after introducing Ti$^{4+}$ ions gradually in the matrix of BaZrO$_3$, which has very low dielectric constant (~ 27). Dielectric behavior of BaZr$_x$Ti$_{1-x}$O$_3$ (x=1.00, 0.95, 0.90, 0.85) ceramics is studied in the temperature range from 300K to 30K. Polar cluster like behavior becomes more prominent with the increase in content of Ti$^{4+}$ ion. The dielectric relaxation is analyzed by Vogel-Fulcher relation.

5.2.1 Dielectric Behavior

The temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ compositions with x=1.00, 0.95, 0.90 and 0.85 is shown in figure 5.1 and 5.2. In case of pure BaZrO$_3$ the change in dielectric constant is very small (~ 10%) in the temperature range from 300K to 15K. However, the increasing trend of dielectric constant with decrease in temperature has been observed up to 40K. Below 40K the signature of weak quantum paraelectric behavior has been observed, as the dielectric permittivity tends to saturate in the low temperature. Whereas, for the composition $x = 0.95$ plateau shaped dielectric behavior is observed which disappeared with the further increase in Ti concentrations. For $0.85 \leq x \leq 0.95$ strong frequency dispersion is observed around the $\varepsilon$ and tan$\delta$ peak, which becomes broader with increase in Ti content. One of the common features noticed in dielectric behavior of all the BZT compositions is that, with increasing frequency $\varepsilon'$ decreases and the temperature ($T_m$)
where the maxima occur is shifted to higher temperatures. In the same manner the temperature of the loss maxima increases with increase in frequency whereas peak value increases unlike $\varepsilon'$. This kind of dielectric behavior is one of the characteristics of a typical ferroelectric like relaxors. Unlike the typical ferroelectric relaxor materials, no thermal hysteresis has been observed during the heating and cooling cycles of the dielectric behavior of all the BZT ceramics as shown in figure 5.3 for Ba(Zr$_{x}$Ti$_{1-x}$)O$_{3}$ compositions with $x=0.90$ and 0.85. In the following section analysis of the dielectric properties of the BZT compositions has been done.
Fig. 5.1. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan\(\delta\)) at various frequencies for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x=1.00$ and 0.95 (Arrows indicate the direction of increasing frequency).
Fig. 5.2. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at various frequencies for $\text{Ba(Zr}_x\text{Ti}_{1-x})\text{O}_3$ with $x=0.90$ and 0.85 (Arrows indicate the direction of increasing frequency).
Fig. 5.3. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) during cooling and heating in the temperature range from 300K to 30K at various frequencies (1kHz, 10kHz, 100kHz and 1 MHz) for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x=0.90$ and 0.85 (Arrows indicate the direction of increasing frequency).
5.2.2 Characterization of dielectric peak using Curie-Weiss Behavior

For a normal ferroelectric in the para-electric region, the Curie-Weiss law

\[ \frac{1}{\varepsilon} = \frac{T - T_0}{C} \quad (T > T_c) \quad (5.1) \]

is followed where \( T_0 \) is the Curie temperature and \( C \) is the Curie-Weiss constant. The inverse \( \varepsilon \) (for various samples) is plotted in figure 5.4 as a function of temperature at 100 kHz and the experimental data are fitted by equation (5.1) using non-linear curve fitting program for all the BZT compositions. The fitting parameters (\( C \) and \( T_0 \)) calculated only in the high temperature linear part are listed in Table 5.1 for all the BZT compositions. It is apparent from Table 5.1 that the value of \( T_0 \) increases systematically with the increase in Ti concentrations.

**Table 5.1** Summary of the fitting parameters of the dielectric behavior of BZT ceramics using Curie-Weiss law:

<table>
<thead>
<tr>
<th>Composition</th>
<th>( C ) (K)</th>
<th>( T_0 ) (K)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{BaZrO}_3 )</td>
<td>( 1.10 \times 10^5 )</td>
<td>-2933.81</td>
</tr>
<tr>
<td>( \text{Ba(Zr}<em>{0.95}\text{Ti}</em>{0.05})\text{O}_3 )</td>
<td>( 4.29 \times 10^4 )</td>
<td>-1115.84</td>
</tr>
<tr>
<td>( \text{Ba(Zr}<em>{0.90}\text{Ti}</em>{0.10})\text{O}_3 )</td>
<td>( 4.34 \times 10^4 )</td>
<td>-499.08</td>
</tr>
<tr>
<td>( \text{Ba(Zr}<em>{0.85}\text{Ti}</em>{0.15})\text{O}_3 )</td>
<td>( 4.27 \times 10^4 )</td>
<td>-255.69</td>
</tr>
</tbody>
</table>

* * Values below the absolute zero suggest the overlapping quantum effect deviating from the ideal curve fit near the \( T_m \).
Fig. 5.4. The inverse dielectric constant ($1/\varepsilon$) as a function of temperature at 100 kHz for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x=1.00$, 0.95, 0.90 and 0.85. (The symbols: experimental data; the solid line: fitting to the Curie-Weiss law). The insets show the plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ Vs $\ln(T - T_m)$ for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x=0.95$, 0.90 and 0.85 (The symbols: experimental data; the solid line: fitting to the Equation 5.2.).
It is seen that the dielectric constant of all the BZT compositions follows Curie-Weiss law at temperatures much higher than the $T_m$. The values of $T_0$ are not the realizable numbers but suggest some secondary influential features (such as quantum fluctuations etc.), near and below the relaxation peak, deviating from the ideal fit of Curie-Weiss behavior.

To describe the diffuseness of the phase transition of relaxor ferroelectrics a modified Curie-Weiss law has been proposed as the following [Uchino et.al. (1982)]:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C_1}$$

(5.2)

where, $\gamma$ and $C_1$ are assumed to be constant and $1 < \gamma < 2$. The limiting values $\gamma = 1$ and $\gamma = 2$ reduce the expression to Curie-Weiss law valid for the case of normal ferroelectric and to the quadratic dependence valid for an ideal relaxor ferroelectric, respectively. The values of $\gamma$ obtained from the experimental data fitted by equation (5.2) using non-linear curve fitting program for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ compositions are 1.51, 1.55 and 1.35 for $x = 0.95$, 0.90 and 0.85, respectively as shown in the insets of the figure 5.4. The values of $\gamma$ greater than 1 for all the BZT compositions show the gradual departure from the behavior of normal Curie-Weiss behavior and simultaneously perhaps the evolution or the presence of polar cluster like behavior.

### 5.2.3 Temperature dependence of the relaxation time

In a dielectric material, if the dielectric relaxation process is governed by a thermally activated motion, the temperature dependence of the relaxation time ($\tau$) follows the Arrhenius law:

$$\tau = \tau_0 \exp\left[\frac{E_{\text{relax}}}{(K_B T)}\right]$$

(5.3)
Table 5.2 Summary of the Arrhenius fitting parameters of BZT ceramics:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Activation energy ($E_{\text{relax}}$) (eV)</th>
<th>$\tau_0$ (Pico-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(Zr$<em>{0.95}$Ti$</em>{0.05}$)O$_3$</td>
<td>0.085 (±0.004)</td>
<td>30.83</td>
</tr>
<tr>
<td>Ba(Zr$<em>{0.90}$Ti$</em>{0.10}$)O$_3$</td>
<td>0.087 (±0.002)</td>
<td>8.13</td>
</tr>
<tr>
<td>Ba(Zr$<em>{0.85}$Ti$</em>{0.15}$)O$_3$</td>
<td>0.081 (±0.002)</td>
<td>6.36</td>
</tr>
</tbody>
</table>

Fig. 5.5. Arrhenius-type temperature dependence of relaxation time ($\tau$) for BaZr$_x$Ti$_{1-x}$O$_3$ ceramics with $x =$0.95, 0.90 and 0.85.

where, $\tau_0$ is the relaxation time at infinite temperature, $E_{\text{relax}}$ the activation energy for relaxation, $K_B$ the Boltzmann’s constant and $T$ the temperature. Experimental data are fitted with the equation (5.3) using non-linear curve fitting program for all the BZT compositions and the results are tabulated in Table 5.2. The temperature dependences of relaxation rate ($\tau$) for the BaZr$_x$Ti$_{1-x}$O$_3$ ceramics with $x =$0.95, 0.90 and 0.85 are shown in figure 5.5.
To understand the possible linkage with the ferroelectric relaxor like behavior the relaxation time in general should follow Vogel-Fulcher relations more closely rather than Arrhenius law. The relaxation time ($\tau$) following Vogel-Fulcher relation is one of the characteristics of the relaxor ferroelectrics. The Vogel-Fulcher [1921 and 1925] law originally derived for the spin-glass systems is described as follows:

$$\tau = \tau_0 \exp \left[ \frac{E_a}{K_B(T - T_{VF})} \right]$$  \hspace{1cm} (5.4)

where $\tau_0$ is the pre-exponential factor, $E_a$ is the activation energy and $T_{VF}$ is the characteristic Vogel-Fulcher temperature. It is found that temperature dependence of relaxation time can be well-fitted as shown in figure 5.6. The fitting parameters are summarized in Table 5.3. It is seen that fitting of the relaxation time to Vogel-Fulcher law is little better than that to the Arrhenius equation.

Fig. 5.6. Temperature dependence of relaxation time ($\tau$) for BaZr$_x$Ti$_{1-x}$O$_3$ ceramics with $x$ = 0.95, 0.90 and 0.85. (The symbols: experimental data; the solid curve: fitting to the Vogel-Fulcher relation).
Table 5.3 Summary of the Vogel-Fulcher fitting parameters of BZT ceramics:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Freezing temperature ($T_{VF}$) (K)</th>
<th>Activation energy ($E_a$) (eV)</th>
<th>Pre-exponential factor ($\tau_0$) (Pico-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ba}(\text{Zr}<em>{0.95}\text{Ti}</em>{0.05})\text{O}_3$</td>
<td>-29 ($\pm$12)</td>
<td>0.17 ($\pm$0.004)</td>
<td>0.050</td>
</tr>
<tr>
<td>$\text{Ba}(\text{Zr}<em>{0.90}\text{Ti}</em>{0.10})\text{O}_3$</td>
<td>-20 ($\pm$9)</td>
<td>0.15 ($\pm$0.003)</td>
<td>0.049</td>
</tr>
<tr>
<td>$\text{Ba}(\text{Zr}<em>{0.85}\text{Ti}</em>{0.15})\text{O}_3$</td>
<td>-18 ($\pm$6)</td>
<td>0.14 ($\pm$0.006)</td>
<td>0.034</td>
</tr>
</tbody>
</table>

The fitted, $T_{VF}$, freezing temperature values below the absolute zero suggest the dynamic nature of the clusters down to near 0 K. It also suggests that dynamic behavior near 0 K may be influenced or superimposed by the quantum fluctuations.

5.2.4. Discussion

In our present work we have introduced polar clusters of BaTiO$_3$ in the matrix of BaZrO$_3$ breaking the long range translational symmetry of BaZrO$_3$ lattice. The evidence of the dynamic disorder due to the incorporation of polar clusters is suggested by the excellent fitting of Vogel-Fulcher relations to the experimental data of BZT ceramics. As the amount of polar BaTiO$_3$ clusters in very low dielectric BaZrO$_3$ (~27) matrix is scanty, the chances of interaction between the individual polar clusters are very slim which is evident in the E-field dependent studies of the dielectric behavior of all the BZT composition as shown in figure 5.7 for $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ compositions with $x=0.90$ and 0.85.
Fig. 5.7. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at 100 kHz for Ba(ZrxTi1-x)O3 compositions with x=0.90 and 0.85 with E = 0 kV/cm and under bias of E = 25 kV/cm and 35 kV/cm.
It is seen that there is no change in dielectric constant ($\varepsilon$) and loss tangent (tan$\delta$) with the application of D.C. field in the temperature range from 300K to 30K for all the BZT compositions. In addition, the observation of no thermal hysteresis in the dielectric behavior can be attributed to the fact that the enough polar clusters to the close enough proximities are not available to communicate with each other in BZT ceramics. Nevertheless, those small amounts of BaTiO$_3$ are good enough to involve the relaxor like behavior in a low dielectric material like BaZrO$_3$ ceramics.

5.2.5 Summary

In summary, the polar cluster like behavior is observed with the incorporation of Ti$^{4+}$ ion in BaZrO$_3$ Ceramics. Although enough polar clusters are not available to communicate with each other even with the application of d.c. field, those small amounts of BaTiO$_3$ are sufficient to show the relaxor like behavior in a low dielectric material like BZT ceramics.

The studies on BZT compositions with higher titanium concentrations may shed more understanding of the observed relaxation behavior and its evolution in this system.
5.3 Evolution of relaxor behavior in BaZr$_x$Ti$_{1-x}$O$_3$ Ceramics

In this section, we have studied how the relaxor behavior has gradually been evolved with the increasing substitution of Ti$^{4+}$ ions for the Zr$^{4+}$ in the matrix of BaZrO$_3$, which has very low dielectric constant (~ 27). Dielectric behavior of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics is studied in the temperature range from 300K to 15K. Relaxor behavior becomes more prominent with the increase in content of Ti$^{4+}$ ion i.e. with increasing amount of the polar regions. The dielectric relaxations in these ceramics are found to follow Vogel-Fulcher type behavior originally derived for the spin-glass systems. Dielectric behavior of BZT ceramics shows more electric field dependence with the increase in Ti$^{4+}$ rich polar regions. Based on the dielectric behavior of BZT ceramics both with E-field and without field, the observed relaxor behavior has been hypothesized due to the increasing amount of long range ordering of nano size Ti$^{4+}$ rich polar regions in the Zr$^{4+}$ rich non polar matrix. Beyond an optimum content of BaTiO$_3$ in the non polar matrix of BaZrO$_3$ ($x \leq 0.75$) probably a critical size and density of the polar regions are reached when polar cluster like BaZr$_x$Ti$_{1-x}$O$_3$ ($x \geq 0.80$) ceramics start showing the relaxor behavior.

5.3.1 Dielectric Behavior without Bias Electric Field

The temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at various frequencies for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ compositions with $x = 0.80, 0.75, 0.70, 0.60, 0.50, 0.45, 0.40$ and $0.35$ are shown in figure 5.8, 5.9, 5.10 and 5.11. Strong frequency dispersion is observed around the $\varepsilon$ and tan$\delta$ peak for all the BZT compositions. Similar
Fig. 5.8 Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at various frequencies for Ba(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ and for Ba(Zr$_{0.75}$Ti$_{0.25}$)O$_3$ (Arrows indicate the direction of increasing frequency).
Fig. 5.9 Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at various frequencies for Ba(Zr$_{0.70}$Ti$_{0.30}$)O$_3$ and for Ba(Zr$_{0.60}$Ti$_{0.40}$)O$_3$ (Arrows indicate the direction of increasing frequency).
Fig. 5.10. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at various frequencies for Ba(Zr$_{0.50}$Ti$_{0.50}$)O$_3$ and for Ba(Zr$_{0.45}$Ti$_{0.55}$)O$_3$ (Arrows indicate the direction of increasing frequency).
Fig. 5.11. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at various frequencies for Ba(Zr$_{0.40}$Ti$_{0.60}$)O$_3$ and for Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$ (Arrows indicate the direction of increasing frequency).
Fig. 5.12. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tanδ) during cooling (solid line) and heating (dash line) in the temperature range from 300K to 15K at various frequencies (100 Hz, 1kHz, 10kHz and 100kHz) for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x=0.70$, 0.60, 0.45 and 0.40 (Arrows indicate the direction of increasing frequency).
to a typical ferroelectric relaxor it is seen in all the BZT compositions that, with increasing frequency $\varepsilon'$ decreases and the temperature ($T_m$) where the dielectric maxima occur is shifted to higher temperatures. In the same manner the temperature of the loss maxima increases with increase in frequency whereas peak value increases unlike $\varepsilon'$. It is also evident from figures that two relaxor peaks, which are more visible in the loss tangent (tan$\delta$) curve for the composition $x=0.80$, gradually merged into single relaxor peak with increasing Ti$^{4+}$ content giving rise the classical relaxor behavior for $0.35 \leq x \leq 0.60$. Figure 5.12 shows the temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) during cooling and heating cycle in the temperature range from 300K to 15K at various frequencies for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x=0.70$, 0.60, 0.45 and 0.40. As shown in the figure no thermal hysteresis in the dielectric behavior of Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics is observed above the Zr content $x \geq 0.70$. With further increase in Ti content Ba(Zr$_x$Ti$_{1-x}$)O$_3$ compositions with $x \leq 0.60$ start showing thermal hysteresis behavior like a typical relaxor ferroelectric. From the dielectric behavior of all the BZT compositions, it is suggested that after certain concentrations of Ti$^{4+}$, polar cluster like Ba(Zr$_x$Ti$_{1-x}$)O$_3$ compositions behave like a classical relaxor ferroelectric as the amount of Ti$^{4+}$ polar regions in nonpolar BaZrO$_3$ matrix reach a percolation limit.

5.3.2 Analysis of dielectric relaxation using Curie-Weiss Behavior

A normal ferroelectric in the para-electric region generally follows the Curie-Weiss law:

$$\frac{1}{\varepsilon} = \frac{C}{T - T_0} \quad (T > T_c) \quad (5.5)$$

where $T_0$ is the Curie temperature and $C$ is the Curie-Weiss constant. The inverse $\varepsilon$ (for various samples) as a function of temperature at 100 kHz is plotted in figure 5.13 and figure 5.14.
Fig. 5.13. The inverse dielectric constant ($1/\varepsilon$) as a function of temperature at 100 kHz for Ba(ZrxTi1-x)O3 with x = 0.80, 0.75, 0.70 and 0.60. (The symbols: experimental data; the solid line: fitting to the Curie-Weiss law). The insets show the plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ vs $\ln(T - T_m)$ for Ba(ZrxTi1-x)O3 ceramics (The symbols: experimental data; the solid line: fitting to the Equation 5.6).
Fig. 5.14. The inverse dielectric constant \((1/\varepsilon)\) as a function of temperature at 100 kHz for Ba\((Zr_xTi_{1-x})O_3\) with \(x=0.50, 0.45, 0.40\) and 0.35. (The symbols: experimental data; the solid line: fitting to the Curie-Weiss law). The insets show the plot of \(\ln(1/\varepsilon - 1/\varepsilon_m)\) vs \(\ln(T - T_m)\) for Ba\((Zr_xTi_{1-x})O_3\) ceramics (The symbols: experimental data; the solid line: fitting to the Equation 5.6).
Table 5.4: Summary of the fitting parameters of the dielectric behavior of BZT ceramics using Curie-Weiss law:

<table>
<thead>
<tr>
<th>Composition</th>
<th>C (K)</th>
<th>T₀(K)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(Zr₀.₈₀Ti₀.₂₀)O₃</td>
<td>4.43 × 10⁴</td>
<td>-170.60</td>
</tr>
<tr>
<td>Ba(Zr₀.₇₅Ti₀.₂₅)O₃</td>
<td>5.22 × 10⁴</td>
<td>-89.43</td>
</tr>
<tr>
<td>Ba(Zr₀.₇₀Ti₀.₃₀)O₃</td>
<td>6.04 × 10⁴</td>
<td>-43.99</td>
</tr>
<tr>
<td>Ba(Zr₀.₆₀Ti₀.₄₀)O₃</td>
<td>4.36 × 10⁴</td>
<td>36.81</td>
</tr>
<tr>
<td>Ba(Zr₀.₅₀Ti₀.₅₀)O₃</td>
<td>6.96 × 10⁴</td>
<td>114.19</td>
</tr>
<tr>
<td>Ba(Zr₀.₄₅Ti₀.₅₅)O₃</td>
<td>6.36 × 10⁴</td>
<td>137.82</td>
</tr>
<tr>
<td>Ba(Zr₀.₄₀Ti₀.₆₀)O₃</td>
<td>1.20 × 10⁵</td>
<td>189.42</td>
</tr>
<tr>
<td>Ba(Zr₀.₃₅Ti₀.₆₅)O₃</td>
<td>1.45 × 10⁵</td>
<td>213.34</td>
</tr>
</tbody>
</table>

* * Values below the absolute zero suggest the possibly overlapping quantum effect deviating from the ideal curve fit near the Tₘ.

The experimental data are fitted by equation (5.5) using non-linear curve fitting program for all the BZT compositions. The fitting parameters (C and T₀) calculated only in the high temperature linear part are listed in Table 5.4 for all the BZT compositions. It is apparent from Table 5.4 that the value of T₀ increases systematically with the increase in Ti concentrations. It is seen that the dielectric constant of all the BZT compositions follows Curie-Weiss law at temperatures much higher than the Tₘ. For x= 0.80, 0.75 and 0.70 the values of T₀ are not the realizable numbers but suggest some secondary influential features (possibly quantum fluctuations), near and below the relaxation peak,
deviating from the ideal fit of Curie-Weiss behavior. It is also evident from the realistic value of $T_0$ for $0.35 \leq x \leq 0.60$ that with increasing Ti content relaxor behavior becomes more prominent in BZT ceramics as the amount of Ti$^{4+}$ polar regions is increased and finally showing the classical relaxor behavior.

To describe the diffuseness of the phase transition of relaxor ferroelectrics a modified Curie-Weiss law has been proposed as the following [Uchino et.al. (1982)]:

\[
\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^\gamma}{C_1}
\]

where, $\gamma$, called as degree of relaxation and $C_1$ are assumed to be constant and $1 < \gamma < 2$. The limiting values $\gamma=1$ and $\gamma=2$ reduce the expression to Curie-Weiss law valid for the case of normal ferroelectric and to the quadratic dependence valid for an ideal relaxor ferroelectric, respectively. The values of $T_m$ and $\gamma$ obtained from the experimental data fitted by equation (5.6) using non-linear curve fitting program for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ compositions are listed in Table 5.5 and the fitting curves are shown in the insets of the figure 5.13 and 5.14. It is apparent from the Table 5.5 that with the increase in Ti contents there is systematic increase in $T_m$ and $\gamma$. The $\gamma$ value slowly increases to 2 with increase in Ti concentration, which shows the evolution of ferroelectric relaxations giving rise to the classical relaxor behavior.
Table 5.5 Summary of the fitting parameters of the dielectric anomaly of BZT ceramics:

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\gamma$</th>
<th>$T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba($Zr_{0.80}Ti_{0.20}$)O$_3$</td>
<td>1.83</td>
<td>124.69</td>
</tr>
<tr>
<td>Ba($Zr_{0.75}Ti_{0.25}$)O$_3$</td>
<td>1.85</td>
<td>135.04</td>
</tr>
<tr>
<td>Ba($Zr_{0.70}Ti_{0.30}$)O$_3$</td>
<td>1.86</td>
<td>139.26</td>
</tr>
<tr>
<td>Ba($Zr_{0.60}Ti_{0.40}$)O$_3$</td>
<td>1.90</td>
<td>145.29</td>
</tr>
<tr>
<td>Ba($Zr_{0.50}Ti_{0.50}$)O$_3$</td>
<td>1.89</td>
<td>143.11</td>
</tr>
<tr>
<td>Ba($Zr_{0.45}Ti_{0.55}$)O$_3$</td>
<td>1.92</td>
<td>155.15</td>
</tr>
<tr>
<td>Ba($Zr_{0.40}Ti_{0.60}$)O$_3$</td>
<td>1.93</td>
<td>167.55</td>
</tr>
<tr>
<td>Ba($Zr_{0.35}Ti_{0.65}$)O$_3$</td>
<td>1.92</td>
<td>187.00</td>
</tr>
</tbody>
</table>

5.3.3 Temperature dependence of the relaxation time

It is believed [Cross, 1987] that so called nano-size polar regions exist in the vicinity of $T_m$ in any classic relaxor system. Each of those polar nano regions (PNR) has a net polarization ($P_s$) and has a characteristic relaxation time ($\tau$) controlled by the local field configuration in them and their characteristic size. The energy barrier that separates the switching of its polarization states decreases as the size of the PNR decreases and when the barrier height becomes comparable to thermal energy ($k_BT$), the direction of $P_s$ fluctuates with temperature. It is proposed [Viehland et.al. (1990)] that the short-range interactions between the polar regions control the fluctuation of $P_s$ leading to its freezing
at a characteristic temperature. Like the spin glass systems the relaxation time \( \tau \) in relaxors can be described by the Vogel-Fulcher relation as follows:

\[
\tau = \tau_0 \exp \left[ \frac{E_a}{k_B (T_m - T_{VF})} \right]
\]

(5.7)

where \( \tau_0 \) is the pre-exponential factor, \( E_a \) is the activation energy for polarization fluctuations of an isolated cluster, \( k_B \) is the Boltzmann constant, \( T_m \) is the temperature corresponding to dielectric maxima and \( T_{VF} \) is the characteristic Vogel-Fulcher freezing temperature. It is found that temperature dependence of relaxation time can be well-fitted with Vogel-Fulcher relation for all the BZT compositions as shown in figure 5.15. The fitting parameters are summarized in Table 5.6. Within the fitting error, it is clearly seen that with increase in \( Ti^{4+} \) content the freezing temperature \( (T_{VF}) \) is increased systematically. Whereas, the activation energy initially decreases with increase in \( Ti^{4+} \) content and then it becomes almost constant in the composition region \( 0.40 \leq x \leq 0.60 \) and then it further decreases with increase in \( Ti^{4+} \) content. The fitted value of the freezing temperature \( (T_{VF}) \) below the absolute zero for \( Ba(Zr_{0.80}Ti_{0.20})O_3 \) suggests that the dynamic behavior of the polar clusters near 0 K may be influenced or superimposed by some other factors possibly the quantum fluctuations as we saw in our earlier studies in \( Ba(Zr_xTi_{1-x})O_3 \) compositions \( (0.85 \leq x \leq 0.95) \). Beyond an optimum composition \( (x \leq 0.75) \) in \( Ba(Zr_xTi_{1-x})O_3 \) ceramics, the realistic increasing values of \( T_{VF} \) indicate the gradual evolution of relaxor behavior with the increase in content of polar \( BaTiO_3 \) in non polar \( BaZrO_3 \) matrix. It is suggested from our previous and present studies that with the gradual incorporation of polar \( BaTiO_3 \) in the non-polar dielectric \( BaZrO_3 \) matrix, BZT ceramics start showing polar-cluster like behavior from a simple dielectric (for pure
BaZrO$_3$) and then probably a critical size and density of the polar regions are reached when it starts showing relaxor behavior. This is reconfirmed from our d.c. field dependent dielectric studies of all the BZT ceramics.

![Graph](attachment:image.png)

**Fig. 5.15.** Temperature dependence of relaxation time ($\tau$) for BaZr$_x$Ti$_{1-x}$O$_3$ ceramics with $x=0.80, 0.75, 0.70, 0.60, 0.50, 0.45, 0.40$ and $0.35$ (The symbols: experimental data; the solid curve: fitting to the Vogel-Fulcher relation).
Table 5.6 Summary of the Vogel-Fulcher fitting parameters of BZT ceramics

<table>
<thead>
<tr>
<th>Composition</th>
<th>**Freezing temperature ((T_{VF})) (K)</th>
<th>Activation energy ((E_a)) (eV)</th>
<th>Pre-exponential factor ((\tau_0)) (Pico-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ba(Zr}<em>{0.80}\text{Ti}</em>{0.20})\text{O}_3)</td>
<td>-7 (±8)</td>
<td>0.26 (±0.003)</td>
<td>0.001</td>
</tr>
<tr>
<td>(\text{Ba(Zr}<em>{0.75}\text{Ti}</em>{0.25})\text{O}_3)</td>
<td>4 (±5)</td>
<td>0.25 (±0.002)</td>
<td>0.004</td>
</tr>
<tr>
<td>(\text{Ba(Zr}<em>{0.70}\text{Ti}</em>{0.30})\text{O}_3)</td>
<td>11 (±4)</td>
<td>0.21 (±0.001)</td>
<td>0.04</td>
</tr>
<tr>
<td>(\text{Ba(Zr}<em>{0.60}\text{Ti}</em>{0.40})\text{O}_3)</td>
<td>21 (±11)</td>
<td>0.17 (±0.003)</td>
<td>0.80</td>
</tr>
<tr>
<td>(\text{Ba(Zr}<em>{0.50}\text{Ti}</em>{0.50})\text{O}_3)</td>
<td>26 (±10)</td>
<td>0.16 (±0.003)</td>
<td>1.05</td>
</tr>
<tr>
<td>(\text{Ba(Zr}<em>{0.45}\text{Ti}</em>{0.55})\text{O}_3)</td>
<td>48 (±3)</td>
<td>0.16 (±0.001)</td>
<td>0.14</td>
</tr>
<tr>
<td>(\text{Ba(Zr}<em>{0.40}\text{Ti}</em>{0.60})\text{O}_3)</td>
<td>68 (±2)</td>
<td>0.17 (±0.002)</td>
<td>0.02</td>
</tr>
<tr>
<td>(\text{Ba(Zr}<em>{0.35}\text{Ti}</em>{0.65})\text{O}_3)</td>
<td>122 (±3)</td>
<td>0.09 (±0.001)</td>
<td>0.56</td>
</tr>
</tbody>
</table>

** The fitted, \(T_{VF}\), freezing temperature value below the absolute zero suggests the dynamic nature of the clusters down to near 0 K. It also suggests that dynamic behavior near 0 K may be influenced or superimposed by the quantum fluctuations.
5.3.4 Dielectric Behavior with Applied Electric Field

Dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) for $\text{Ba(Zr}_x\text{Ti}_{1-x})\text{O}_3$ compositions with $x=0.80, 0.75, 0.70, 0.60, 0.50, 0.45, 0.40$ and $0.35$ studied in cryogenic to room temperature range at $100$ kHz under various d.c. biases are shown in figures 5.16 to 5.19. It is evident from the figures that there is almost no change in dielectric constant and loss tangent for $\text{Ba(Zr}_{0.80}\text{Ti}_{0.20})\text{O}_3$ under the bias electric field. Where as effects of electric field for the composition $x=0.75$ and $0.70$ are similar, a little decrease in both dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) (~3% and 5% decrease at $T_m$ respectively). In case of the dielectric behavior of $\text{Ba(Zr}_x\text{Ti}_{1-x})\text{O}_3$ compositions with $0.35\leq x \leq 0.60$ strong response to the applied electric field has been observed. It is evident that for these compositions, both dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) are gradually suppressed with the increase in electric field and the peaks of $\varepsilon'$ and $\tan\delta$ become increasingly broadened. The interesting feature of these materials is that the loss ($\tan\delta$) remains almost constant and low of the order of $10^{-3}$ up to ~$200K$ from room temperature for all these BZT compositions, which may be useful for various, microwave tunable device applications point of view as described in more details in Appendix A and B.

It is evident from the figure 5.19 that in case of $\text{BaZr}_{0.35}\text{T}_{0.65}\text{O}_3$ and $\text{BaZr}_{0.40}\text{T}_{0.60}\text{O}_3$ compositions, the temperature of the dielectric maxima ($T'_m$) shifted to the higher temperature with increasing d.c. bias whereas the temperature of the loss maxima ($T''_m$) shifted to the lower temperature as the applied bias field increases. However, the $T_m$ of both $\varepsilon'$ and $\tan\delta$ remains almost constant with the various d.c. bias for $\text{Ba(Zr}_x\text{Ti}_{1-x})\text{O}_3$ compositions with $0.45\leq x \leq 0.75$. 
Fig. 5.16. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at 100 kHz for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics with $x$ = 0.80 and 0.75 under bias of various E-field with maximum $E = 35$ kV/cm. Arrows indicate the direction of increasing d.c. electric field.
Fig. 5.17. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at 100 kHz for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics with $x = 0.70$ and 0.60 under bias of various E-field with maximum $E = 35$ kV/cm. Arrows indicate the direction of increasing d.c. electric field.
Fig. 5.18. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at 100 kHz for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics with $x=0.50$ and 0.45 under bias of various E-field with maximum E= 30 and 40 kV/cm respectively. Arrows indicate the direction of increasing d.c. electric field.
Fig. 5.19. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at 100 kHz for Ba(Zr$_{x}$Ti$_{1-x}$)O$_{3}$ ceramics with $x=0.40$ and 0.35 under bias of various E-field with maximum $E=40$ kV/cm. Arrows indicate the direction of increasing d.c. electric field.
5.3.5 Clusters and Percolation Density

In our present attempt, the gradual evolution of relaxation in the BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) solid solution system has been hypothesized due to the increasing amount of ordering and density of nano size Ti$^{4+}$ rich polar regions in the Zr$^{4+}$ rich matrix as Ti$^{4+}$ is gradually incorporated in the BaZrO$_3$ lattice. In our previous work [section 5.2 in this chapter], the polar cluster like behavior has been observed in the BaZr$_x$Ti$_{1-x}$O$_3$ solid solution system ($0.85 \leq x \leq 1.00$), by proposing the introduction of polar clusters of BaTiO$_3$ in the matrix of BaZrO$_3$ breaking the long range translational symmetry of BaZrO$_3$. With further increase in Ti content ($0.35 \leq x \leq 0.80$) gradual evolution of relaxor behavior has been observed in BaZr$_x$Ti$_{1-x}$O$_3$ solid solution, which eventually becomes completely relaxor for $0.35 \leq x \leq 0.60$. It can be hypothesized from its dielectric behavior that the amount of Ti-rich nano polar regions become sufficient enough to build up a long range polar regions interactions to show relaxor ferroelectricity. It is also evident from the field dependent dielectric behavior of all the BZT ceramics where the response of electric field becomes stronger with increase in Ti content as more and more BaTiO$_3$ polar clusters become available to communicate with each other in the presence of external electric field. From the thermal hysteresis in dielectric behavior and Vogel-Fulcher fitting of the temperature dependence of relaxation time as well as from the E-field dependent studies of dielectric behavior for all the BZT compositions it is suggested that beyond an optimum content of polar BaTiO$_3$ in the non polar matrix of BaZrO$_3$ ($x \leq 0.75$) probably a critical size and distribution density of the polar regions are reached when polar cluster like BaZr$_x$Ti$_{1-x}$O$_3$ ($x \geq 0.80$) ceramics start showing the relaxor behavior.
The gradual departure from a non ferroelectric material \((x= 1.00)\) to polar cluster like \((x \geq 0.80)\) behavior to relaxor \((x \leq 0.75)\) behavior with the subsequent increase in Ti\(^{4+}\) content in BaZr\(_{x}\)Ti\(_{1-x}\)O\(_3\) solid solution makes this system interesting to further investigate the nature of polar clusters which is responsible for ferroelectric relaxor behavior.

### 5.4 The Phase Diagram of Barium Zirconate Titanate or BaZr\(_{x}\)Ti\(_{1-x}\)O\(_3\) system

Since BaTiO\(_3\)-BaZrO\(_3\) system was identified as a solid solution as in early 1950s [McQuarrie et.al. (1954)] many research workers [Kell et.al. (1956), Hennings et.al. (1982), Farhi et.al. (1999) and Yu et.al. (2002)] studied this materials in lower concentration \((x < 0.40)\) of Zr in Ba(Ti\(_{1-x}\)Zr\(_x\))O\(_3\) system over the years and have developed the phase diagram of Ba(Ti\(_{1-x}\)Zr\(_x\))O\(_3\) system in lower concentration of Zr i.e. BaTiO\(_3\) rich side of the phase diagram similar to the figure 2.9 as shown in Chapter 2. To the best of our knowledge there are no reports on the dielectric behavior in the higher BaZrO\(_3\) concentration of this solid solution system.

In the current investigation, we have prepared the BaZr\(_{x}\)Ti\(_{1-x}\)O\(_3\) \((0.35 \leq x \leq 1.00)\) ceramics by conventional solid state route. From the dielectric study of this solid solution system we have observed the gradual evolution of relaxor behavior with the increase in Ti\(^{4+}\) content. Unlike the classic relaxor ferroelectrics like PMN, PZN etc where intrinsic disorderness prevails, in our present investigation we have introduced the disorderness gradually through the incorporation of Ti\(^{4+}\) ion in BaZrO\(_3\) lattice to observe the relaxor
behavior in a non-ferroelectric material like BaZrO$_3$ with low dielectric constant. From the thermal hysteresis in dielectric behavior and d.c. field dependent dielectric studies it has been concluded that with the incorporation of Ti$^{4+}$ ion in the BaZrO$_3$ matrix BaZr$_x$Ti$_{1-x}$O$_3$ compositions ($x \geq 0.80$) start showing polar-cluster like behavior and after a percolation limit BZT compositions ($x \leq 0.75$) show relaxor-like behavior. This has been further confirmed from the calculation of degree of relaxation ($\gamma$) and Vogel-Fulcher freezing temperature ($T_{VF}$). Figure 5.20 shows the variation of degree of relaxation ($\gamma$) and Vogel-Fulcher freezing temperature ($T_{VF}$) as a function of Zr content ($x$) in BaZr$_x$Ti$_{1-x}$O$_3$.
$\gamma$O$_3$ compositions. The values of $\gamma$ and $T_{VF}$ for the BaZr$_{0.30}$Ti$_{0.70}$O$_3$ composition are taken from the work of Zhi et. al. [2002]. Based on our current investigations on dielectric anomaly of BaZr$_x$Ti$_{1-x}$O$_3$ compositions with $0.35\leq x \leq 1.00$, we have updated the phase diagram of BaZr$_x$Ti$_{1-x}$O$_3$ after including the work on composition $x<0.30$ from the earlier reports. The new whole phase diagram of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics is shown in figure 5.21. Data for the composition $0 \leq x \leq 0.30$ are taken from the paper by Zhi et. al. [2002]. As shown in the phase diagram when we look at it with a “bottom-up” approach i.e. BaZrO$_3$ as matrix, BaZr$_x$Ti$_{1-x}$O$_3$ compositions show polar cluster like behavior for $x \geq 0.80$ from a simple dielectric i.e. pure BaZrO$_3$ ($x=1.00$). On the other hand with the “top-down” approach to the phase diagram one can see that with the increase in amount of Zr$^{+4}$ incorporation, proper ferroelectric BaTiO$_3$ ($x=0.0$) transforms into a pinched phase transition at $x \sim 0.15$. In the composition range $0.15 < x < 0.25$ BaZr$_x$Ti$_{1-x}$O$_3$ compositions show almost 2$^{nd}$ order ferroelectric like diffuse phase transition behavior. The region showing relaxor behavior in BaZr$_x$Ti$_{1-x}$O$_3$ system has been detected in the composition range $0.25 < x < 0.75$.

In summary Barium Zirconate Titanate, Ba(Zr$_x$Ti$_{1-x}$)O$_3$ system depending on the composition, successively depicts the properties extending from simple dielectric (pure BaZrO$_3$) to polar cluster dielectric, relaxor ferroelectric, 2$^{nd}$ order like diffuse phase transition, ferroelectric with pinched phase transitions and then to a proper ferroelectric (pure BaTiO$_3$). So far there has been no other single solid solution system that demonstrates all complex aspects of ferroelectricity.
Fig. 5.21. Phase diagram (composition vs. temperature) of BaZr$_x$Ti$_{1-x}$O$_3$ compositions with $0 \leq x \leq 1.00$ based on the dielectric permittivity measurements.
5.5 Thermal strain behavior of Barium Zirconate Titanate or BaZrxTi1-xO3

As discussed in chapter 2.3.3, the interesting properties of relaxors are attributed to nano-structural features. In relaxors, the chemistry is believed to prevent the establishment of long–range polar ordering at the temperature of the permittivity maximum (Tm) as in the case of normal ferroelectrics. Instead, the system fashions polar moments on the scale of the local chemistry. At the Tm, the polarization is not suddenly lost, but decays gradually to zero as the scale of the local chemistry changes such that the orientation of the polarization is thermally reversible. Bhalla et.al. (1987) and Burns et.al. (1990) have shown that Polar cluster embryos originate at the temperature much higher than Tf and Tm. At very high temperature, thermal fluctuations are so large that there are no well-defined dipole moments. However, on cooling, these dipolar entities grow into small polar clusters below the so-called Burns temperature, TD [Burns and Dacol (1990)]. A local polarization is believed to exist at temperatures up to the deviation temperature, Td, implying that the local symmetry of relaxor ferroelectrics is typically lower than the global symmetry. The relaxor parameter that corresponds to the onset of the polarization i.e. the deviation temperature, Td, can be estimated from the temperature dependent thermal strain behavior.

Dilatometry experiments were performed to measure the thermal strain of BaZrxTi1-xO3 compositions. Figure 5.22 and figure 5.23 show typical thermal strain behavior as a function of temperature for BaZrxTi1-xO3 relaxor compositions with x= 0.40, 0.60 and 0.70. All the BZT compositions show hysteresis in the temperature dependent strain behavior during heating and cooling cycles as shown in the insets of the figures.
Fig. 5.22. Typical thermal strain plot for BaZr$_x$Ti$_{1-x}$O$_3$ compositions with $x=0.40$ and $0.60$ showing linear relation in paraelectric phase (solid line: experimental strain data; dot line: linear fit to the experimental data). The insets show the hysteresis behavior of thermal strain during heating and cooling cycle.
Fig. 5.23. Typical thermal strain plot for BaZr$_{0.70}$Ti$_{0.30}$O$_3$ composition showing linear relation in paraelectric phase (solid line: experimental strain data; dot line: linear fit to the experimental data). The insets show the hysteresis behavior of thermal strain during heating and cooling cycle.
It is seen that the strain follows a linear relation at very high temperature in all the BaZr$_x$Ti$_{1-x}$O$_3$ ceramics with a slope of $9.87$, $9.74$ and $8.45$ ppm/°C for compositions $x=0.40$, $0.60$ and $0.70$ respectively. At the deviation temperature, $T_D^o$, a departure from the linear relation is observed in all the three BZT compositions indicating electrostrictive strain due to the onset of a local polarization. The $T_D^o$ values obtained for BaZr$_x$Ti$_{1-x}$O$_3$ relaxor compositions with $x=0.40$, $0.60$, and $0.70$ are $\sim 443$ K, $\sim 439$ K and $\sim 475$ K respectively. The values of $T_D^o$ can also be obtained from the inverse dielectric permittivity versus temperature curve estimating the temperature where it deviates from the linear behavior or the C–W behavior. In the previous section we can see from the Curie-Weiss plot in figures 5.13 and 5.14 that the value of $T_D^o$ looks much lower than the same obtained from the thermal strain behavior in the BZT relaxors. Nevertheless, it is misleading as in figures 5.13 and 5.14 dielectric data are taken upto room temperature whereas, in the thermal strain behavior we measured upto 650 K. This further brings the dispute on the relevance and very origin of the Burns temperature. This temperature can not be considered as the usual phase transition temperature. Rather it should be considered as a temperature, which signifies the onset of local polar singularities depending on the experimental limit that can detect that local structure. From our thermal strain measurement it can be concluded that in these BZT compositions polar nano regions exist upto $\sim 440$ K. This implicates that the local structure of BZT ceramics is not cubic till the temperature $\sim 440$ K although the global symmetry is cubic in BZT relaxors even in very low temperature as observed in our Neutron diffraction measurements shown in chapter 4. This is further confirmed from the study of our Raman spectra on BZT ceramics.
5.6 Raman Spectra of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($0.5 \leq x \leq 1.00$) Ceramics

In addition to the dielectric measurement, which remains the most instrumental technique for the characterization of relaxor ferroelectricity, Raman scattering has been proven to be a powerful tool for studying the onset of ferroelectric order in the polar disordered systems. It is known that experimentally obtained parameters depend on the spatial magnitude and time scale of the measured physical phenomena. In general the results of the dielectric measurements on polycrystalline ceramic samples are averaged over a larger volume. Micro-Raman spectroscopy on the other hand can provide local information because of the shorter coherence length and time scale of the phonons. Because of the ceramic character of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT), which gives rise to a strong depolarization of the incident and scattered light, Raman spectra are not expected to be polarized. In addition, because of the random grain orientation in the ceramics, the directions of the phonon wave vectors are randomly distributed with respect to the crystallographic axes from one grain to another, and mode mixing together with long range electrostatic force effects should be therefore responsible for a broadening of the lines.

Figure 5.24 shows the depolarized Raman spectra of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ compositions at 300K. For pure $\text{BaZrO}_3$ no first order Raman scattering is expected as at room temperature $\text{BaZrO}_3$ has been reported to be a nearly cubic perovskite and shows x-ray patterns corresponding to $P_{m\text{3m}}$ symmetry. However the Raman spectrum of $\text{BaZrO}_3$ shows weak bands in agreement with previous reports [Dobal et.al. (2001) and Chemarin et.al. (2000)]. Such observations from Raman and x-ray studies could be due to the different coherence length and time scale involved in these processes. A slight local
Fig. 5.24. Room Temperature Raman spectra of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics with $0.5 \leq x \leq 1.00$. Inset shows the Raman spectra of BaTiO$_3$ at 300 and 410 K.

distortion of oxygen octahedral can result in the breakdown of Raman selection rules and thereby giving rise to weak bands in BaZrO$_3$ Raman spectrum. Measurements of Raman spectra under pressure revealed that the Raman spectra of BaZrO$_3$ most probably originate from the dynamical disorder in the material. With incorporation of Ti ions in the non-polar matrix (BaZrO$_3$), there are considerable changes in the room temperature Raman spectrum of BaZr$_x$Ti$_{1-x}$O$_3$ compositions as evident from figure 5.24. To analyze these spectra conveniently, room temperature Raman spectrum of pure BaTiO$_3$ is shown
in the inset of figure 5.24. BaTiO$_3$ is cubic with P$_{m3m}$ symmetry above 400 K and at temperatures below 393 K it is tetragonal belonging to P$_{4mm}$ symmetry, which further transforms into orthorhombic and rhombohedral structures at 278 K and 183 K respectively. Both in the paraelectric and ferroelectric phase, BaTiO$_3$ has one molecule (5 atoms) per unit cell giving rise to 12 ($3 \times 5 - 3$) long wavelength optical modes. In the paraelectric phase ($> 400$K) the optical modes transform according to the triply degenerate irreducible representations $3F_{1u} + F_{2u}$ of the P$_{m3m}$ symmetry. The $F_{2u}$ mode is silent and the $F_{1u}$ modes are only infrared active, so there is no Raman active mode in the paraelectric phase with perfect cubic symmetry. In the ferroelectric phase with tetragonal structure (P$_{4mm}$ symmetry), each of $F_{1u}$ modes splits into a doubly degenerate E mode and a nondegenerate A$_1$ mode and the $F_{2u}$ mode split into E and B$_1$ modes. Thus $\Gamma_{tet}^{optical} = 3(A_1 + E) + (E + B_1)$. All the A$_1$ and E modes are both Raman and infrared active and the B$_1$ mode is only Raman active. Each of these optical modes further splits into longitudinal (LO) and transverse (TO) modes due to the presence of the long-range electrostatic forces associated with lattice ionicity. The assignment of phonons as LO or TO modes in the ferroelectric phase is valid as long as the phonon wave vector lies along one of the principal symmetry directions of the crystal. For the phonons propagating in between the principal axis, mixing of A$_1$ and E modes occurs and quasimodes are allowed in the spectra [Freire et.al. (1987)].

The room temperature Raman spectrum of BaTiO$_3$ shows the over damped transverse E$_1$ (TO) mode, detected through the increase of the scattered intensity below 100 cm$^{-1}$ and other E$_1$ and A$_1$ modes. The strong anti-resonance effect, which arises from the interference of the sharp A$_1$ (TO) mode at $\sim$180 cm$^{-1}$ wit a broad A$_1$ (TO) mode $\sim$
270 cm $^{-1}$ is clearly visible ~ 180 cm $^{-1}$. A third A$_1$ (TO) mode appears at ~ 516 cm $^{-1}$. The E (TO) mode appears ~ 309 cm $^{-1}$ and the A$_1$ (LO) mode appears ~ 720 cm $^{-1}$. The disappearance of the strong anti-resonance effect at ~ 180 cm $^{-1}$ and the E (TO) mode ~ 309 cm $^{-1}$ along with A$_1$ (LO) mode ~ 720 cm $^{-1}$ is considered as the signature of the tetragonal to cubic phase transition in BaTiO$_3$. Thus the cubic phase of BaTiO$_3$ is characterized by two very broad lines centered ~ 285 cm $^{-1}$ and ~ 520 cm $^{-1}$, which are also shown in the inset of figure 5.24. Even though a perfect cubic symmetry forbids any Raman modes, appearance of these two modes in cubic BaTiO$_3$ suggests that a strong disorder is already occurring at the microscopic level at high temperatures.

The room temperature Raman spectra of Zr rich BaZr$_x$Ti$_{1-x}$O$_3$ compositions (0.5 $\leq x \leq$ 1.00) evolves considerably with incorporation of Ti into nonpolar BaZrO$_3$ matrix. However, they are dominated by BaTiO$_3$ spectrum at room temperature as seen from fig. 5.24. First the anti-resonance band ~ 183 cm $^{-1}$, which is a signature of ferroelectric BaTiO$_3$ is present in all compositions with Ti. Notable changes occur in the region 200–400 cm $^{-1}$ spectral region, which have been attributed to vibration associated to polar BO$_6$ octahedra. With increasing amount of Ti bands in this region become sharper and well defined. Similar behavior is also observed in the region 400–600 cm $^{-1}$, here too the bands become sharper and well defined with increasing Ti content. The main band in this region gains intensity and moves to higher wave number with increasing Ti content as well. Evolution of room temperature Raman spectra in the region 600–800 cm $^{-1}$ is perhaps most interesting with increasing Ti amount. A sharp band (LO) evolves (in place of the weak bands associated with the locally distorted ZrO$_6$ octahedra), which shifts to higher wave number and gains intensity as Ti amount increases. Furthermore, as can be seen
from figure 5.24 that a second band at \( \sim 754 \text{ cm}^{-1} \) starts evolving for \( x = 0.6 \) and which is clearly visible for \( x = 0.5 \) having higher intensity than the LO mode \( \sim 710 \text{ cm}^{-1} \). This extra line has already been observed with a weaker intensity in less Zr rich compounds and which has been described as a clear signature of the relaxor phase [Farhi et.al. (1999)]. This observation agrees very well with our dielectric results, discussed in the previous sections, in Zr rich compositions, BaZr\(_x\)Ti\(_{1-x}\)O\(_3\) \((0.50 \leq x \leq 1.00)\), where it has been shown from dielectric measurements that there is a gradual evolution of relaxor behavior from nonpolar BaZrO\(_3\) with increasing Ti content and compositions with \( x = 0.60 \) and 0.50 show classical relaxor behavior. Another interesting feature in the room temperature Raman spectrum of compositions with Ti, is the presence of a dip \( \sim 120 \text{ cm}^{-1} \), which is more intense than the antiresonance feature \( \sim 180 \text{ cm}^{-1} \). The current feature has also been observed in the Raman spectrum of Ti rich BaZr\(_x\)Ti\(_{1-x}\)O\(_3\) [Farhi et.al. (1999) and Dobal et.al. (2001)]. This feature has never been reported before in BaTiO\(_3\), but previously detected in the infrared spectrum of BaZrO\(_3\) [Perry et.al. (1965)]. Based on this observation Farhi et. al. [1999] have proposed that the feature arises from a normal mode involving Zr ions, which implies that nanometer size Zr (or Zr rich) domains exist, because otherwise the phonon lifetime would have been too short to result in a defined separated Raman feature. However, based on high pressure Raman studies Kreisel et. al. [2004] excluded local pure BaZrO\(_3\) zones and rather proposed Zr rich domains as BaZrO\(_3\) presents for \( p > 12 \text{ Gpa} \) a well defined Raman signature with sharp and intense bands \( \sim 400 \) and \( \sim 620 \text{ cm}^{-1} \), which were not observed in the high pressure Raman spectra.
Fig. 5.25 Raman spectra of BaZr$_{0.6}$Ti$_{0.4}$O$_3$ ceramic at different temperatures.

Fig. 5.26 Raman spectra of BaZr$_{0.75}$Ti$_{0.25}$O$_3$ ceramic at different temperatures.
Extrapolation of the BZT phase diagram as has been reported [Farhi et al. (1999) and Dobal et al. (2001)] to the higher Zr side suggests that the room temperature structure of BaZr$_x$Ti$_{1-x}$O$_3$ with, $0.5 \leq x \leq 1.00$ would be cubic. Also our XRD and Neutron scattering results suggest that the room temperature structure of BaZr$_x$Ti$_{1-x}$O$_3$ would be cubic as discussed in Chapter 3. However, the presence of all the bands corresponding to the ferroelectric BaTiO$_3$ along with the feature at $\sim 120$ cm$^{-1}$, in the present room temperature Raman spectra of BaZr$_x$Ti$_{1-x}$O$_3$ with, $0.50 \leq x \leq 1.00$ suggests that the local structure around BO$_6$ octahedra deviates from perfect cubic symmetry.

Raman spectra of BaZr$_{0.6}$Ti$_{0.4}$O$_3$ and BaZr$_{0.75}$Ti$_{0.25}$O$_3$ ceramic at different temperatures are shown in figure 5.25 and figure 5.26, respectively. It is seen from the temperature dependent Raman spectra in BaZr$_{0.6}$Ti$_{0.4}$O$_3$ as shown in figure 5.25 that the presence of a dip $\sim 120$ cm$^{-1}$ and the corresponding relaxor peak at $\sim 754$ cm$^{-1}$ along with other features exist even at 450 K, which is far above the temperature of its dielectric maxima ($T_m \sim 145$ K). Moreover this temperature is far above the temperature corresponding tetragonal to cubic phase transition in pure BaTiO$_3$. As shown in the inset of figure 5.24, pure BaTiO$_3$ become cubic above 400 K. Similarly in case of BaZr$_{0.75}$Ti$_{0.25}$O$_3$ the antiresonance band $\sim 183$ cm$^{-1}$, which is a signature of ferroelectric BaTiO$_3$, is present in at the temperature of 550 K. Although some fine features in the Raman spectra getting disappear with the increase in temperature, all the major peaks are observed even at 550 K. This implies that polar BaTiO$_3$ regions distributed in the non-polar BaZrO$_3$ matrix exist with local polarization at the temperature far above the corresponding $T_m$ of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics.
5.7 Pyroelectric behavior of Barium Zirconate Titanate or BaZr$_x$Ti$_{1-x}$O$_3$

Relaxor ferroelectric materials can be manipulated by the application of a stress, either mechanical or electrical. In either case, the zero–field cooled materials can be transformed from a short–range to a long–range domain structure with the application of a suitable field. The field overrides the internal symmetry–breaking process, which lead to the short–range (5–50nm) polar regions typical of zero–field cooled relaxor materials [Xu et al. (2006)]. Under the influence of suitable electric fields, the nano or micro–polar domains present in the material “switch” to a metastable macro–domain state at temperatures below freezing temperature which can be considered as Vogel-Fulcher freezing temperature, $T_{VF}$. At $T > T_{VF}$ there is sufficient thermal energy to disorder the microstructure to a frustrated micro–polar and dispersive state [Viehland et al. (1991)].

From the pyroelectric behavior of relaxor ferroelectrics it can be easily seen if the application of suitable electric field can induce a long range ordering ferroelectric phase below the freezing temperature in BaZr$_x$Ti$_{1-x}$O$_3$ relaxor compositions. In the pyroelectric measurement, a zero-field heating after field cooling (ZFH / FC) experiment should consequently result in a depolarization current peak leading to a peak in pyroelectric coefficient below the freezing temperature, $T_{VF}$. Figures 5.27 and 5.28 show the pyroelectric coefficient ($p$) and the polarization (P) resulting from its integration obtained from a Zero-field heating after field cooling experiment in BaZr$_x$Ti$_{1-x}$O$_3$ compositions with $x= 0.35, 0.40, 0.45$ and $0.50$. The values of Vogel-fulcher freezing temperature ($T_{VF}$) and the temperature of the dielectric maxima ($T_{\epsilon_m}$) for the corresponding composition obtained from the dielectric measurements are given in the insets of the figures.
Fig. 5.27. Pyroelectric coefficient (left scale) and the polarization resulting from its integration (right scale) obtained from a Zero-field heating after field cooling experiment in BaZr$_x$Ti$_{1-x}$O$_3$ compositions with $x=0.35$ and 0.40. The values of Vogel-fulcher freezing temperature ($T_{VF}$) and the temperature of the dielectric maxima ($T_{\varepsilon_m}$) for the corresponding composition are given in the insets.
Fig. 5.28. Pyroelectric coefficient (left scale) and the polarization resulting from its integration (right scale) obtained from a Zero-field heating after field cooling experiment in BaZr$_x$Ti$_{1-x}$O$_3$ compositions with $x=0.45$ and 0.50. The values of Vogel-fulcher freezing temperature ($T_{VF}$) and the temperature of the dielectric maxima ($T_{\varepsilon_m}$) for the corresponding composition are given in the insets.
The applied electric fields during cooling in BaZr$_x$Ti$_{1-x}$O$_3$ are 30 kV/cm for $x = 0.35$, 50 compositions and 40 kV/cm for the compositions $x = 0.40$ and 0.45. BaZr$_x$Ti$_{1-x}$O$_3$ relaxor compositions with $x = 0.35$ and 0.40 show a pyroelectric peak at $\sim 81$ K and $\sim 46$ K respectively. The freezing temperatures, $T_{VF}$ for these two materials are $122 \pm 3$ K and $68 \pm 2$ K for BZT-35 and BZT-40 compositions respectively. The occurrence of pyroelectric peak at the temperature lower than the freezing temperature in these two relaxor compositions reflects the transition from the field induced ferroelectric state to the ergodic relaxor phase. In BaZr$_{0.45}$Ti$_{0.55}$O$_3$ composition two pyroelectric peaks are observed as shown in figure 5.28. The low temperature pyroelectric peak at $\sim 33$ K is lower than its Vogel-Fulcher freezing temperature of $48 \pm 3$ K determined from the dielectric measurements. This in good agreement with the transformation from the field induced metastable macro–domain state to micro–polar domains. The high temperature pyroelectric peak at $\sim 221$ K observed in this composition may occur from the phase transition of polar BaTiO$_3$ clusters distributed in the non-polar BaZrO$_3$ matrix. Infact this is highly probable as Raman spectra shows that peak corresponding to BaTiO$_3$ in these BZT compositions at the temperatures much higher than the temperature of dielectric maxima which is $155$ K for the BZT-45 composition. As the temperature of the dielectric maxima ($T_m$) increases with decrease in Zr content in BaZr$_{0.45}$Ti$_{0.55}$O$_3$ composition (figure 5.21) this high temperature pyroelectric peak is not observed in BZT-35 composition within the measurement temperature range. It is seen that the values of pyroelectric coefficient decreases gradually with increase in Zr content in BaZr$_x$Ti$_{1-x}$O$_3$ compositions. In the BaZr$_x$Ti$_{1-x}$O$_3$ compositions with $x \geq 0.50$ the pyroelectric coefficient
values are very small as shown in the figure 5.28 for BaZr_{0.50}Ti_{0.50}O_3 as an example. Probably the sample does not get poled well during field cooling as the amount of polar BaTiO_3 in non-polar BaZrO_3 decreases. However, the maximum pyroelectric coefficient obtained for BaZr_xTi_{1-x}O_3 compositions with x= 0.35, 40, 45 are \( \sim 1731 \, \mu \text{C/m}^2\text{-K} \) at 81 K, \( \sim 1820 \, \mu \text{C/m}^2\text{-K} \) at 46 K and \( \sim 675 \, \mu \text{C/m}^2\text{-K} \) at 221 K, respectively. These high values of pyroelectric coefficients make these BZT composition promising candidates for low temperature pyroelectric device applications.

### 5.8 Relaxor Ferroelectricity in BaZr_xTi_{1-x}O_3 or Barium Zirconate Titanate ceramics

Although, over the years, extensive research works have been carried out on relaxor ferroelectrics since it was first observed by Smolenskii et al. in Ba(Ti, Sn)O_3 solid solution in 1954, the step forward understanding of the physical phenomena of relaxor ferroelectrics has still been going on. As discussed in chapter 2.3.3, several models have been proposed by various authors to explain the relaxor behavior which includes super-paraelectric model [Cross (1987)], “dipolar-glass” model [Viehland et.al. (1990)], random field model [Westphal et.al. (1992)] etc. In our current investigation, the gradual evolution of relaxation in the BaZr_xTi_{1-x}O_3 (BZT) solid solution system has been hypothesized due to the increasing amount of ordering and density of nano size Ti^{4+} rich polar regions in the Zr^{4+} rich matrix as Ti^{4+} is gradually incorporated in the BaZrO_3 lattice. The typical characteristics of BaZrO_3 are its simple perovskite structure with relatively large lattice constant, smaller thermal expansion coefficient, lower dielectric constant and loss as compared to that of BaTiO_3. From the whole phase diagram of BZT developed
from our dielectric measurements as discussed in the section 5.4, the region showing relaxor behavior in \( \text{BaZr}_x\text{Ti}_{1-x}\text{O}_3 \) system has been identified in the composition range \( 0.25<x<0.75 \).

In the classic \( \text{A(B}_x\text{B}_{1-x})\text{O}_3 \) ferroelectric relaxors like \( \text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 \) (PMN), \( \text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3 \) (PZN) etc., the nano-size cation ordered charged regions (suggested to be \( 1:1 :: \text{Mg:Nb or Zn:Nb} \)) distributed in a disordered matrix are known to be responsible for their relaxor behavior. Apparently, in a solid solution system like \( \text{BaZr}_x\text{Ti}_{1-x}\text{O}_3 \) (BZT), such kind of charge imbalanced order-disorder is not expected between homovalent \( \text{Ti}^{4+} \) and \( \text{Zr}^{4+} \). It is also reported that the presence of lone pair electron in \( \text{Pb}^{2+} \) cation in lead based relaxors contributes large displacement leading the order-disorder mechanism. In this \( \text{Ba}^{2+} \) based (no lone pair electron) system such kind of possibilities are not expected. Viehland et al. [1991] looked at the field dependence of the dielectric response in PMN and observed suppression in the frequency dispersion, a reduction in the permittivity maximum, and an increase in the temperature of the permittivity maximum with application of dc bias. In \( \text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 \), the relaxor behavior is assigned to the non-homogeneous distribution of the \( \text{Mg}^{2+} \) and \( \text{Nb}^{5+} \) cations over the B site of the perovskite structure. The difference of charge of the two cations creates space charges and hence, electric field fluctuations on an atomic length scale. The quenched local random fields may oppose any increase of the polar domain size [Klemann (2005)]. The application of an external field suppresses the influence of the random fields and permits a macro ferroelectric state to be induced.
Fig. 5.29 Temperature dependent dielectric constant ($\varepsilon'$) at 10 kHz and 100 kHz for Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$ ceramics under bias of various E-field. Arrows indicate the direction of increasing frequency.
Fig. 5.30 Temperature dependent dielectric constant ($\varepsilon'$) at 10 kHz and 100 kHz for Ba(Zr$_{0.40}$Ti$_{0.60}$)O$_3$ ceramics under bias of various E-field. Arrows indicate the direction of increasing frequency.
In case of our $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ relaxor compositions it happens to be interesting to see if such kind of behavior is possible as the homovalent $\text{Ti}^{4+}$ and $\text{Zr}^{4+}$ cannot induce strong random fields. Recently, Sciau et al. [2000] have not observed any induced long range polar-order in their X-ray diffraction study under the applied electric field $\leq 9.6 \text{ kV/cm}$ in $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$ composition in contrast to the classical relaxor like PMN [Mathan et al. (1991) and Calvarin et al. (1995)] where long range ordering can be established by applied E-field.

In our current studies on electric field response on the dielectric permittivity, $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ relaxor compositions with $x=0.35$ and $0.40$ show a reduction in permittivity maximum and an increase in the temperature of the permittivity maximum with application of d.c. bias as shown in figure 5.19. This is the common feature observed in the classical relaxor like PMN. Temperature dependent dielectric constant ($\varepsilon'$) at 10 kHz and 100 kHz for $\text{Ba(Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics with $x=0.35$ and $0.40$ under bias of various E-field are shown in figure 5.29 and 5.30 respectively. Maximum applied electric field is 40 kV/cm in the temperature range from 300 K to 15 K. It is apparent from the figures that with the application of electric field the frequency dispersion behavior in the dielectric permittivity is gradually disappeared and the dielectric peak become broaden in these two BZT ceramics. This behavior is more prominent in $\text{Ba(Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ composition than in $\text{Ba(Zr}_{0.40}\text{Ti}_{0.60})\text{O}_3$. As shown in figure 5.29, in $\text{Ba(Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ ceramics the frequency dispersion in dielectric permittivity, which is a typical characteristics of relaxor ferroelectrics become lessen with the application of electric field and become almost disappeared at $E=40 \text{ kV/cm}$. This implies that applied electric field gradually induces the long range ordering in this BZT relaxor composition.
Fig. 5.31. The plot of $\Delta T_m$ vs $E^{2/3}$ for Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$ ceramics. $\Delta T_m$ is the shift in temperature of the maximum dielectric permittivity due to the applied E field. (Symbols: experimental data; solid line: linear fit).

and after a critical electric field ferroelectric long range ordering is established with the build up of so called macro–domains. From the temperature dependence of dielectric constant of these two compositions it can be seen that the temperature of the maximum dielectric permittivity, $T_m$ shifts to the higher temperature with the increasing applied electric field. In these BZT relaxor compositions after a critical electric field the shift $\Delta T_m$ is found to follow a relation with E-field as below:

$$\Delta T_m \sim E^{2/3} \quad (5.8)$$

Figure 5.31 shows the plot of $\Delta T_m$ vs $E^{2/3}$ for Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$ ceramics. It can be seen from the figure that after a critical electric field Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$ ceramics follow
the equation 5.8 which is a relationship generally observed in a normal ferroelectric with second order phase transition. This implies that ferroelectric long range ordering can be established in Ba(Zr0.35Ti0.65)O3 ceramics with the application of enough electric field. However, very high electric field is required to induce the long range ordering in Ba(ZrxTi1-x)O3 ceramics due to the homovalent nature of Ti⁴⁺ and Zr⁴⁺ cations unlike the classical relaxor like PMN. That is why probably Sciau et.al. [2000] have not observed any induced long range polar-order in their X-ray diffraction study under the applied electric field \( \leq 9.6 \text{ kV/cm} \) in BaZr0.35Ti0.65O3 composition.

Interestingly, the other Ba(ZrxTi1-x)O3 relaxor compositions with \( 0.45 \leq x \leq 0.75 \) show almost no change in \( T_m \) with the application of electric field. Although, strong electric field response in the dielectric permittivity has been observed with the reduction in maximum dielectric constant especially in the compositions \( 0.45 \leq x \leq 0.60 \) as shown in the figure 5.19 in the earlier section of this chapter.

From our electric field dependent dielectric studies and pyroelectric behavior it can be suggested that the relaxor regions of the Ba(ZrₓTi₁₋ₓ)O₃ phase diagram as shown in figure 5.21, can be further classified as two different kinds of relaxor ferroelectrics as Type-I and Type-II. Type-I is the higher Ti content Ba(ZrₓTi₁₋ₓ)O₃ relaxors dominated by polar BaTiO₃ and \( T_m \) of the BZT compositions in this region decreases with increase in Zr content. On the other hand, Type-II is higher Zr content Ba(ZrₓTi₁₋ₓ)O₃ relaxors which is dominated by non polar BaZrO₃ and in this region \( T_m \) of the BZT compositions remain almost constant irrespective of Zr content as shown by the flat region in the temperature vs composition phase diagram of BZT in figure 5.21. Type-I BZT relaxors behave much closer to the classical relaxor like PMN exhibiting pyroelectric peaks below the freezing
temperature and capable of inducing long range ferroelectric ordering with the application of electric field. In contrast Type-II is a kind of relaxors, which show the suppression of dielectric permittivity with the applied E-field, but does not show the long range ordering with E-field. It can not be poled easily as this is dominated by non-polar BaZrO$_3$. Probably very high applied electric field can show some long range ordering in these relaxors.

Recently researchers [Farhi et al. (1999 and 2000), Laulhe et al. (2006)] have proposed that the difference in size of Ti$^{4+}$ (ionic radius= 0.745 Å) and Zr$^{4+}$ (ionic radius= 0.86 Å) cations in BZT induces random elastic fields. Such fields could affect the displacement of the ferroelectrically active Ti$^{4+}$ ions in the oxygen octahedral. In the extended X-ray absorption fine structure experiments (EXAFS) Laulhe et al. [2006] have suggested that BaZrO$_3$ inclusions in BaTiO$_3$ do not adopt the cubic bulk structure of BaZrO$_3$ but present considerable distortions away from it observing the presence of buckled Zr-O-Zr bonds which suggests the presence of octahedron tilts. In the high pressure Raman investigation Kreisel et al. [2004] have shown that the change of spectrum of BaZr$_{0.35}$Ti$_{0.65}$O$_3$ is different from that of PMN. They suggested that BaZr$_{0.35}$Ti$_{0.65}$O$_3$ behaves as a relaxor with temperature but with pressure it is similar to a classic ferroelectric. Nagasawa et al. [2006] have not observed any anomaly in the heat capacity measurement by adiabatic calorimetry in the temperature range from 13 K to 420 K in BaZr$_{0.35}$Ti$_{0.65}$O$_3$ relaxor composition. This behavior is in contrast to the classical relaxor like PMN in which a broad heat capacity anomaly is observed in the same temperature range as that of the broad peak in dielectric constant.

From our electrical, thermal measurements of BZT ceramics it is suggested that difference in size of Zr$^{4+}$ and Ti$^{4+}$ cations ($r_{Zr^{4+}} / r_{Ti^{4+}} = 1.18$) induces shear strain causing
the elastic interaction between polar Ti$^{4+}$ rich regions and non-polar Zr$^{4+}$ rich regions in BaZr$_{x}$Ti$_{1-x}$O$_{3}$ system. Considering that the lattice parameter hence the cell volume of BaZrO$_{3}$ is larger than that of BaTiO$_{3}$, a significant strain between the TiO$_{6}$ octahedra with the adjacent ZrO$_{6}$ octahedra is expected. Hence different Ti$^{4+}$ displacements causing the polarity are expected considering the high stiffness of ZrO$_{6}$ octahedra. These displacements, which depend on the local strain, would naturally induce the random electric fields. However, the elastic interaction among polar and non-polar regions is not expected so strong and that is the probable reason why we observed that beyond an optimum content of polar BaTiO$_{3}$ in the non polar matrix of BaZrO$_{3}$ probably a critical size and density of the polar regions are reached when polar cluster like BaZr$_{x}$Ti$_{1-x}$O$_{3}$ ceramics start showing the relaxor behavior. As the larger amount of Ti$^{4+}$ displacements are expected due to the local strain in BaZr$_{x}$Ti$_{1-x}$O$_{3}$ with the higher Ti$^{4+}$ concentration, we observe more random electric field induced by local strain resulting the Type-I relaxor ferroelectrics in BZT system. On the other hand in Type-II relaxors in BZT system not so much random electric fields expected compared to the Type-I relaxors as the amount of Ti$^{4+}$ rich polar regions become lesser in the BaZrO$_{3}$ nonpolar matrix. That is why we do not observe the field induced long range ordering in the Type-II relaxors. As a whole it can be hypothesized that relaxor behavior in Type-I is largely electric field driven whereas, in the Type-II region dielectric relaxation is mostly driven by elastic field. Most importantly BaZr$_{x}$Ti$_{1-x}$O$_{3}$ relaxors should not be considered in the sense of a model relaxors like PMN. Rather, this should be considered as an engineered material where dielectric relaxation has been engineered by introducing elastic strain. Hence we observe the some unusual properties, which are not common in a classical relaxors like PMN.
Although the global symmetry of the BZT relaxors are pseudocubic the local symmetry deviates far from the global symmetry as observed in our thermal strain measurement and Raman investigation. It is seen that local polar regions exist in the BZT ceramics even at 550 K at which temperature both end members of the phase diagram BaZrO$_3$ and BaTiO$_3$ are cubic in pure form.

As a whole BaZr$_x$Ti$_{1-x}$O$_3$ can be considered an engineered material in which case the self-assembled polar nano-regions resulting some unusual properties, hard to be predicted from its constituents BaTiO$_3$ and BaZrO$_3$. Hence BaZr$_x$Ti$_{1-x}$O$_3$ is qualified as meta-material.
Chapter 6

Ferroelectric Relaxor Behavior in

$\text{Ba(Zr}_x\text{Ti}_{1-x})\text{O}_3:\text{MgO Composites}$

6.1 Introduction

As discussed in the previous chapter relaxor behavior can be manipulated by electric and elastic field. Moreover one can engineer a material, which can show the relaxor behavior even none of the constituents of the materials show such properties. In turns, one can engineer a meta-material, which can show dielectric relaxation behavior. Based on our understanding in relaxor behavior of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics in this chapter we have shown a potential approach to fabricate the relaxor materials by making the ceramic composite of environmental friendly Ba-based diffuse ferroelectric $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x= 0.20$ and 0.25) with non-ferroelectric MgO.

The composites of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x= 0.20$ and 0.25) and 50 wt% dielectric MgO have been prepared by conventional solid state route. $\text{BaZr}_{0.20}\text{Ti}_{0.80}\text{O}_3$ (BZT-20) and $\text{BaZr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ (BZT-25) compositions both in bulk [Yu et.al. (2000 and 2007)] and thin film [Dixit et.al. 2004] show diffuse phase transition behavior as shown in figure 6.1. In the present work, relaxor behavior has been induced in these two $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT-20 and BZT-25) ceramics by making composite with non-ferroelectric MgO. The degree of relaxation ($\gamma$) has been estimated using modified Curie-Weiss law. The dielectric relaxations in these composites are found to follow Vogel-Fulcher type behavior originally derived for the spin-glass systems. These $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ composites have also shown strong dc electric field dependent dielectric behavior.
Fig. 6.1. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at various frequencies for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x = 0.20$ and 0.25 (Arrows indicate the direction of increasing frequency).
6.2 Phase and Structural Characterization

Dense ceramic samples of Ba(Zr$_x$Ti$_{1-x}$)O$_3$ : MgO composites with $x$= 0.20 and 0.25 [abbreviated as BZT20:MgO and BZT25:MgO respectively] were prepared by the conventional solid-state route.

![SEM image and EDS analysis](image)

Fig. 6.2. Microstructure of Ba(Zr$_{0.25}$Ti$_{0.75}$)O$_3$ : MgO composite: (Top) SEM image (800X magnification), (bottom) Distribution of Mg and Ba as determined by EDS (energy dispersive spectroscopy).

Scanning electron microscope (SEM) study and the composition profile analysis by energy dispersive spectroscopy (EDS) were carried out to reveal the microstructure features and identification of the phases in the composites. It was observed that MgO was
randomly dispersed in the BZT matrix without any detectable new phase as shown in figure 6.2.

Figure 6.3. XRD pattern of sintered Ba(Zr0.2Ti0.8)O3 and Ba(Zr0.2Ti0.8)O3:MgO ceramics.

The room temperature X-ray diffraction study was carried out on all the sintered BZT:MgO ceramic composites. In both the BZT composites two crystalline phases, BZT and MgO were observed but no other phase was detected. Figure 6.3 shows the XRD patterns of BZT-20 and BZT20:MgO composite. BZT-20 was verified to be single-phase perovskite solid solution whereas two distinguished crystalline phases, BZT and MgO were observed in the XRD patterns of BZT20:MgO composite as shown in the figure.
From the XRD and SEM study, it is apparent that during the ceramic processing, the initially mixed BZT and MgO powders do not make the solid solution and they are distributed as individual phases in the final composite bulk ceramics.

### 6.3 Dielectric Behavior without Bias Electric Field

The temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan\(\delta\)) at various frequencies for BZT20:MgO and BZT25:MgO composites is shown in figure 6.4. Strong frequency dispersion is observed around the $\varepsilon$ and tan\(\delta\) peak for all the BZT composites. Similar to a typical ferroelectric relaxor it is seen in both the BZT composites that, with increasing frequency $\varepsilon'$ decreases and the temperature ($T_m$) where the dielectric maxima occur are shifted to the higher temperatures. In the same manner the temperature of the loss maxima increases with increase in frequency whereas peak value increases unlike $\varepsilon'$. It is also evident from figure 6.4 that the values of dielectric constant become on the order of hundreds in BZT composites whereas pure BZT compositions have the dielectric constant on the order of $10^4$ (as shown in figure 6.1). It is expected as MgO has very low dielectric constant (~ 9.8 at room temperature). It is also seen that the temperature ($T_m$) of the dielectric maxima is much lower for BZT:MgO composites than that of pure BZT compositions.

### 6.4. Characterization of dielectric peak using Curie-Weiss Behavior

A normal ferroelectric in the para-electric region generally follows the Curie-Weiss law:

$$\frac{1}{\varepsilon} = \frac{T - T_0}{C}$$

(6.1)
Figure 6.4. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at various frequencies for Ba(Zr$_{0.20}$Ti$_{0.80}$)O$_3$: MgO and Ba(Zr$_{0.25}$Ti$_{0.75}$)O$_3$: MgO composites (Arrows indicate the direction of increasing frequency).
Figure 6.5. The inverse dielectric constant ($1/\varepsilon$) as a function of temperature at 100 kHz for Ba($Zr_xTi_{1-x}$)O$_3$:MgO composites with $x=0.20$ and 0.25. (The symbols: experimental data; the solid line: fitting to the Curie-Weiss law). The insets show the plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ vs $\ln(T - T_m)$ for Ba($Zr_xTi_{1-x}$)O$_3$:MgO composites (The symbols: experimental data; the solid line: fitting to the Equation 6.3).
where $T_0$ is the Curie temperature and $C$ is the Curie-Weiss constant. The inverse $\varepsilon$ (for both the composites) as a function of temperature at 100 kHz is plotted in figure 6.5 and the experimental data are fitted by equation (6.1) using non-linear curve fitting program for all the BZT composites. The fitting parameters ($C$ and $T_0$) calculated only in the high temperature linear part and the temperature ($T_m$) where the dielectric maxima occur are listed in Table 6.1 for the BZT composites. It is apparent from Table-I that the values of $T_0$ and $T_m$ for BZT20:MgO composite are higher than that of BZT25:MgO composite.

Table 6.1: Summary of the fitting parameters of the dielectric behavior of BZT:MgO composites using Curie-Weiss law:

<table>
<thead>
<tr>
<th>Composition</th>
<th>$C$ (K)</th>
<th>$T_0$ (K)</th>
<th>$T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZT20:MgO</td>
<td>$3.30 \times 10^4$</td>
<td>151.91</td>
<td>192.33</td>
</tr>
<tr>
<td>BZT25:MgO</td>
<td>$2.76 \times 10^4$</td>
<td>133.24</td>
<td>153.73</td>
</tr>
</tbody>
</table>

It is seen that the dielectric constant of both the BZT composites follows Curie-Weiss law at temperatures much higher than the $T_m$. Deviation from Curie-Weiss law can be described by an empirical parameter $\Delta T_m$, which is defined as

$$\Delta T_m = T_{\text{dev}} - T_m$$

(6.2)

Where $T_{\text{dev}}$ is the temperature at which $\varepsilon$ starts to deviate from the Curie-Weiss law. The estimated values of $\Delta T_m$ at 100 kHz for BZT20:MgO and BZT25:MgO composites are 74.83 and 92.82 respectively.
To describe the diffuseness of the phase transition of relaxor ferroelectrics a modified Curie-Weiss law has been proposed as the following [uchino et.al. (1982)]:

\[
\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C_1}
\]  \hspace{1cm} (6.3)

where, \(\gamma\) is called the degree of relaxation, \(1 < \gamma < 2\), and \(C_1\) is assumed to be constant. The limiting values \(\gamma = 1\) and \(\gamma = 2\) reduce the expression to Curie-Weiss law valid for the case of normal ferroelectric and to the quadratic dependence valid for an ideal relaxor ferroelectric, respectively. To obtain the values of \(\gamma\), the experimental data is fitted to the equation (6.3) using non-linear curve-fitting program for BZT : MgO composites and the fitting curves are shown in the insets of the figure 6.5. The calculated values of \(\gamma\) are 2 and 1.91 for BZT20:MgO and BZT25:MgO composites respectively, implying a typical ferroelectric relaxor behavior.

**6.5 Temperature dependence of the relaxation time**

To understand the possible linkage with the ferroelectric relaxor like behavior, the temperature dependence of relaxation time is analyzed by Vogel-Fulcher relations. The relaxation time (\(\tau\)) following Vogel-Fulcher relation is one of the characteristics of the relaxor ferroelectrics. The Vogel-Fulcher [1921 and 1925] law originally derived for the spin-glass systems is described as follows:

\[
\tau = \tau_0 \exp \left[ \frac{E_a}{K_B(T - T_{VF})} \right]
\]  \hspace{1cm} (6.4)

where \(\tau_0\) is the pre-exponential factor, \(E_a\) is the activation energy, \(k_B\) is the Boltzmann constant, \(T_m\) is the temperature corresponding to dielectric maxima and \(T_{VF}\) is the characteristic Vogel-Fulcher freezing temperature. It is found that temperature
dependence of relaxation time can be well fitted with Vogel-Fulcher relation for all the BZT : MgO composites as shown in figure 6.6. The fitting parameters are summarized in Table 6.2. Within the fitting error, it is clearly seen that with increase in Zr$^{4+}$ content in BaZr$_x$Ti$_{1-x}$O$_3$ : MgO composites the freezing temperature (T$_{VF}$) is decreased.

Figure 6. Temperature dependence of relaxation time ($\tau$) for BaZr$_x$Ti$_{1-x}$O$_3$ : MgO composites with $x=0.20$ and 0.25 (The symbols: experimental data; the solid curve: fitting to the Vogel-Fulcher relation).

Table 6.2 Summary of the Vogel-Fulcher fitting parameters of BZT:MgO composites.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Freezing temperature ($T_{VF}$) (K)</th>
<th>Activation energy ($E_a$) (eV)</th>
<th>Pre-exponential factor ($\tau_0$) (Pico-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZT20:MgO</td>
<td>149 ($\pm$6)</td>
<td>0.06 ($\pm$0.002)</td>
<td>0.47</td>
</tr>
<tr>
<td>BZT25:MgO</td>
<td>102 ($\pm$5)</td>
<td>0.07 ($\pm$0.001)</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Figure 6.7. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at 10 kHz for Ba(Zr$_x$Ti$_{1-x}$)$_3$:MgO composites with $x=0.20$ and $0.25$ under bias of various E-field with maximum E= 35 kV/cm and 30 kV/cm for BZT20:MgO and BZT25:MgO respectively (Arrows indicate the direction of increasing dc electric field).
6.6 Dielectric Behavior with Applied Electric Field

Dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) for BZT20:MgO and BZT25:MgO composites studied in the cryogenic to room temperature range at 10 kHz under various d.c. biases are shown in figure 6.7. It is evident from the figure that for these two composites, both dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) are gradually suppressed with the increase in electric field and the peaks of $\varepsilon'$ and tan$\delta$ become increasingly broadened. The interesting feature of these two materials is that the loss (tan$\delta$) remains almost constant and low on the order of $10^{-4}$ up to ~200K from room temperature. BZT20:MgO and BZT25:MgO composites show the maximum tunability of 51% at ~175K with 35kv/cm bias and 32% at ~151K with 30 kV/cm dc bias respectively. Strong dc field dependence of these composites having such a low loss with low dielectric permittivity (on the order of hundreds) may be useful for various microwave tunable device applications as described in more details in Appendix C.

6.7 Discussion

In the previous chapter it is discussed that the difference in size of Zr$^{4+}$ and Ti$^{4+}$ cations ($\frac{r_{Zr^{4+}}}{r_{Ti^{4+}}} = 1.18$) induces shear strain causing the elastic interaction between polar Ti$^{4+}$ rich regions and non-polar Zr$^{4+}$ rich regions in BaZr$_x$Ti$_{1-x}$O$_3$ system. It has been suggested that dielectric relaxation occurs in BZT system due to the significant local strain developed because of the misfit of the TiO$_6$ octahedra with the adjacent ZrO$_6$ octahedra, which in turns induces the random electric fields.

In our present investigation, we have categorically chosen BaZr$_{0.20}$Ti$_{10.80}$O$_3$ (BZT-20) and BaZr$_{0.25}$Ti$_{0.75}$O$_3$ (BZT-25) compositions, which show diffuse phase transition
behavior. In other words, these are the two compositions prior to becoming relaxor in the BaTiO$_3$ rich side of the BaZr$_x$Ti$_{1-x}$O$_3$ phase diagram as discussed in chapter 5.4. The two compositions have been made as composites with MgO, which is highly refractory material and does not make solid solution with BZT. Interestingly, these two compositions (BZT-20 and BZT-25) show ferroelectric relaxor behavior in the composite form. The good fitting of the temperature dependence of relaxation time to the Vogel-Fulcher relations and the $\gamma$ values close to 2 (2 and 1.97 for BZT-20 and BZT-25 respectively) further ensure the ferroelectric relaxor behavior.

It is hypothesized that, enough elastic field differences have been induced among BZT and MgO grains due to the mechanical impedance mismatch, so that relaxor behavior has been induced in the composite form of those BaZr$_x$Ti$_{1-x}$O$_3$ compositions, which are prior to become relaxor in pure form rather say, in which compositions already significant amount of local strain exists but not enough to show the relaxor behavior.

6.8 Summary

In summary, we have prepared the BaZr$_{0.20}$Ti$_{0.80}$O$_3$ : 50 wt% MgO (BZT20 : MgO) and BaZr$_{0.25}$Ti$_{0.75}$O$_3$ : 50 wt% MgO (BZT25 : MgO) composites by conventional solid state route. In the dielectric study, the ferroelectric relaxor behavior has been observed in those composites which otherwise have not shown such behavior in the pure form. Unlike the classic relaxor ferroelectrics like PMN, PZN etc., where the intrinsic disorder prevails, the present study have shown the relaxor behavior in diffuse ferroelectric BaZr$_x$Ti$_{1-x}$O$_3$ by making composite with MgO due to the induced elastic
field differences between BZT and MgO grains. Relaxor behavior of these BZT:MgO composites has been shown to follow the Vogel-Fulcher relations. Strong dc field dependence of these composites having low loss with low dielectric permittivity (on the order of hundreds) has been observed which may have the potentials for applications in various microwave tunable device.
Chapter 7

Magnetoelectric Composite

7.1 Introduction

In the search of engineered magnetoelectric metamaterials earlier in our lab research works have been done on the composites of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ with several individual ferrite components such as $\text{CoFe}_2\text{O}_4$, $\text{Mn}_{0.1}\text{Zn}_{0.9}\text{Fe}_2\text{O}_4$ and $\text{NiMn}_{0.1}\text{Fe}_{1.9}\text{O}_4$ [Agrawal (2006)]. According to the previous understanding $\text{CoFe}_2\text{O}_4$ and $\text{Mn}_{0.1}\text{Zn}_{0.9}\text{Fe}_2\text{O}_4$ exhibit the better magnetoelectric coefficients with BST. Hence we have forwarded the previous work by replacing BST with $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$-31% $\text{PbTiO}_3$ (PMN-PT) as PMN-PT shows the better piezoelectric properties than BST.

In thesis work $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$-31% $\text{PbTiO}_3$ (PMN-PT) has been used as the ferroic material and ferrites like $\text{CoFe}_2\text{O}_4$ and $\text{Mn}_{0.1}\text{Zn}_{0.9}\text{Fe}_2\text{O}_4$ are used as the magnetostrictive materials to make the magnetoelectric meta material composites. The magneto-electric coefficients on these samples were calculated by applying the magnetic field and observing the changes in the electric polarization in the composites.

7.2 Magnetoelectric behavior of PMN-PT : $\text{CoFe}_2\text{O}_4$ composite

Magnetoelectric composite of PMN-31%PT : $\text{CoFe}_2\text{O}_4$ (60:40) were prepared by both conventional and E-field microwave sintering. Figure 7.1 depicts the comparison of the magnetoelectric coefficient of PMN-31%PT : $\text{CoFe}_2\text{O}_4$ composite (60:40) prepared
Fig. 7.1 Comparison of the magnetoelectric coefficient of PMN-31%PT : CoFe$_2$O$_4$ composite (60:40) prepared by conventional and E-field microwave sintering.

Fig. 7.2 The magnetoelectric coefficient of PMN-31%PT : CoFe$_2$O$_4$ (80:20) composite prepared by E-field microwave sintering.
by conventional and E-field microwave sintering. Magnetoelectric coefficient was measured at 1 kHz frequency in room temperature. As shown in the figure a broad peak of the magnetoelectric coefficient has been observed. It can be seen from the figure 7.1 that composites prepared by E-field microwave sintering exhibit better property than that prepared by conventional sintering method. The maximum magnetoelectric coefficient in conventional sintered composite is ~ 54 mV/cm.Oe and in E-field single mode microwave sintered composite is ~ 87 mV/cm.Oe. Fig. 7.2 shows the magnetoelectric coefficient of PMN-31%PT : CoFe_2O_4 (80:20) composite prepared by E-field microwave sintering. The maximum coefficient found in this composition is ~56 mV/cm.Oe. It may be due to the reduced amount of ferrite in the composites.

### 7.2 Magnetoelectric behavior of PMN-PT : Mn_{0.1}Zn_{0.9}Fe_2O_4 composite

Figure 7.3 shows the measured magneto-electric coefficient in the case of PMN-PT (31%): Mn_{0.1}Zn_{0.9}Fe_2O_4 composite with 40 % and 20 % by weight the content of ferrite in the composites. Both the composites were prepared by conventional sintering method. It is seen that 60:40 composite gives the better coefficient than the 80:20 composite similar to what we observe in case of PMN-PT : CoFe_2O_4 composites. The maximum magnetoelectric coefficient for the PMN-PT (31%): Mn_{0.1}Zn_{0.9}Fe_2O_4 composites are ~71 mV/cm.Oe and 60 mV/cm.Oe for 60:40 and 80:20 composites respectively.
Fig. 7.3 Comparison of the magnetoelectric coefficient as a function of d.c. bias field for PMN-31%PT : $\text{Mn}_{0.1}\text{Zn}_{0.9}\text{Fe}_2\text{O}_4$ composites with (60:40) and (80:20) weight ratio. Both the composites were prepared by convention sintering.
Chapter 8

Summary and Future Work

The aim of this thesis work was to develop two different kinds of engineered metamaterials (a) a new family of the environmental friendly relaxor ferroelectrics and (b) novel magnetoelectric composites. The results of the research works are summarized in the following sections along with the suggested future work that could be carried out to enhance the understanding of polar nano regions in relaxor ferroelectrics and magnetoelectric nano-composites.

8.1 Relaxor Ferroelectrics

The ceramic compositions of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT) with $x = 0.35, 0.40, 0.45, 0.50, 0.60, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95$ and $1.00$ were successfully prepared by conventional solid state route. Structural characterizations have been done by XRD and neutron diffraction studies in a wide range of temperatures. All the ceramic compositions were verified to be single phase perovskite. Local structure of the BZT ceramics has been investigated by Raman spectroscopy. Dielectric, pyroelectric, and thermal strain measurements have been carried out from cryogenic temperature to high temperatures. Further we have shown a potential approach to fabricate the relaxor materials by making the ceramic composite of environmental friendly Ba-based diffuse ferroelectric $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.20$ and $0.25$) with non-ferroelectric MgO. Following is the summary of the research works:
Fig. 8.1 The Phase diagram (composition vs. temperature) of BaZr$_x$Ti$_{1-x}$O$_3$ compositions with $0 \leq x \leq 1.00$. 
1. In the course of searching environmental friendly lead free relaxor system a new phase diagram of Barium Zirconate Titanate, $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ has been developed in the composition range $0 \leq x \leq 1.00$ as shown in figure 8.1.

2. Barium Zirconate Titanate, $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ system depending on the composition, successively depicts the properties extending from simple dielectric (pure $\text{BaZrO}_3$) to polar cluster dielectric, relaxor ferroelectric, $2^{nd}$ order like diffuse phase transition, ferroelectric with pinched phase transitions and then to a proper ferroelectric (pure $\text{BaTiO}_3$). So far there has been no other single solid solution system that demonstrates all complex aspects of ferroelectricity.

3. When we look at the phase diagram with a “bottom-up” approach i.e. $\text{BaZrO}_3$ as the matrix, $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ compositions show polar cluster like behavior for $x \geq 0.80$ from a simple dielectric i.e. pure $\text{BaZrO}_3$ ($x=1.00$). On the other hand with the “top-down” approach to the phase diagram one can see that with the increase in amount of $\text{Zr}^{4+}$ incorporation, proper ferroelectric $\text{BaTiO}_3$ ($x=0.0$) transforms into a pinched phase transition at $x \approx 0.15$. In the composition range $0.15 < x < 0.25$ $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ compositions show almost $2^{nd}$ order ferroelectric like diffuse phase transition behavior. The region showing relaxor behavior in $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ system has been detected in the composition range $0.25 < x < 0.75$.

4. In contrary to the classic relaxor ferroelectrics like PMN, PZN etc where intrinsic disorder prevails, in our present investigation we have introduced the disorderness gradually through breaking the long range translational symmetry of $\text{BaZrO}_3$ by the incorporation of $\text{Ti}^{4+}$ ion in $\text{BaZrO}_3$ lattice to observe the relaxor behavior in a non-ferroelectric material like $\text{BaZrO}_3$ with low dielectric constant ($<40$). From
the thermal hysteresis in dielectric behavior and d.c. field dependent dielectric studies it has been concluded that with the incorporation of Ti$^{4+}$ ion in the BaZrO$_3$ matrix BaZr$_x$Ti$_{1-x}$O$_3$ compositions ($x \geq 0.80$) start showing polar-cluster like behavior. Beyond an optimum content of polar BaTiO$_3$ in the non polar matrix of BaZrO$_3$ probably a critical size and distribution density of the polar regions are reached when polar cluster like BaZr$_x$Ti$_{1-x}$O$_3$ ceramics start showing the relaxor-like behavior ($x \leq 0.75$). This has been further confirmed from the calculation of degree of relaxation ($\gamma$) and Vogel-Fulcher freezing temperature ($T_{VF}$).

5. From our electric field dependent dielectric studies and pyroelectric behavior, the relaxor regions of the Ba(Zr$_x$Ti$_{1-x}$)O$_3$ phase diagram as shown in figure 8.1, are further classified as two different kinds of relaxor ferroelectrics as Type-I and Type-II. Type-I is the higher Ti content Ba(Zr$_x$Ti$_{1-x}$)O$_3$ relaxors dominated by polar BaTiO$_3$ and $T_m$ of the BZT compositions in this region decreases with increase in Zr content. On the other hand, Type-II is higher Zr content Ba(Zr$_x$Ti$_{1-x}$)O$_3$ relaxors which is dominated by non polar BaZrO$_3$ and in this region $T_m$ of the BZT compositions remain almost constant irrespective of Zr content as shown by the flat region in the temperature vs composition phase diagram of BZT in figure 8.1.

6. Type-I BZT relaxors behave much closer to the classical relaxor like PMN exhibiting pyroelectric peaks below the freezing temperature and capable of inducing long range ferroelectric ordering with the application of electric field. In contrast Type-II is a kind of relaxors, which show the suppression of dielectric permittivity with the applied E-field, but does not show the long range ordering
with E-field. It can not be poled easily as this is dominated by non-polar BaZrO$_3$. Probably very high applied electric field can show some long range ordering in these relaxors.

7. From our electrical, thermal measurements of BZT ceramics it is suggested that difference in size of Zr$^{4+}$ and Ti$^{4+}$ cations ($r_{Zr^{4+}} / r_{Ti^{4+}} = 1.18$) and larger cell volume of BaZrO$_3$ than that of BaTiO$_3$, induces shear strain causing different Ti$^{4+}$ displacements which in turns induce the random electric fields. As the larger amount of Ti$^{4+}$ displacements are expected in BaZr$_x$Ti$_{1-x}$O$_3$ with the higher Ti$^{4+}$ concentration it is hypothesized that relaxor behavior in Type-I is largely electric field driven whereas, in the Type-II region dielectric relaxation is mostly driven by elastic field.

8. Although the global symmetry of the BZT relaxors are predicted as pseudocubic from the powder neutron diffraction data as well as from the high q-resolution neutron scattering by triple axis spectrometer, the local symmetry deviates far from the global symmetry as observed in our thermal strain measurements and Raman investigations.

9. It is seen that local polar regions exist in the BZT ceramics even at 550 K at which temperature both end members of the phase diagram BaZrO$_3$ and BaTiO$_3$ are cubic in pure form.

10. In an overview picture of BaZr$_x$Ti$_{1-x}$O$_3$ compositions it is noted that depending on the composition range, the system has unique capabilities of resulting materials with properties different than the conventional solid solution and those do not follow the simple mixing rules considering the properties of the constituents,
BaTiO₃ and BaZrO₃. In this context the BaZrₓTi₁₋ₓO₃ relaxor compositions can be classified as a unique example of metamaterials where the polar clusters result in the relaxor materials with the unusually large dielectric properties not present in either of the end member compositions.

11. Further we have shown that one can engineer a meta-material, which can show dielectric relaxation behavior even none of the constituents of the materials does not show such properties. We have categorically chosen BaZr₀.₂₀Ti₁₀.₈₀O₃ and BaZr₀.₂₅Ti₀.₇₅O₃ compositions, which show diffuse phase transition behavior. In other words, these are the two compositions prior to becoming relaxor in the BaTiO₃ rich side of the BaZrₓTi₁₋ₓO₃ phase diagram. Relaxor behavior has been induced in these two BaZrₓTi₁₋ₓO₃ ceramics by making composite with non-ferroelectric MgO. This further ensures that elastic field plays a major role in the relaxor ferroelectricity in BaZrₓTi₁₋ₓO₃ system.

12. Strong field dependent dielectric behavior of the BaZrₓTi₁₋ₓO₃ composition in both bulk and composite form can be useful for the tunable microwave device applications as discussed in details in the cross-reference from paper in Appendix A, B and C.

13. The maximum pyroelectric coefficient obtained for BaZrₓTi₁₋ₓO₃ compositions with x= 0.35, 40, 45 are ~1731 μC/m²·K at 81 K, ~1820 μC/m²·K at 46 K and ~675 μC/m²·K at 221 K, respectively. These high values of pyroelectric coefficients make these BZT composition promising candidates for low temperature pyroelectric device applications.
8.2 Magnetoelectric Composite

Magnetoelectric meta material composites of PbMg$_{1/3}$Nb$_{2/3}$O$_3$-31% PbTiO$_3$ with several ferrites like CoFe$_2$O$_4$, Mn$_{0.1}$Zn$_{0.9}$Fe$_2$O$_4$ were prepared using both conventional and single mode microwave sintering techniques. These composites were successfully processed and characterized. The results of the magnetoelectric composites are summarized below:

(i) The composites of PMN-PT : ferrite were prepared by both conventional and microwave sintering technique in an E-field environment in a single mode microwave oven. Magnetoelectric behaviors of several composite samples prepared by different synthesis route are studied and compared.

(ii) PMN-31%PT : CoFe$_2$O$_4$ composites showed good magnetoelectric coefficient values. These values obtained from the composites sintered in E-field single mode microwave are better than those prepared in conventional furnace.

(iii) Both PMN-PT : CoFe$_2$O$_4$ and PMN-PT : Mn$_{0.1}$Zn$_{0.9}$Fe$_2$O$_4$ composites exhibit better magnetoelectric behavior in the compositions of 60:40 weight ratio than those of 80:20 compositions.

8.3 Future Work

As with any thesis, there always remain more questions than answers and not enough time to sort through it all. This section is devoted to the suggestions for future work on the relaxor and magnetoelectric composite systems from both practical and scientific viewpoints.
1. To understand the nature and origin of polar nano regions which is believed to be responsible for relaxor ferroelectricity, BaZr$_x$Ti$_{1-x}$O$_3$ system can be very interesting as this system demonstrates all complex aspects of ferroelectricity. Moreover one can systematically control the amount of polar clusters in this system to see the evolution of relaxor behavior.

2. More detailed investigation should be carried out on pure BaZrO$_3$, which shows the signature of weak quantum ferroelectricity in the low temperature dielectric behavior below 40 K. Furthermore, this will be interesting to see the role of quantum fluctuations in the BaZr$_x$Ti$_{1-x}$O$_3$ compositions with higher Zr content, which in turns may shed some light on the quantum phenomena behind the relaxor ferroelectricity.

3. TEM study should be carried out to locate the local ordering in the BaZr$_x$Ti$_{1-x}$O$_3$ compositions.

4. So far the global symmetry of the BaZr$_x$Ti$_{1-x}$O$_3$ relaxors has been determined to be cubic from the neutron diffraction patterns. However E-field dependent neutron diffraction study should be carried out to see whether any splitting appears in any of the Bragg peaks due to the induced long range ferroelectric ordering by electric field as observed in our dielectric study.

5. High energy synchrotron X-ray scattering can give the subtle features of the structure of these BZT relaxor compositions.

6. Piezoelectric and electrostrictive measurements should be carried out on BaZr$_x$Ti$_{1-x}$O$_3$ compositions as relaxor ferroelectric materials generally exhibit very high piezoelectric coefficients.
7. As strain has been found to play a major role behind the relaxor ferroelectric behavior in BaZr$_x$Ti$_{1-x}$O$_3$ system, further study on high purity thin film prepared by novel techniques like MBE may produce very interesting results as more local strain can be induced in the BaZr$_x$Ti$_{1-x}$O$_3$ lattice.

8. In the research of magnetoelectric composites, samples can be prepared by E-field and H-field microwave sintering as the initial research done in this thesis shows that rapid sintering by E-field microwave manifests better properties than conventional sintering.

9. Further work should be done on the composites of PMN-PT with other high magnetostrictive materials like terfenol.


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Appendix A

Electric field dependent dielectric properties and high tunability of BaZr$_x$Ti$_{1-x}$O$_3$ relaxor ferroelectrics


In recent years, extensive research$^{1,2}$ has been carried out on electric field tunable dielectric materials due to their potential applications in tunable filters, phase shifters, antennas etc. Dielectric material of high tunability, low dielectric loss and desired permittivity is required for such applications. Among the environmental friendly lead free perovskites (Ba,Sr)TiO$_3$ solid solution is mostly studied both as pure$^3$ and composite with MgO$^4$ for tunable microwave applications. But their temperature stability and reproducibility are required to be improved. Recently BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) solid solution has shown promises for these applications both in bulk$^5$ and thin film$^6$ due to its high tunability and low loss. For some applications the desired combination of high tunability with low dielectric permittivity with low loss is required which is difficult to achieve i.e. low permittivity with high tunabilty. In this letter, it is reported that manipulating the Zr:Ti concentration in BZT system one can engineer the tunable properties for optimum device application using different bias fields.

The system (BaZr$_x$Ti$_{1-x}$O$_3$) exhibits a pinched phase transition$^7$ at x~ 0.15, i.e. all the three phase transitions correspond to pure BaTiO$_3$ are merged or pinched into one broad peak. Further increase in Zr concentration a typical ferroelectric relaxor behavior has been observed$^8$. More recently present authors have shown the polar cluster like behavior in the higher BaZrO$_3$ concentration of BaZr$_x$Ti$_{1-x}$O$_3$ solid solution system$^9$
and then the gradual evolution of relaxor behavior\textsuperscript{10} (0.50\leq x\leq 0.80) with the increasing substitution of Ti\textsuperscript{4+} ions for the Zr\textsuperscript{4+} in the matrix of BaZrO\textsubscript{3} which has very low dielectric constant (~ 27). In the present investigation we have studied d.c. field dependence of dielectrics behavior of Ba(Zr\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3} (BZT-50) and Ba(Zr\textsubscript{0.6}Ti\textsubscript{0.4})O\textsubscript{3} (BZT-60) for the potential application as microwave tunable materials. Results show high tunability with low loss and low dielectric constant of BZT relaxors.

Dense Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} ceramics were prepared by the conventional solid-state route using BaCO\textsubscript{3} (99.997\%), TiO\textsubscript{2} (99.995\%) and ZrO\textsubscript{2} (99.978\%) powders as the starting materials. To prepare the stoichiometric compositions of Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} ceramics with x=0.50 and 0.60, powders in appropriate ratios were mixed in ball-mill for 30 h using alcohol as the milling media. Calcination of the mixed powder was carried out at 1473K for 2 h. Before pelletization, the calcined powders were ball-milled for breaking the agglomerates. Sintering of the pellets was carried out at 1773K for 15 h.

Gold electrodes were sputtered on the ceramic samples for dielectric measurements. The dielectric constant and loss tangent of the samples were measured using HP4284 LCR meter from 100 Hz to 1 MHz in the temperature range from 300K to 30K with a cooling rate of 1 K/min in a cryogenic system and a high temperature oven (Delta 9023). Tunability was measured by measuring the dielectric constant of the sample under an applied electric field using a voltage source (TREK 610, Trek Inc.) and a high voltage blocking circuit, which effectively separates the LCR meter from the voltage (0 to 2kV) applied to the sample.

The temperature dependence of dielectric constant (\varepsilon') and loss tangent (\tan\delta) for BZT-50 and BZT-60 are shown in Fig. A.1. Strong frequency dispersion is observed
Fig. A.1. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at various frequencies for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x=0.50$ and 0.60 (Arrows indicate the direction of increasing frequency)

around the $\varepsilon$ and tan$\delta$ peak for both the BZT compositions. Similar to a typical ferroelectric relaxor it is seen in both the BZT compositions that, with increasing frequency $\varepsilon'$ decreases and the temperature ($T_m$) where the dielectric maxima occur is shifted to higher temperatures. In the same manner the temperature of the loss maxima increases with increase in frequency whereas peak value increases unlike $\varepsilon'$.

Because of its better temperature stability having only one broad and diffuse peak as shown in Fig. A.1, D.C. electric field dependent dielectric studies have been carried out on BZT samples to investigate its potentiality for tunable microwave applications as Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics show extremely low loss tangent (tan$\delta$) like 0.0008 and 0.007 at 100kHz for $x=0.50$ and 0.60 compositions respectively in the temperature range from 200K to 300K. Dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) as a function of temperature at 100kHz for BZT-50 and BZT-60 under different bias electric fields are
Fig. A.2. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at 100 kHz for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x=0.50$ and 0.60 under bias of various E-field with maximum $E=30$ kV/cm and 35 kV/cm for BZT-50 and BZT-60 respectively (Arrows indicate the direction of increasing d.c. electric field).

shown in Fig. A.2. It is evident from the figure that both dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) are gradually suppressed with the increase in electric field and the peaks of $\varepsilon'$ and tan$\delta$ become increasingly broadened. The interesting feature of these two materials is that the loss (tan$\delta$) remains almost constant and low on the order of $10^{-3}$ up to $\sim200$K from room temperature for both of the BZT compositions. The tunability is determined by finding the change in dielectric constant at zero-field compared to those dielectric values when there is an applied electric field at a given temperature, using the equation$^1$:

$$Tunability(\%) = \frac{\varepsilon(E_0) - \varepsilon(E)}{\varepsilon(E_0)} \times 100\%$$

Where $E_0=0$ kV/cm and $E$ is the electric field at which we calculate the tunability. The temperature dependence of tunability at 100 kHz for both BZT compositions under
Fig. A.3. Temperature dependence of tunability (%) at 100 kHz for \( \text{Ba(Zr}_{0.50}\text{Ti}_{0.50})\text{O}_3 \) under 30kV/cm bias and for \( \text{Ba(Zr}_{0.60}\text{Ti}_{0.40})\text{O}_3 \) under 35kV/cm bias.

different d.c. biases shows a broad and diffuse peak in the temperature range from 100K to 300K as shown in Fig. A.3. The maximum dc field applied to BZT-50 and BZT-60 is 30 and 35kV/cm respectively. From Fig. A.3 it is seen that BZT-50 and BZT 60 show the maximum tunability of ~37% at ~144K under 30kV/cm bias and ~21% at ~153K under 35kV/cm bias respectively. High tunabilty of these two BZT compositions indicates the existence of enough amounts of BaTiO\(_3\) polar clusters breaking the translational symmetry of BaZrO\(_3\) matrix unlike the compositions of higher Zr\(^{4+}\) concentrations in \( \text{Ba(Zr}_x\text{Ti}_{1-x})\text{O}_3 \) system\(^9\). Even at room temperature BZT-50 and BZT-60 show ~9% (30kV/cm bias) and ~7% (35kV/cm bias) tunabilty respectively. It indicates the existence of Barium Titanate polar clusters at room temperature which is ~150K higher than transition temperature (\( T_m \)). The figure of merit (or K-factor) for the tunable dielectric materials is defined as:
\[ K - \text{factor} = \frac{\varepsilon(E_0) - \varepsilon(E)}{\varepsilon(E_0)} \times (1/\tan \delta) \]

K-factor is calculated considering the losses at zero bias. As the bias is increased tunability increases resulting the increase in K-factor. As shown in Fig. A.4 maximum K-factor achieved for BZT-50 and BZT-60 are \( \sim 148 \) at 264K under 30kV/cm and \( \sim 54 \) at \( \sim 223K \) under 35kV/cm bias respectively. Such values are impressive for the materials having low dielectric constant in order of hundreds instead of thousands. At the temperature \( (T_m) \) where the dielectric maxima occur, K-factor is low though the tunability values are higher because losses are high around \( T_m \). But above the temperature \( T_m \), because of the constant low losses in both BaZr\(_x\)Ti\(_{1-x}\)O\(_3\) ceramics (0.0008 and 0.007 for \( x=0.50 \) and 0.60 respectively) suitable dielectric properties can be tailored in the temperature range from 200K to 300K using different bias fields and manipulating the Zr:Ti concentration ratio in this BZT system.

Fig. A.4. Temperature dependence of K-factor at 100 kHz for Ba(Zr\(_x\)Ti\(_{1-x}\))O\(_3\) ceramics with \( x=0.50 \) and 0.60 under different dc biases: 10, 15, 20, 25, 30 and 35 kV/cm as labeled by numbers 1-6 respectively (For BZT-50 maximum applied dc field is 30 kV/cm).
In summary BaZr$_x$Ti$_{1-x}$O$_3$ (x= 0.50 and 0.60) ceramics prepared by conventional solid state route give suitable dielectric constant (hundreds instead of thousands) showing ferroelectric relaxor behavior. High tunability [~37% at ~144K under 30kV/cm bias for Ba(Zr$_{0.50}$Ti$_{0.50}$)O$_3$ and 21% at ~153K under 35kV/cm bias for Ba(Zr$_{0.60}$Ti$_{0.40}$)O$_3$] and high K-factor (~148 at ~264K and ~54 at ~223K for BZT-50 and BZT-60 respectively) of these materials can be useful for potential microwave tunable applications. The broad peak observed in temperature dependent study of K-factor and tunability gives the flexibility with which one can tailor the tunable properties for optimum device application using different bias fields and manipulating the Zr:Ti concentration ratio in BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) ceramics.

References
Appendix B

Enhanced electric field tunable dielectric properties of BaZr$_x$Ti$_{1-x}$O$_3$ relaxor ferroelectrics


In the course of searching the environmental friendly lead free materials, recently, lot of research works have been carried out on Barium Titanate (BaTiO$_3$) based materials for various device applications. Among the BaTiO$_3$ based perovskites (Ba,Sr)TiO$_3$ (BST) system which exhibits high dielectric constant and relatively lower leakage current, has attracted considerable attention for dynamic random access memory (DRAM)\(^1\) and tunable microwave applications\(^2,3\). But their temperature stability and reproducibility are required to be improved. Recently BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) system has shown great potential for the application as DRAM\(^4,5\) and tunable microwave devices\(^6,7\) like tunable filters, phase shifters, antennas etc. For such applications, materials with large electric field tunable dielectric constant as well as low loss are required which is difficult to achieve i.e. high tunability with low loss. In this paper, it is reported that manipulating the Zr:Ti concentration in BZT system one can engineer the tunable properties for optimum device application using different bias fields.

The system BaZr$_x$Ti$_{1-x}$O$_3$ exhibits a pinched phase transition\(^8\) at $x \sim 0.15$, i.e. all the three phase transitions corresponding to pure BaTiO$_3$ are merged or pinched into one broad peak. Further increase in Zr concentration a typical ferroelectric relaxor behavior has been observed\(^9\). More recently present authors\(^10,11\) have shown the polar cluster like
behavior in the higher BaZrO$_3$ concentration of BaZr$_x$Ti$_{1-x}$O$_3$ solid solution system ($0.80 \leq x \leq 1.00$) and then the gradual evolution of relaxor behavior ($0.50 \leq x \leq 0.75$) with the increasing substitution of Ti$^{4+}$ ions for the Zr$^{4+}$ in the matrix of BaZrO$_3$ which has very low dielectric constant (~27). Authors have also shown the potentiality of BZT system for the tunable microwave device applications$^7$. As a part of our investigation on the whole phase diagram of BaZr$_x$Ti$_{1-x}$O$_3$ system, in the present paper we have reported the d.c. field dependence of dielectrics behavior of Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$ (BZT-35), Ba(Zr$_{0.4}$Ti$_{0.6}$)O$_3$ (BZT-40) and Ba(Zr$_{0.45}$Ti$_{0.55}$)O$_3$ (BZT-45) for the potential application as microwave tunable materials. Results show very high tunability with low loss of BZT relaxors compositions.

Dense Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics were prepared by the conventional solid-state route using BaCO$_3$ (99.997%), TiO$_2$ (99.995%) and ZrO$_2$ (99.978%) powders as the starting materials. To prepare the stoichiometric compositions of Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics with $x=0.35$, 0.40 and 0.45, powders in appropriate ratios were mixed in ball-mill for 30 h using alcohol as the milling media. Calcination of the mixed powder was carried out at 1473K for 2 h. Before pelletization, the calcined powders were ball-milled for breaking the agglomerates. Sintering of the pellets was carried out at 1773K for 10 h.

Gold electrodes were sputtered on the ceramic samples for dielectric measurements. The dielectric constant and loss tangent of the samples were measured using HP4284 LCR meter from 100 Hz to 1 MHz in the temperature range from 300K to 30K with a cooling rate of 2 K/min in a cryogenic system and a high temperature oven (Delta 9023). Tunability was measured by measuring the dielectric constant of the sample under an applied electric field using a voltage source (TREK 610, Trek Inc.) and a high
voltage blocking circuit, which effectively separates the LCR meter from the voltage (0 to 2kV) applied to the sample.

Fig. B.1. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at various frequencies for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x$= 0.35, 0.40 and 0.45 (Arrows indicate the direction of increasing frequency).

The temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) for BZT-35, BZT-40 and BZT-45 are shown in Fig. B.1. Strong frequency dispersion is observed around the $\varepsilon$ and tan$\delta$ peak for all three BZT compositions. It is seen in all the BZT compositions that, with increasing frequency $\varepsilon'$ decreases and the temperature ($T_m$) where
the dielectric maxima occur is shifted to higher temperatures. In the same manner the temperature of

![Graph showing dielectric constant and loss tangent as a function of temperature for various electric fields.](image)

Fig. B.2. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent (tanδ) at 100 kHz for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ with $x =$ 0.35, 0.40 and 0.45 under bias of various electric field with maximum $E =$ 40 kV/cm (Arrows indicate the direction of increasing d.c. electric field).

the loss maxima increases with increase in frequency whereas peak value increases unlike $\varepsilon'$. These are the characteristics typically related to the relaxor ferroelectrics.

These BZT compositions show good temperature stability having only one broad and diffuse peak as shown in Fig. B.1. Furthermore, it is seen that one can achieve
dielectric constant on the order of hundreds as well as thousands by manipulating the 
Zr:Ti concentration ratio in BaZr_xTi_{1-x}O_3 (BZT) ceramics. D.C. electric field dependent 
dielectric studies have been carried out on BZT samples to investigate its potentiality for 
tunable microwave applications as Ba(Zr_xTi_{1-x})O_3 ceramics show extremely low loss 
tangent (tan\(\delta\)) on the order of 10^{-3} at 100kHz for all the compositions in the temperature 
range from 200K to 300K. Electric field dependent dielectric constant (\(\varepsilon'\)) and loss 
tangent (tan\(\delta\)) at 100kHz are measured in the temperature range from 300K to 15K for 
these BZT compositions as shown in Fig. B.2. Maximum d.c. bias of 40 kV/cm has been 
applied to all the BZT ceramics. As shown in the figure, both dielectric constant (\(\varepsilon'\)) and 
loss tangent (tan\(\delta\)) are gradually suppressed with the increase in electric field and the 
peaks of \(\varepsilon'\) and tan\(\delta\) become increasingly broadened. The dielectric constant (\(\varepsilon'\)) becomes 
on the order of hundreds with the applied d.c. bias for BZT-35 and BZT-40 in 
comparison to the order of thousands when it is measured at zero bias. It is evident from 
the Fig. B.2 that in case of BZT-35 and BZT-40 compositions, the temperature of the 
dielectric maxima (T'_m) shifted to the higher temperature with increasing d.c. bias 
whereas the temperature of the loss maxima (T''_m) shifted to the lower temperature as the 
applied bias field increases. But the T_m of both \(\varepsilon'\) and tan\(\delta\) remains almost constant with 
the various d.c. bias for BZT-45 composition.

The tunability is determined by finding the change in dielectric constant with an 
applied d.c. bias compared to those dielectric values at zero-field at a given temperature, 
using the equation^{12}: 

\[
\text{Tunability(\%)} = \frac{\varepsilon(E_0) - \varepsilon(E)}{\varepsilon(E_0)} \times 100\%
\]
Fig. B.3. Temperature dependence of tunability (%) and K-factor at 100 kHz for Ba(Zr_{0.35}Ti_{0.65})_3O_3 ceramics under different dc biases: 10, 15, 20, 25, 30 and 40 kV/cm as labeled by numbers 1-6 respectively (Arrows indicate the direction of increasing d.c. electric field).

Fig. B.4. Temperature dependence of tunability(%) and K-factor at 100 kHz for Ba(Zr_xTi_{1-x})_3O_3 ceramics with x= 0.35, 0.40 and 0.45 under 40 kV/cm dc bias.
Where $E_0 = 0 \text{ kV/cm}$ and $E$ is the electric field at which we calculate the tunability. For the applications as tunable microwave material in tunable filters, phase shifters, antennas etc., besides high tunability one should achieve high $Q = 1/\tan \delta$ or low loss to reduce the power loss from heat. The figure of merit (or $K$-factor) for the tunable dielectric materials is defined as:

$$K \text{ - factor} = \text{tunability} \times Q$$

$$= \frac{\varepsilon(E_0) - \varepsilon(E)}{\varepsilon(E_0)} \times (1/ \tan \delta)$$

In all the three BZT compositions tunability is increased with the increasing d.c. bias resulting the increase in $K$-factor. The temperature dependence of tunability (%) and $K$-factor at 100 kHz for all the BZT compositions under different d.c. biases shows a broad and diffuse peak as shown in Fig. B.3 for Ba(Zr$_{0.35}$Ti$_{0.65}$)O$_3$ (BZT-35) compositions as an example. At the temperature ($T_m$) where the dielectric maxima occur, $K$-factor is low though the tunability values are high because losses are high around $T_m$. But above the temperature $T_m$, because of the constant low losses on the order of $10^{-3}$ in all the BaZr$_x$Ti$_{1-x}$O$_3$ ceramics suitable dielectric properties can be tailored in the temperature range from 150K to 300K using different bias fields and manipulating the Zr:Ti concentration ratio in this BZT system. The temperature dependence of tunability (%) and $K$-factor at 100 kHz for BaZr$_x$Ti$_{1-x}$O$_3$ ceramics with $x = 0.35$, 0.40 and 0.45 under the maximum d.c. bias of 40 kV/cm is shown in the Fig. B.4. The summary of the tunable dielectric behavior of these three BZT compositions is shown in Table B.1. It is seen that with the decrease in Zr$^{4+}$ content in Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics both the tunability and $K$-factor are increased. At room temperature under 40 kV/cm bias BZT-35 and BZT40 show
44% and 36% tunability respectively. Because of the low losses very high K-factor like 234 and 208 are achieved at room temperature for BZT-35 and BZT40 compositions respectively. In comparison to these two materials BZT-45 shows lower tunability (24%) and K-factor (97) at room temperature. But such values are impressive for the materials having low dielectric constant on the order of hundreds instead of thousands.

Table B.1 Summary of the tunable dielectric behavior of BZT ceramics:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Room Temperature Tunable Properties</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ε’ at zero bias</td>
<td>tanδ at zero bias</td>
<td>Tunability (%) at 40 kV/cm bias</td>
<td>K-factor at 40 kV/cm bias</td>
<td>εmax at zero bias</td>
<td>Max. Tunability (%) at 40 kV/cm bias</td>
</tr>
<tr>
<td>BZT-35</td>
<td>1632</td>
<td>0.002</td>
<td>44</td>
<td>234</td>
<td>9165 at ~187K</td>
<td>93% at ~182K</td>
</tr>
<tr>
<td>BZT-40</td>
<td>1071</td>
<td>0.003</td>
<td>36</td>
<td>208</td>
<td>4978 at ~168K</td>
<td>85% at ~164K</td>
</tr>
<tr>
<td>BZT-45</td>
<td>382</td>
<td>0.003</td>
<td>24</td>
<td>97</td>
<td>1060 at ~155K</td>
<td>56% at ~154K</td>
</tr>
</tbody>
</table>

It is observed that one can bring down the dielectric constant from the order of thousands to the order of hundreds using d.c. bias resulting the maximum tunability of 93% at ~182K and 85% at ~164K for BZT-35 and BZT-40 respectively under 40 kV/cm bias field. Extremely high K-factor is achieved for these two materials in the temperature range from 150K to 300K having the maximum of 468 at ~212K and 400 at ~237K for BZT-35 and BZT-40 respectively. The unique combination of such a high tunability with
very high K-factor is very rare amongst the tunable dielectric materials so far known. BZT-45 which has the dielectric constant on the order of hundreds at zero bias shows the maximum tunability of 56% at ~154K and maximum K-factor of 160 at ~232K under 40kV/cm bias.

In summary environmental friendly lead free relaxor ferroelectric BaZr$_x$Ti$_{1-x}$O$_3$ (x= 0.35, 0.40 and 0.45) ceramics are prepared by conventional solid state route. Very high tunability [93% for BZT-35 at ~182K, 85% for BZT-40 at 164K and 56% for BZT-45 at ~154K] under 40kV/cm bias and high K-factor [468 for BZT-35 at ~212K, 400 for BZT-40 at ~237K and 160 for BZT-45 at ~232K] of these materials can be useful for potential microwave tunable device applications. The broad peak observed in temperature dependent study of K-factor and tunabilty gives the flexibility with which one can tailor the tunable properties for optimum device application using different bias fields and manipulating the Zr:Ti concentration ratio in BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) ceramics. Very high tunability (above 90%) and low losses with high dielectric constant (in the order of thousands) of some of the BZT compositions open up the option for the application in DRAM.

References


Appendix C

Tailored dielectric properties and tunability of lead free relaxor

Ba(Zr$_x$Ti$_{1-x}$)$_3$O$_5$:MgO composites


INTRODUCTION

Extensive research [1, 2] has been carried out in recent years on the electric field tunable microwave dielectric materials for their potential applications in tunable filters, phase shifters, antennas etc. Dielectric material showing high tunability (electric field dependent $\varepsilon$), low dielectric loss ($\tan\delta$) and desired permittivity ($\varepsilon'$) is required for such applications. Among the environmental friendly lead free perovskites, (Ba,Sr)TiO$_3$ solid solution system [3,4,5] has attracted considerable attention both as pure and composite with MgO for tunable microwave applications. But their temperature stability and reproducibility are required to be improved. Recently BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) system [6,7,8] has shown great potential for the application as tunable microwave devices due to its high tunability and low loss. For some tunable device applications, along with high tunability, materials having low dielectric permittivity ($\varepsilon'$) is required to match the device impedance for designing purpose. The excess of $\varepsilon'$ than the required values for planar integrated microwave components causes the complications which lead to the less efficient power transfer in the device thereby degrading the device performance. High dielectric Q (= 1/$\tan\delta$) is also another important parameter to achieve for these applications as high dielectric loss ($\tan\delta$) attenuates the microwave signal resulting the inferior device
performances. The desired combination of high tunability with low dielectric permittivity with low loss is required which is difficult to achieve i.e. low permittivity with high tunability. In our present investigation we have reported high tunability and low loss \( \tan \delta \) of the \( \text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 : \text{MgO} \) (BZT:MgO) composites which show the dielectric permittivity \( \varepsilon' < 400 \) in the temperature range from 300K to 11K.

The system \( \text{(BaZr}_x\text{Ti}_{1-x})\text{O}_3 \) exhibits a pinched phase transition [9] at \( x \approx 0.15 \), i.e. all the three phase transitions correspond to pure BaTiO\(_3\) are merged or pinched into one broad peak. Further increase in Zr concentration a typical ferroelectric relaxor behavior has been observed [10]. More recently present authors have shown the polar cluster like behavior in the higher BaZrO\(_3\) concentration of \( \text{BaZr}_x\text{Ti}_{1-x}\text{O}_3 \) solid solution system [11] \((0.85 \leq x \leq 1.00)\) and then the gradual evolution of relaxor behavior [12] \((0.50 \leq x \leq 0.80)\) with the increasing substitution of Ti\(^{4+}\) ions for the Zr\(^{4+}\) in the matrix of BaZrO\(_3\) which has very low dielectric constant \((\sim 27)\). Authors have also shown the potentiality of BZT system for the tunable microwave device applications [7,8]. To further enhance the suitability of BZT solid solution, MgO has been introduced to fabricate the BZT:MgO composites for tunable microwave device applications. MgO, a well known microwave dielectric material with low dielectric constant and loss, tailored the dielectric properties of BZT ceramics to make it useful in an array of different applications similar to the \( \text{(Ba,Sr)}\text{TiO}_3 : \text{MgO} \) [4] and \( \text{(Sr,Pb)}\text{TiO}_3 : \text{MgO} \) [13] composites. Recently authors [14] have observed the induced ferroelectric relaxor behavior in those \( \text{BaZr}_x\text{Ti}_{1-x}\text{O}_3 : \text{MgO} \) \((x = 0.20 \text{ and } 0.25)\) composites which do not show such behavior in the pure form. In the present work, the composites of \( \text{BaZr}_x\text{Ti}_{1-x}\text{O}_3 \) \((x = 0.20, 0.25, 0.30 \text{ and } 0.35)\) and 50 wt% dielectric MgO have been prepared by conventional solid state route. D.C. field
dependence of dielectrics behavior of the BZT composites have been studied for the potential application as microwave tunable materials. It is reported that manipulating the Zr:Ti concentration in Ba(ZrₙTi₁₋ₙ)O₃:MgO composites one can engineer the tunable properties for optimum device applications using different bias fields.

**EXPERIMENTAL PROCEDURE**

Dense ceramic samples of Ba(ZrₙTi₁₋ₙ)O₃:MgO composites with x= 0.20, 0.25, 0.30 and 0.35 [abbreviated as BZT₂₀:MgO, BZT₂₅:MgO, BZT₃₀:MgO and BZT₃₅:MgO respectively] were prepared by the conventional solid-state route. To prepare the stoichiometric compositions of Ba(ZrₙTi₁₋ₙ)O₃ with x=0.20, 0.25, 0.30 and 0.35, powders of BaCO₃ (99.997%), TiO₂ (99.995%) and ZrO₂ (99.997%) in appropriate ratios were mixed in ball-mill for 30 h using alcohol as the milling media. Then the mixed powders were calcined at 1473K for 2 h and milled again. Then, high purity grade magnesium oxide (MgO) was added to the Ba(Zr,Ti)O₃ powder, in the weight ratio of 50:50 (BZT:MgO) and the mixture was ball milled again. After adding the binder the composite powder was pressed into pellets. Sintering of the pellets was carried out at 1773K for 10 h.

Well sintered dense ceramics were polished and annealed. Then, gold electrodes were sputtered on the ceramic samples for dielectric measurements. The dielectric constant and loss tangent of the samples were measured using HP4284 LCR meter from 100 Hz to 1 MHz in the temperature range from 300K to 11K with a cooling rate of 2 K/min in a cryogenic system and a high temperature oven (Delta 9023). Tunabilty was
measured by measuring the dielectric constant of the sample under an applied electric field using a voltage source (TREK 610, Trek Inc.) and a high voltage blocking circuit, which effectively separates the LCR meter from the voltage (0 to 2kV) applied to the sample.

RESULTS AND DISCUSSION

Dielectric Behavior without Bias Electric Field

The temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) for BZT:MgO composites are shown in Fig. C.1. Strong frequency dispersion is observed around the $\varepsilon$ and tan$\delta$ peak for all the BZT composites. Similar to a typical ferroelectric

Fig. C.1. Temperature dependence of dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at various frequencies for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ : MgO composites with $x$= 0.20, 0.25, 0.30 and 0.35 (Arrows indicate the direction of increasing frequency).
relaxor it is seen in all the BZT composites that, with increasing frequency $\varepsilon'$ decreases and the temperature ($T_m$) where the dielectric maxima occur is shifted to higher temperatures. In the same manner the temperature of the loss maxima increases with increase in frequency whereas peak value increases unlike $\varepsilon'$.

These BZT composites show better temperature stability having only one broad and diffuse peak as shown in Fig. C.1. Furthermore, it is seen that the values of dielectric constant become a few hundreds ($<400$) in the temperature range from 300K to 11K in all the BZT:MgO composites whereas pure BZT compositions have the dielectric constant on the order of $10^4$ [15]. It is expected as MgO has very low dielectric constant ($\sim 9.8$ at room temperature). It is also observed that the ferroelectric-paraelectric phase transition temperature is shifted to the lower temperature with increasing Zr$^{4+}$ content in the Ba(Zr$_x$Ti$_{1-x}$)O$_3$: MgO composites. The notable features of the dielectric behavior of these composites are that both dielectric constant and loss become nearly independent of frequency and the loss tangent becomes almost constant ($<10^{-3}$) in the temperature range from 200K to 300K. Such a phenomena is useful for tunable microwave applications point of view which leads us to further study of the dielectric behavior of these composites in the presence of d.c. bias field.

**Dielectric Behavior with an Applied Electric Field**

D.C. electric field dependent dielectric studies have been carried out on BZT:MgO composites to investigate its potentiality for tunable microwave applications. Electric field dependent dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at 10kHz are measured in the temperature range from 300K to 11K for these BZT composites as
shown in Fig. C.2. Maximum d.c. bias of 30 kV/cm has been applied to all the BZT:MgO composites. As shown in the figure, both dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) are gradually suppressed with the increase in electric field and the peaks of $\varepsilon'$ and tan$\delta$ become increasingly broadened. It is observed that the effect of electric field on the dielectric properties becomes noticeably stronger with decrease in Zr$^{4+}$ content in Ba(Zr$_x$Ti$_{1-x}$)O$_3$ : MgO composites.

Fig. C.2. D.C. field dependent dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) at 10 kHz for Ba(Zr$_x$Ti$_{1-x}$)O$_3$ : MgO composites with x = 0.20, 0.25, 0.30 and 0.35 under bias of various E-field with maximum E = 30 kV/cm (Arrows indicate the direction of increasing d.c. electric field).

The tunability is determined by finding the change in dielectric constant with an applied d.c. bias compared to those dielectric values at zero-field at a given temperature, using the equation [12]:

$$\varepsilon'_{\text{bias}} - \varepsilon'_{\text{zero-field}} = \varepsilon'_{\text{tunable}}$$
\[ Tunability(\%) = \frac{\varepsilon(E_0) - \varepsilon(E)}{\varepsilon(E_0)} \times 100\% \]

Where \( E_0 = 0 \text{ kV/cm} \) and \( E \) is the electric field at which we calculate the tunability. For the applications as tunable microwave material in tunable filters, phase shifters, antennas etc., besides high tunability one should achieve high \( Q = 1 / \tan(\delta) \) or low loss to reduce the power loss from heat. The figure of merit (or K-factor) for the tunable dielectric materials is defined as:

\[ K - factor = \frac{tunability \times Q}{1 / \tan(\delta)} \]

Fig. C.3. Temperature dependence of tunability (%) at 10 kHz for \( \text{Ba(Zr}_x\text{Ti}_{1-x})_3\text{O}_9 : \text{MgO} \) composites with \( x = 0.20, 0.25, 0.30 \) and \( 0.35 \) under different dc biases: 9, 15, 21, 27 and 30 kV/cm as labeled by numbers 1-5 respectively.

In all the BZT:MgO composites tunability is increased with the increasing d.c. bias resulting the increase in K-factor. The temperature dependence of tunability at 10 kHz for all the BZT:MgO composites under different d.c. biases shows a broad and diffuse peak.
in the temperature range from 75K to 300K as shown in Fig. C.3. The temperature dependence of K-factor at 10 kHz for Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} : MgO composites with x= 0.20, 0.25, 0.30 and 0.35 under the maximum d.c. bias of 30 kV/cm is shown in the fig. C. 4. The summary of the tunable dielectric behavior of all the BZT:MgO composites at 10 kHz is illustrated in Table C.1. At the temperature (T\textsubscript{m}) where the dielectric maxima occur, K-factor is low though the tunability values are higher because losses are high around T\textsubscript{m}. But above the temperature T\textsubscript{m}, because of the constant low losses (less than 10\textsuperscript{3} at 10kHz) in all the BZT:MgO composites suitable dielectric properties can be tailored in the temperature range from 150K to 300K using different bias fields and manipulating the

![Graph](https://via.placeholder.com/150)

Fig. C.4. Temperature dependence of K-factor at 10 kHz for Ba(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} : MgO composites with x= (a)0.20, (b)0.25, (c)0.30 and (d)0.35 under 30 kV/cm dc bias.
Zr:Ti concentration ratio in this Ba(Zr$_x$Ti$_{1-x}$)O$_3$ composites. It is seen that with the decrease in Zr$^{4+}$ content in Ba(Zr$_x$Ti$_{1-x}$)O$_3$: MgO composites both the tunability and K-factor are increased as the value of dielectric constant without d.c. bias increases. It is noticeable from the figures that BZT35:MgO composite shows although the lower values of k-factor and tunability than the other compositions but the temperature dependence of the tunable properties becomes much lower than the other compositions.

At room temperature, 22% tunability with very high k-factor ($\sim$273) is achieved for BZT20:MgO composite at 30 kV/cm bias field which is very impressive for the materials having low dielectric constant on the order of couple of hundreds instead of thousands. Varying the Zr:Ti concentration ratio in Ba(Zr$_x$Ti$_{1-x}$)O$_3$ composites one can achieve 10-20% tunability at room temperature for the materials having the dielectric
permittivity of 100-200 at zero bias, as shown in the Table-C.1. As all the BZT:MgO composites show the loss tangent (tanδ) on the order of $10^{-4}$ very high values of K-factor in the range from 140 to 275 are achieved for various compositions at room temperature under 30kV/cm bias.

From the temperature dependence study of tunability and k-factor, it is seen that by manipulating the Zr:Ti concentration ratio in this Ba(Zr$_x$Ti$_{1-x}$)O$_3$ composites, under 30kV/cm bias one can achieve maximum tunability of 20% to 45% in the temperature range from 130K to 175K and the maximum K-factor of about 300 to 400 in the temperature range from 190K to 260K. The unique combination of such a high tunability with very high K-factor is very rare amongst the tunable dielectric materials which show the dielectric permittivity <400 at zero bias in the temperature range 300K to 11k.

**CONCLUSIONS**

In summary environmental friendly lead free relaxor Ba(Zr$_x$Ti$_{1-x}$)O$_3$ : MgO composites with x= 0.20, 0.25, 0.30 and 0.35 are prepared by conventional solid state route. From the dielectric study, we have observed the ferroelectric relaxor like behavior in all the BaZr$_x$Ti$_{1-x}$O$_3$ :MgO composites. All the BZT:MgO composites show the dielectric permittivity <400 in the temperature range from 300K to 11k. It is shown that by fabricating the composite of BZT with dielectric MgO one can achieve the excellent optimization for electric field tunability and minimized dielectric loss (less than 0.001) without compromising the integrated device component impedance matching ($\varepsilon/'<400$) in the wide range of temperature from 150K to 300K. Results show very high tunability [45% at ~175K for BZT20:MgO composite under 30 kV/cm bias] and high K-factor [387
at ~238K for BZT25:MgO composite under 30 kV/cm bias] in these low dielectric composite materials which can be used for the potential tunable microwave device applications such as tunable filters, resonators, phase shifters, antennas etc.. The broad peak observed in temperature dependent study of K-factor and tunability gives the flexibility with which one can tailor the tunable properties for optimum device application using different bias fields, manipulating the Zr:Ti concentration ratio and optimizing the percentage of MgO phase in the BaZr$_x$Ti$_{1-x}$O$_3$ :MgO composites.

References


VITA
Tanmoy Maiti

Tanmoy Maiti was born on 2nd January 1980 in India to Prabhas Chandra Maiti and Abha Maiti. He got married to Ms. Akansha Dwivedi on 6th December 2007.

EDUCATION:

- **Doctor of Philosophy**, Materials Science and Engineering (December 2007)
  The Pennsylvania State University

- **Master of Technology**, Ceramic Engineering (2004)
  Institute of Technology, Banaras Hindu University, India
  THESIS: “Structure Property Correlations and Phase Transitions in Nb$_{5+}$ substituted Pb(Zr$_{0.520}$Ti$_{0.480}$)O$_3$ (PZT) Ceramics”

- **Bachelor of Technology**, Ceramic Technology (2002)
  College of Ceramic Technology, University of Calcutta, India
  THESIS: “Some studies on ultra low cement castables prepared with Alumina and Silica sol”

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