CERIUM CLUSTERING AND RADIATION DAMAGE RESISTANCE IN 
ALUMINOPHOSPHATE AND SILICOPHOSPHATE GLASSES

A Dissertation in
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by
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ABSTRACT

Cerium oxide is a well-known additive for increasing resistance to radiation damage in glass by preventing electrons and holes freed by irradiation from becoming trapped at defect sites and inducing optical absorption bands which can severely darken the glass. Phosphate glasses provide a unique opportunity for studying radiation damage resistance due to their high rare-earth solubility, ~25 mol%. Two series of glasses, nominally AlP$_3$O$_9$-CeP$_3$O$_9$ and CeP$_3$O$_9$-SiP$_2$O$_7$, were synthesized to investigate structure-property relationships in a range of compositions near the metaphosphate.

The presence of cerium clustering, or sharing of oxygen between cerium cations, was predicted using the chain fragment cluster model, an extension of earlier models for rare-earth phosphate glasses. Using the atom% composition determined by XPS from vacuum fracture surfaces, and cation coordination measured by Ce K-edge EXAFS, $^{29}$Si CPMG NMR, and $^{27}$Al MAS NMR, it was determined that clustering occurs for glasses containing $\geq 14$ mol% Ce$_2$O$_3$ in the aluminophosphate glass series and $\geq 18$ mol% Ce$_2$O$_3$ in the silicophosphate glass series. Many measured properties have been observed to correlate with the presence or absence of cerium clustering, cluster size, or other concomitant structural changes, including: visible coloration, density, refractive index, Ce$^{3+}$ photoluminescence, and Ce$^{3+}$ paramagnetic resonance.

Additionally, radiation damage resistance was identified in the aluminophosphate and silicophosphate glasses which were predicted to have clustered cerium cations through the absence of radiation-induced phosphorus-related paramagnetic defects. This resistance is attributed to a structural implication of clustering. Specifically, cerium
cations will be in close proximity to defect precursor sites at the concentrations required for clustering and are thus able to prevent localization of electrons and holes on those sites.

Finally, irradiation-induced optical absorption was measured in all glass compositions and was attributed to a change in the local electronic structure of cerium which is similar to intervalence charge transfer. This induced absorption provides evidence for the mechanism of radiation damage resistance where cerium acts as a preferential electron- or hole-trap and either changes oxidation state or forms Ce$^{3+}$ and Ce$^{4+}$e$^-$. 
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CHAPTER 1

INTRODUCTION

Cerium is a well-known glass additive for decolorization, fining, UV absorption, and blue luminescence.\textsuperscript{1-4} However, it is perhaps best known for providing radiation damage resistance in glasses.\textsuperscript{5} The ability to withstand high radiation environments without darkening, or solarization, is a desired property for glass used to protect optical and electronic devices, including solar cells, i.e. coverglass. Solar energy is becoming a more prominent part of the energy portfolio through a push toward green, renewable, energy sources.\textsuperscript{6} As part of this movement, solar cells are becoming more widespread in both terrestrial and space-based applications, from solar roofs on private homes to telecommunications satellites. Understanding the phenomenon of radiation damage resistance within the context of glass structure, will allow for the design of glass compositions specifically suited for high energy environments, where long-term performance is required with minimal darkening of the coverglass over time.

Phosphate glasses were selected for this study, rather than silicate glasses, due to their high rare-earth solubility, > 25 mol\% versus 2-3 mol\%. The difference in RE$_2$O$_3$ solubility between these two glassformers is readily apparent from the binary phase diagrams of La$_2$O$_3$-P$_2$O$_5$ and La$_2$O$_3$-SiO$_2$ shown in Figures 1.1 and 1.2.\textsuperscript{7,8} In particular, a region of high temperature liquid-liquid immiscibility at > 2.5 mol\% La$_2$O$_3$ indicates the low solubility of La$_2$O$_3$ in SiO$_2$. The high solubility for luminescent RE$^{3+}$ cations in phosphate glasses, in particular aluminophosphate glasses with their increased durability,\textsuperscript{9,10} makes them an ideal laser host material.\textsuperscript{11}
Two glass series, centered on cerium metaphosphate (CeP$_3$O$_9$) were chosen for the characterization of the local structure of cerium in a range of compositions, with subsequent study of radiation damage resistance. Cerium metaphosphate glasses, and rare-earth phosphate glasses in general, are of interest due to the possibility of rare-earth clustering. Clustering, the sharing of oxygen between rare-earth cations, could occur, or be avoided, depending on the coordination assumed by these large cations, typically between 6 and 12. While many ultraphosphate and metaphosphate glasses have been studied, including cerium metaphosphate, clustering has not been directly measured by EXAFS, neutron diffraction, or x-ray diffraction. Instead, an R…R distance indicative of clustering has been measured for a samarium metaphosphate and terbium metaphosphate glass by anomalous dispersion neutron diffraction and magnetic difference neutron diffraction respectively.

The first ternary compositional series, CeP$_3$O$_9$-AlP$_3$O$_9$ (CAP), is of interest because clustering could be avoided if cerium assumes octahedral coordination, as aluminum does in the metaphosphate crystal. In AlP$_3$O$_9$, octahedrally coordinated Al$^{3+}$ cations connect chains of Q$^2$ phosphate tetrahedra. However, in CeP$_3$O$_9$, 8-fold Ce$^{3+}$ form edge-shared dodecahedra chains, which cross-link Q$^2$ phosphate chains.

While properties of CAP glasses have been measured previously, their structure was not characterized. Alternatively, two series of lanthanum aluminophosphate glasses were the subject of structure studies, but also did not study rare-earth coordination across the compositional series. This work examines both aluminum and cerium coordination in a series of cerium aluminophosphate glasses and subsequently predicts the presence or absence of cerium clustering.
The second ternary compositional series, Ce$_3$O$_9$-SiP$_2$O$_7$ (CSP), raises the possibility of both octahedrally coordinated silicon cations and intermediate range segregation similar to the modified random network model. The presence of two different silicon coordinations suggests the possibility of SiO$_2$-like regions composed of Q$^4$ silicate tetrahedra, SiP$_2$O$_7$-like regions incorporating octahedrally coordinated silicon and Q$^1$ phosphate tetrahedra, and modified ultraphosphate-like regions. Studies of 6-coordinated silicon in sodium silicophosphate glasses have provided evidence for this type of preferential intermediate range bonding. However, work on octahedral silicon has largely been limited to binary silicophosphate glasses, and alkali or alkaline-earth silicophosphate glasses. Though properties for cerium silicophosphate glasses have been reported previously, this study on CSP glasses expands silicophosphate systems where silicon coordination has been examined to include a rare-earth silicophosphate. Additionally, it makes a prediction for cerium clustering through the examination of cerium coordination.

There have been many studies of radiation damage resistance in cerium-doped glasses, both silicate and phosphate, detailing changes in both optical absorption and radiation-induced paramagnetic defects. However, to the author’s knowledge, only one study on high-cerium phosphate glasses was published, which focused on the cerium metaphosphate to barium metaphosphate compositional series. The work reported here examines radiation damage across both the CAP and CSP series described above, and correlates the presence or absence of radiation-induced defects to the measured structure.

Chapter 2 reviews the uses of cerium oxide in glass while Chapter 3 reviews the structure of phosphate glasses. Chapter 4 describes the glass melting and sample
preparation procedure, as well experimental methods used to determine glass transition
temperature, density, refractive index, optical transmission, and Ce$^{3+}$ photoluminescence.

Chapter 5 describes the use of x-ray photoelectron spectroscopy (XPS) to
determine the composition of the CAP and CSP glasses from vacuum fracture surfaces
and to determine the Ce$^{3+}$/Ce$^{4+}$ ratio from the Ce 3d spectra.

Chapter 6 discusses the determination of average cerium coordination in CAP and
CSP glasses through the use of Ce K-edge extended x-ray absorption fine structure
(EXAFS) spectroscopy.

Chapter 7 reports resonances from Ce$^{3+}$ and radiation-induced phosphate-related
defects identified by electron paramagnetic resonance (EPR) in irradiated CAP and CSP
glasses. A procedure is also defined for the determination of hyperfine splitting
parameters for the measured paramagnetic defects.

Chapter 8 introduces a new chain fragment cluster model for calculation of
average cluster size based upon the existing models presented in Chapter 3. Aluminum
and silicon cation coordination is reported for the CAP and CSP glasses as measured by
$^{27}$Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy and
$^{29}$Si Carr–Purcell–Meiboom–Gill (CPMG) MAS NMR spectroscopy respectively.
Cerium clustering is predicted for a range of compositions in both glass series based upon
measured composition and cation coordination, and correlated to density, refractive index,
optical transmission, and Ce$^{3+}$ photoluminescence.

Chapter 9 discusses radiation damage resistance in the CAP and CSP glasses as
measured by changes in optical transmission and the presence of radiation-induced
paramagnetic defects. The resistance to damage, or lack thereof, is correlated to the measured glass structure.

This study provides new structural information for cerium, silicon, and aluminum across two series of cerium aluminophosphate and silicophosphate glasses, expanding the range of data available from the binary cerium metaphosphate (CeP$_3$O$_9$) endpoint. It also presents a significant expansion of the study of radiation damage resistance past cerium-doping, into these two compositional series, and correlates their resistance to damage to the measured structure. Finally, a model for calculation of average cerium cluster size is also proposed which is applicable to binary rare-earth phosphate, rare-earth aluminophosphate, rare-earth silicophosphate glasses, and rare-earth aluminosilicophosphate glasses, where RE$_2$O$_3 < 25$ mol%.
Figure 1.1: La$_2$O$_3$-P$_2$O$_5$ phase diagram.*

*Adapted from Phase Diagrams for Ceramists: 11:9312.7
Figure 1.2: La$_2$O$_3$-SiO$_2$ phase diagram.*

*Adapted from Phase Diagrams for Ceramists: 2:2372.®
CHAPTER 2
CERIUM OXIDE IN GLASS

Cerium oxide is a well-known glass additive for several properties, including: decolorization, fining, UV absorption, blue luminescence, and radiation damage resistance. The stability of both Ce\textsuperscript{3+} and Ce\textsuperscript{4+} in glass impacts several of these properties and the ability of cerium to function as a decolorizing and fining agent depends upon it.

2.1 Ce\textsuperscript{3+}/Ce\textsuperscript{4+} REDOX EQUILIBRIA

The oxidation state of cerium has been found to be highly dependant on composition. Cerium is found exclusively as Ce\textsuperscript{3+} in phosphate glasses such as gadolinium sodium phosphate glasses,\textsuperscript{30} calcium metaphosphate glasses,\textsuperscript{31} and sodium phosphate glasses.\textsuperscript{32} In silicate glasses, the predominance of both oxidation states has been determined with yttrium aluminosilicate glasses,\textsuperscript{33} 2\% Al\textsubscript{2}O\textsubscript{3} doped silica,\textsuperscript{34} 2\% P\textsubscript{2}O\textsubscript{5} doped silica,\textsuperscript{34} and lanthanum aluminosilicate glasses\textsuperscript{35} containing mostly Ce\textsuperscript{3+} and cerium-doped silica reported to contain mainly Ce\textsuperscript{4+} or Ce\textsuperscript{3+} based on synthesis conditions.\textsuperscript{3,34} Additionally, in sodium silicate glasses containing ≤ 7.5 mol\% CeO\textsubscript{2}, cerium is present almost exclusively as Ce\textsuperscript{3+}, while in a sodium silicate glass with 10 mol\% CeO\textsubscript{2}, ~40\% of the cerium is present as Ce\textsuperscript{4+}.\textsuperscript{36}

As a multivalent cation known for reaching oxidation-reduction equilibrium in glass, it is instructive to compare this experimental data with the predictions of standard redox equilibria for cerium oxides. Using the equations for standard Gibbs free energy as
a function of temperature \((\Delta G^o_1)\) given by Paul\(^3\) for \(\langle Ce \rangle + \langle O_2 \rangle = \langle CeO_2 \rangle\) and \(\frac{4}{3}\langle Ce \rangle + \langle O_2 \rangle = \frac{2}{3}\langle CeO_3 \rangle\) it is possible to calculate the change in free energy as a function of temperature \((\Delta G_T)\) for the reaction of ceric oxide to form cerous oxide and oxygen shown in Equation 2.1. This redox reaction may also be written in terms of the ionic species that would be present in glass as shown in Equation 2.2.a, with the equilibrium constant, \(K\), as shown in Equation 2.2.b where \(R = \) ideal gas constant, \(T = \) temperature, and \(pO_2 = \) partial pressure oxygen. For a melting temperature of 1500 °C (~1800 K) and ambient atmospheric conditions, \(pO_2 \approx 0.21\) atm, the percentage of cerium present as Ce\(^{4+}\) is expected to be 40%. This value differs significantly from the Ce\(^{3+}\) predominance measured in phosphate glasses as well as some silicate glasses, though agrees well with that measured from a sodium silicate glass containing 10 mol% CeO\(_2\).

\[
4CeO_2 \leftrightarrow 2Ce_2O_3 + O_2 \quad (2.1)
\]

\[
4Ce^{4+} + 2O^{2-} \leftrightarrow 4Ce^{3+} + O_2 \quad (2.2.a)
\]

\[
\Delta G_T = -RT \ln K = -RT \ln \frac{[Ce^{3+}]^4}{[Ce^{4+}]^4} pO_2 \quad (2.2.b)
\]

This disparity is most certainly due to the use of standard free energies of formation for CeO\(_2\) and Ce\(_2\)O\(_3\) rather than accounting for the glass composition dependence of the equilibrium constant. For example, in a study of cerium-doped sodium disilicate glasses equilibrated at 1085° C, the cerium redox was measured at several different oxygen partial pressures.\(^3\) From the linear relationship between \(-\log(pO_2)\) and \(\log(Ce^{3+}/Ce^{4+})\), it is possible to estimate that 68% of the cerium would be present as Ce\(^{4+}\) in these glasses melted under ambient atmospheric conditions. A comparison between Ce\(^{4+}\)% and partial pressure of oxygen is shown in Figure 2.1 as
calculated from standard Gibbs free energy given by Paul\textsuperscript{37} at 1800 K (~1500 °C), and for sodium disilicate glasses at 1085° C using Johnston’s data\textsuperscript{38} Clearly, there is a strong influence of both oxygen partial pressure and glass composition on cerium redox equilibria.

2.2 DECOLORIZING AND FINING AGENT

As a polyvalent cation, cerium can form redox couples with other polyvalent cations in glass. This allows cerium to act as a decolorizing agent for some cations by shifting the redox equilibria from a highly absorbing oxidation state that produces visible coloration to a less absorbing oxidation state that does not produce as much visible coloration. To determine which polyvalent cation will oxidize and which will reduce in any given redox couple, it is useful to compare the redox equilibria for each cation in the glass composition of interest, at a defined temperature and partial pressure of oxygen, using a plot of \(-\log(pO_2)\) versus \(\log(M^{x+}/M^{(x+n)+})\). For the generic case shown in Equation 2.3.a, the relationship between \(-\log(pO_2)\) and \(\log(M^{x+}/M^{(x+n)+})\) can be determined as shown in Equation 2.3.b-d, from the equilibrium constant \(K\).\textsuperscript{1,38}

Specifically, a plot of \(-\log(pO_2)\) versus \(\log(M^{x+}/M^{(x+n)+})\) will have a slope of \(4/n\) and an x-intercept of \(E’\), the relative reduction potential.\textsuperscript{1} \(E’\) varies with glass composition, melt temperature, and concentration of the polyvalent cation.\textsuperscript{1} For any defined \(pO_2\), the cation in the redox couple with the greater \(\log(M^{x+}/M^{(x+n)+})\) value will be reduced, while the other will be oxidized.\textsuperscript{1}
\[
\frac{4}{n} M^{(x+n)^+} + 2O^{2-} \leftrightarrow \frac{4}{n} M^{x+} + O_2 \quad (2.3.a)
\]

\[
K = \frac{pO_2 \frac{M^{x+}}{n}}{\left[ M^{(x+n)^+} \right]^4_n} \quad (2.3.b)
\]

\[
\frac{K}{pO_2} = \left( \frac{M^{x+}}{M^{(x+n)^+}} \right)^4_n \quad (2.3.c)
\]

\[
-\log(pO_2) = \frac{4}{n} \log \left( \frac{M^{x+}}{M^{(x+n)^+}} - E' \right) \quad (2.3.d)
\]

Cerium can be used in this manner to decolorize iron-containing silicate glasses by shifting iron from Fe\(^{2+}\), responsible for a blue-green coloration, to Fe\(^{3+}\), which only produces a weak yellow coloration, as shown in Equation 2.4.\(^1\) A \(-\log(pO_2)\) versus \(\log(M^{x+}/M^{(x+n)^+})\) plot for cerium and iron in a sodium disilicate glass as measured by Johnston\(^38\) is given in Figure 2.2, showing that cerium is capable of oxidizing Fe\(^{2+}\) for in this system.

\[
Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+} \quad (2.4)
\]

The polyvalent nature of cerium also allows cerium oxide (CeO\(_2\)) to be used as a fining agent in glasses, similar to arsenic and antimony oxides.\(^2\) Cerium oxide releases oxygen into the melt, according to Equation 2.1, which can enlarge existing bubbles, facilitating their rise to the surface of the melt via buoyancy according to Stoke’s Law, or create new bubbles which can sweep other smaller bubbles to the surface.\(^2\) With the manufacturing industry moving toward ‘environmentally green products and processes,’ cerium oxide is preferred as a fining agent over arsenic oxide and antimony oxide, both of which are toxic and considered hazardous materials.\(^39\)
2.3 ABSORPTION AND PHOTOLUMINESCENCE

Most transition metal and rare-earth cations are notable for having absorption peaks in the visible region of the electromagnetic spectrum, resulting in visible coloration. Both Ce$^{3+}$ and Ce$^{4+}$, however, have absorption peaks in the ultraviolet region, which does not lead to visible coloration. Specifically, the Ce$^{3+}$ absorption peak is due to the lone 4f electron transitioning to the 5d orbital and occurs at 290 nm in calcium metaphosphate glasses, 314 nm in sodium silicate glasses, and 320 nm in silica. Alternatively, the Ce$^{4+}$ absorption peak in oxide glasses is due to the charge transfer transition of an electron from a delocalized oxygen orbital to an empty orbital mainly localized on cerium and occurs at 240 nm in sodium silicate glasses, and 260 nm in silica. The ability to absorb UV radiation without any visual coloration has led to the addition of cerium oxide to glasses intended for eye protection and other applications where UV transmission is not desired.

Rare-earth cations are also known for their luminescence, emission of electromagnetic radiation in the visible range, due to the excitation by electromagnetic radiation, often in the ultraviolet or visible range (photoluminescence), electrons (cathodoluminescence), ionizing radiation (scintillation), etc. In contrast to the line emission exhibited by other rare-earth cations due to well-shielded inner 4f electron transitions, broad luminescence emission bands are displayed for cerous (Ce$^{3+}$) cations due to 4f-5d transitions of its single valence electron. While the 4f ground state is only affected slightly by the local environment, the 5d excited state is an outer electron level and subject to significant influence by the host lattice, or in the case of glasses, local structure. In particular, inhomogeneous broadening of the emission peak is expected due
to differences in local environment between Ce\textsuperscript{3+} sites from the intrinsic disorder of glasses.\textsuperscript{4}

For Ce\textsuperscript{3+} photoluminescence, the single 4f\textsuperscript{1} electron is first excited from the ground state (\textsuperscript{2}F\textsubscript{5/2}) to one of the 5d\textsuperscript{1} states though ultraviolet absorption.\textsuperscript{4,43} For free Ce\textsuperscript{3+} ions, the excited 5d levels are 2,489 cm\textsuperscript{-1} apart at 49,737 cm\textsuperscript{-1} for \textsuperscript{2}D\textsubscript{3/2} and 52,226 cm\textsuperscript{-1} for \textsuperscript{2}D\textsubscript{5/2}, and are further are subject to crystal field splitting according to their local symmetry environment.\textsuperscript{4,43} The excited electron then relaxes to the lowest energy level in the excited state though non-radiative decay.\textsuperscript{4} Finally, the electron returns to one of the two 4f ground states produced by spin-orbit coupling, the \textsuperscript{2}F\textsubscript{5/2} or \textsuperscript{2}F\textsubscript{7/2} level (separated by 2,253 cm\textsuperscript{-1} in a free Ce\textsuperscript{3+} ion), through spontaneous emission, yielding two emission bands.\textsuperscript{4,43} Normally, Ce\textsuperscript{3+} photoluminescence occurs at blue or ultraviolet wavelengths, at 450 nm for SiO\textsubscript{2},\textsuperscript{3,34} and at 350 nm in calcium metaphosphate glasses.\textsuperscript{31} But, by changing the host lattice in crystalline compounds, it is possible to “tune” the luminescence to yellow (550nm) in Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Ce\textsuperscript{3+} (YAG:Ce)\textsuperscript{44}, and red (625 nm) in CaSiN\textsubscript{2}:Ce\textsuperscript{3+}.\textsuperscript{45}

2.4 RADIATION DAMAGE RESISTANCE

Perhaps the most notable reason for using cerium oxide in glass is the observed increase in resistance to damage from gamma rays, x-rays, and other high energy forms of radiation, both wave and particle. Irradiation frees electrons and holes which become trapped at defect sites, intrinsic to glass and its processing, and can induce optical absorption bands which severely darken the glass. Cerium, and other polyvalent cations such as iron, vanadium, and titanium have been observed to prevent radiation-induced
optical absorption bands, thus attributing this property to the multivalent nature of these cations.\textsuperscript{5,46} However, cerium is unique in having intrinsic absorption bands in the ultraviolet region, while these other cations have visible absorption bands, making them less desirable candidates for radiation damage resistance in optical glasses.\textsuperscript{5,29,40}

Several investigations have been conducted on cerium-containing glasses in order to determine if a change in oxidation state occurs due to irradiation. Kreidl and Hensler did not find any evidence for a change cerium redox with irradiation in study of K-Ba-aluminophosphate glasses.\textsuperscript{5} Though they did measure a radiation-induced UV absorption at 270 nm rather than a visible absorption in those glasses containing cerium.\textsuperscript{5} Additionally, Alers’ study of Ce-Ba-phosphate glasses did not detect a change in cerium oxidation state with irradiation by measurement of Ce\textsuperscript{3+} magneto-optic (Faraday) rotations, though a radiation-induced optical absorption peak at 320-340 nm was measured.\textsuperscript{29} Alers postulated that the cerium cations act as intermediate energy traps which allow electrons to leave at ambient temperatures and recombine at their original site, preventing the formation of optical absorption bands without changing oxidation state.\textsuperscript{29} He also noted that this mechanism may only be applicable to high-cerium content glasses.\textsuperscript{29}

Alternatively, other studies of cerium-doped glasses did find evidence for a change in oxidation state with irradiation. Bishay measured a radiation-induced color center at 650 nm in highly reduced cerium-doped Ba- and K-aluminoborate glasses.\textsuperscript{47} This absorption band was attributed to Ce\textsuperscript{3+} trapping an electron, and is not present when Ce\textsuperscript{4+} is available to capture the electron instead.\textsuperscript{47,48} It was also determined that hole capture by Ce\textsuperscript{3+} suppresses formation of a visible absorption band at 525-550 nm,
attributed to an intrinsic hole center in the base glass.\textsuperscript{47,48} Additionally, Bishay attributes opposing electron- and hole-trapping reactions for maintaining the redox ratio of cerium in irradiated K-aluminoborate glasses.\textsuperscript{48} In a study of sodium trisilicate glass, Stroud attributed an induced absorption band at 250 nm to a Ce\textsuperscript{3+} center, a Ce\textsuperscript{3+} which has trapped a hole.\textsuperscript{40,49,50} The suppression of absorption bands from trapped electron sites which extend into the visible was attributed to Ce\textsuperscript{4+} trapping electrons to form Ce\textsuperscript{4+}+e\textsuperscript{-} centers, though a specific absorption band was not identified.\textsuperscript{49,50}

It has been noted in several studies that the initial oxidation-reduction ratio of cerium affects the extent of radiation damage resistance. However, the optimal ratio identified varies with the glass system under investigation. Kreidl and Hensler’s study of aluminophosphate glasses identified highly reduced cerium as the most effective.\textsuperscript{5} Alternatively, studies by Bishay of aluminoborate glasses and of sodium trisilicate glasses by Stroud indicate that the presence of both oxidation states of cerium is required to suppress visible absorption bands.\textsuperscript{47-49}

Thus, two mechanisms for cerium-induced radiation damage resistance in glass have been proposed. In the first, cerium acts as a preferential electron- or hole-trap and either changes oxidation state or forms Ce\textsuperscript{3+} and Ce\textsuperscript{4+}+e\textsuperscript{-}. In the second, cerium acts as an intermediate energy trap and allows e\textsuperscript{-} and h\textsuperscript{+} freed by irradiation to recombine at their original site, producing no change in redox equilibrium. Additionally, induced absorption bands at 250 nm and 320-340 nm have been measured in Ce-containing glasses and are attributed to cerium sites rather than radiation-induced defects. Finally, the optimal initial redox ratio for cerium to prevent radiation-induced defects has been found to vary with composition.
Figure 2.1: Ce$^{4+}$% versus partial pressure oxygen as calculated from standard Gibbs free energy reactions given by Paul$^{37}$ at 1800 K, and from Johnston’s data for sodium disilicate glasses equilibrated at 1085° C.$^{38}$
Figure 2.2: Redox equilibria for cerium and iron in a sodium disilicate glass at 1085° C as measured by Johnston.38
CHAPTER 3

PHOSPHATE GLASS STRUCTURE MODELS

Similar to silicate glasses, the network in phosphate glasses is created by interconnected tetrahedra. In SiO₂, a fully polymerized 3D network is created by SiO₄ tetrahedra with four bridging-oxygen bonds. However, due to the 5+ charge of the phosphorus cation, the 3D network in vitreous P₂O₅ is not fully polymerized, instead being formed from PO₄ tetrahedra with only three bridging oxygen bonds. This important structural difference impacts network formation in phosphate glasses.

3.1 [PO₄]³⁻ STRUCTURAL UNITS

Qⁿ terminology is used to identify the number of bridging oxygens (n) per phosphate tetrahedra.⁵¹ The oxygen to phosphorus ratio (O/P), a measure of the network connectivity in a phosphate glass, can be associated with the predominance of a particular Qⁿ unit.⁵¹ Additionally, the strength of the bonds between the phosphorus cation and the oxygen anions can be expressed in terms of valence units (VU), cation charge divided by cation coordination number, as defined by Pauling’s second rule.¹⁰ Each oxygen anion, having a formal charge of -2, requires bonding that supplies a charge of +2, or 2.0 VU.¹⁰

In ν-P₂O₅ (O/P = 2.5), a cross-linked 3D network is created by Q³ phosphate tetrahedra with 3 bridging oxygen (BO) bonds and one double bond to a non-bridging oxygen (NBO).⁵¹,⁵³ Each BO receives 1.0 VU from each of two phosphorus cations, while the NBO receives 2.0 VU from one double bond with a phosphorus cation.
With the addition of other network formers, modifiers, and intermediates, the O/P ratio increases in phosphate glasses. For metaphosphate glasses (O/P = 3), the phosphate network consists predominantly of Q\(^2\) units, with 2 non-bridging oxygen bonds (NBO), organized into chains and rings.\(^{51,53-55}\) In the Q\(^2\) tetrahedra, each NBO receives 1.5VU from the phosphorus cation, leaving 0.5VU to be provided by other cations present in the glass.\(^{10}\)

Pyrophosphate glasses (O/P = 3.5) have a structure characterized by Q\(^1\) dimers joined by a single bridging oxygen bond.\(^{10,51,55}\) In the Q\(^1\) phosphate tetrahedra, the phosphorus cation contributes 1.33 VU to each of the 3 non-bridging oxygen anions with the remaining 0.67 VU contributed by other cations present in pyrophosphate glasses.\(^{10}\)

Finally, orthophosphate glasses (O/P = 4) consist of isolated Q\(^0\) phosphate tetrahedra with four NBO’s and can be considered ‘invert’ glasses due to the lack of bridging oxygens between phosphorus.\(^{10,51,55}\) In the Q\(^0\) phosphate tetrahedra, the +5 charge of the phosphorus cation is equally divided over the 4 non-bridging oxygen bonds, contributing 1.25VU to each bond.\(^{10}\)

Ultraphosphate glasses are those in the range from \(\nu\)-P\(_2\)O\(_5\) to metaphosphate glasses (2.5 > O/P > 3.0) where the structure transitions from a random 3D network of PO\(_4\) units to chains of phosphate tetrahedra.\(^{51}\) This range encompasses the ultraphosphate crystal, [P\(_5\)O\(_{14}\)]\(^{3-}\), which has a structure comprised of both Q\(^3\) and Q\(^2\) species.\(^{56}\)

The term polyphosphate is applied to those glasses in the range from metaphosphate through pyrophosphate to orthophosphate.\(^{51}\) The decreasing P\(_2\)O\(_5\) content along this series results in shortening of the Q\(^2\) phosphate chains to Q\(^1\) dimers and finally
isolated tetrahedra.\textsuperscript{51} Table 3.1 lists the $Q^n$ structural units associated with different phosphate glass compositions and some of their identifying quantities.

### 3.2 MODEL: BINARY DISTRIBUTION OF $Q^n$ PHOSPHATE TETRAHEDRA

A binary distribution of $Q^n$ phosphate tetrahedra can be predicted from the glass composition for modified phosphate glasses, although inherent disorder and disproportionation will lead to a distribution of $Q^n$ units in actual phosphate glasses.\textsuperscript{51,55} This binary distribution is calculated from the quantity $y$, or the number of oxygen atoms added per $P_2O_5$ from network modifiers, as defined in Equation 3.1, where $c_\alpha$ is the atomic fraction of $\alpha$, $N_\alpha$ is the number of $\alpha$ atoms, and $N$ is the total number of atoms.\textsuperscript{57-60}

\begin{equation}
y = 2 \frac{c_\alpha}{c_p} - 5 \quad (3.1.a)
\end{equation}

\begin{equation}
c_\alpha = \frac{N_\alpha}{N} \quad (3.1.b)
\end{equation}

\begin{equation}
N = \sum_{\alpha} N_\alpha \quad (3.1.c)
\end{equation}

In the ultraphosphate region, $(2.5 > O/P > 3.0)$ or $(0 < y < 1)$, the fraction of $Q^3$ and $Q^2$ phosphate tetrahedra are given by Equation 3.2.\textsuperscript{60}

\begin{equation}
f(Q^3) = 1 - y \quad (3.2.a)
\end{equation}

\begin{equation}
f(Q^2) = y \quad (3.2.b)
\end{equation}

Likewise, the fraction of $Q^2$ and $Q^1$ phosphate tetrahedra for compositions between the metaphosphate and pyrophosphate, $(3.0 > O/P > 3.5)$ or $(1 < y < 2)$, are given by Equation 3.3.\textsuperscript{60}
Finally, the fraction of $Q^1$ and $Q^0$ phosphate tetrahedra for compositions between the pyrophosphate and orthophosphate, $(3.0 > O/P > 3.5)$ or $(2 < y < 3)$, are given by Equation 3.4.60

\[ f(Q^1) = 3 - y \] (3.4.a)
\[ f(Q^0) = y - 2 \] (3.4.b)

The average number of BO and NBO around each phosphorus cation, $\bar{n}_{RE}^{BO}$ and $\bar{n}_{RE}^{NBO}$ respectively, can also be determined as shown in Equation 3.5.60

\[ \bar{n}_{P}^{BO} = 3 - y \] (3.5.a)
\[ \bar{n}_{P}^{NBO} = 1 + y \] (3.5.b)

Values for $y$, $\bar{n}_{RE}^{BO}$, and $\bar{n}_{RE}^{NBO}$ are give in Table 3.1 for $\nu$-P$_2$O$_5$, meta-, pyro-, and ortho-phosphate glasses.

For binary phosphate glasses, the quantity $y$ can also be defined according to composition as shown in Table 3.2 for several different metal oxides. The molar fraction of modifier (x) for the meta-, pyro-, and ortho-phosphate compositions is also given in Table 3.2. As cerium is the trivalent rare-earth oxide of interest in this work, Equations 3.2, 3.3, and 3.4 are rewritten using $y = 3x/(1-x)$ in Equations 3.6-3.8, and are shown graphically in Figure 3.1. The equation for $\bar{n}_{RE}^{BO}$ and $\bar{n}_{RE}^{NBO}$ are also rewritten in Equation 3.9.
\[
f(Q^3) = \frac{1 - 4x}{1 - x} \quad (3.6.a)
\]
\[
f(Q^2) = \frac{3x}{1 - x} \quad (3.6.b)
\]
\[
f(Q^1) = \frac{2 - 5x}{1 - x} \quad (3.7.a)
\]
\[
f(Q^1) = \frac{4x - 1}{1 - x} \quad (3.7.b)
\]
\[
f(Q^0) = \frac{3 - 6x}{1 - x} \quad (3.8.a)
\]
\[
f(Q^0) = \frac{5x - 2}{1 - x} \quad (3.8.b)
\]

\[
\bar{n}_{p}^{BO} = \frac{3 - 6x}{1 - x} \quad (3.9.a)
\]
\[
\bar{n}_{p}^{NBO} = \frac{1 + 2x}{1 - x} \quad (3.9.b)
\]

### 3.3 MODEL: RARE-EARTH PHOSPHATE GLASSES

In binary rare-earth phosphate glasses, rare-earth cations (RE\(^{3+}\)) are expected to bond to NBO’s from phosphate tetrahedra as observed in rare-earth phosphate crystals.\(^{61}\) Three structural regions have been defined for these glasses, in order of increasing RE\(_2\)O\(_3\) concentration, based on the relationship between the average number of oxygen available per rare-earth cation (\(\bar{n}_{RE}^{NBO}\)) and rare-earth coordination (CN\(_{RE}\)) as shown in Table 3.3.\(^{61,62}\) Equation 3.10 gives \(\bar{n}_{RE}^{NBO}\) calculated from both atomic fractions (\(c_\alpha\)) and mole fraction RE\(_2\)O\(_3\) (\(x\)).\(^{58-60,62}\)
Region I is defined by $\bar{n}_{RE}^{NBO} > CN_{RE}$, where the number of non-bridging oxygens available per rare-earth cation exceeds the maximum coordination number assumed by that cation.\textsuperscript{62} As RE$_2$O$_3$ concentration increases in this region, the $\bar{n}_{RE}^{NBO}$ decreases and the phosphate network is repolymerized through increased RE-O-P bonding.\textsuperscript{61}

Once $\bar{n}_{RE}^{NBO} = CN_{RE}$, for the maximum coordination assumed by the rare-earth cation, the glass network is completely repolymerized with all NBO bonds from PO$_4$ tetrahedra bonding to a RE cation.\textsuperscript{61,62} The glass now enters Region II, where $\bar{n}_{RE}^{NBO} = CN_{RE}$ and complete network polymerization is maintained by a decrease in CN$_{RE}$ with increasing RE$_2$O$_3$ content.\textsuperscript{61,62}

In these first two regions, rare-earth cations remain isolated and no RE-O-RE bonding occurs.\textsuperscript{61,62} However, once the coordination of the rare-earth cation reaches its minimum, Region II behavior can no longer be maintained with increasing RE$_2$O$_3$ content and the glass enters Region III, where $\bar{n}_{RE}^{NBO} < CN_{RE}$.\textsuperscript{61,62} As a result, rare-earth clustering, the sharing of corners (1 oxygen), edges (2 oxygen), and possibly faces (3 oxygen) between RE polyhedra, is expected in this region.\textsuperscript{61,62}

A plot of rare-earth coordination versus RE$_2$O$_3$ concentration is given in Figure 3.2 and shows Region I, II, and III behavior for a RE$^{3+}$ that assumes a maximum coordination of 9 and a minimum coordination of 6.

The fraction of NBO’s shared between rare-earth cations ($f_s$) for Region III behavior is given in Equation 3.11.\textsuperscript{60} Furthermore, if rare-earth cations are assumed to
only edge-share, the average number of next-nearest rare-earth neighbors around each rare-earth cation ($\bar{n}_{RE}^{RE}$) can be estimated using Equation 3.12.  

$$f_s = \frac{CN_{RE} - \bar{n}_{RE}^{NBO}}{CN_{RE}}$$  \hspace{1cm} (3.11)$$

$$\bar{n}_{RE}^{RE} = f_s CN_{RE}$$  \hspace{1cm} (3.12)$$

3.4 MODEL: ALUMINOPHOSPHATE GLASSES

With the addition of $\text{Al}_2\text{O}_3$ as a third oxide component to modified phosphate glasses, several Al-NBO-P linkages are possible which fully satisfy the NBO’s charge requirements. For example, an octahedrally coordinated $\text{Al}^{3+}$ supplies 0.5 VU to each of its coordinate oxygens, capable of fully charge satisfying a $Q^2$ NBO which receives 1.5 VU from its phosphorus, as in the $\text{AlP}_3\text{O}_9$ crystal.\textsuperscript{10,21} Additionally, tetrahedral $\text{Al}^{3+}$ cations donate 0.75 VU to their coordinate oxygen and fully charge satisfy $Q^0$ NBO’s which receive 1.25 VU from their phosphorus, as in the $\text{AlPO}_4$ crystal.\textsuperscript{10,52} Finally, 5-coordinate $\text{Al}^{3+}$ cations contribute 0.6 VU to a NBO, nearly satisfying the $Q^1$ NBO, which receives $\sim$1.33 VU from it’s phosphorus. With other modifiers present to donate charge, many other combinations are capable of satisfying the charge requirements of the NBO’s from phosphate tetrahedra.\textsuperscript{10}

The average number of NBO available per RE cation in an aluminophosphate glass can be calculated by modifying Equation 3.10 to take into account the NBO’s required by aluminum cations to satisfy their coordination requirements. If there are no Al-O-Al or Al-O-RE bonds, and NBO’s are not 3-coordinated to a combination of Al and RE cations, then Equation 3.10 can be rewritten as shown in Equation 3.13.  

For the
case of Region III behavior where $\bar{n}^{NBO}_{RE} < CN_{RE}$, the fraction of non-bridging oxygen shared between rare-earth cations is given by Equation 3.11 and the average number of next-nearest rare-earth neighbors around each rare-earth cation is also estimated using Equation 3.12.

$$\bar{n}^{NBO}_{RE} = \frac{2(c_O - 2c_p) - c_{Al}CN_{Al}}{c_{RE}}$$

(3.13)
<table>
<thead>
<tr>
<th></th>
<th>O/P</th>
<th>y</th>
<th>$Q^n$</th>
<th>$\text{PO}_4$ tetrahedra</th>
<th>$\bar{n}^{BO}_P$</th>
<th>$\bar{n}^{NBO}_P$</th>
<th>VU/NBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$-$\text{P}_2\text{O}_5$</td>
<td>2.5</td>
<td>0</td>
<td>$Q^3$</td>
<td>$\overset{-\text{O}}{\text{P}}\overset{-\text{O}}{\text{O}}\overset{-\text{O}}{\text{O}}\overset{-\text{O}}{\text{O}}$</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Metaphosphate</td>
<td>3</td>
<td>1</td>
<td>$Q^2$</td>
<td>$\overset{-\text{O}}{\text{P}}\overset{-\text{O}}{\text{O}}\overset{-\text{O}}{\text{O}}\overset{-\text{O}}{\text{O}}$</td>
<td>2</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Pyrophosphate</td>
<td>3.5</td>
<td>2</td>
<td>$Q^1$</td>
<td>$\overset{-\text{O}}{\text{P}}\overset{-\text{O}}{\text{O}}\overset{-\text{O}}{\text{O}}\overset{-\text{O}}{\text{O}}$</td>
<td>1</td>
<td>3</td>
<td>1.33</td>
</tr>
<tr>
<td>Orthophosphate</td>
<td>4</td>
<td>3</td>
<td>$Q^0$</td>
<td>$\overset{-\text{O}}{\text{P}}\overset{-\text{O}}{\text{O}}\overset{-\text{O}}{\text{O}}\overset{-\text{O}}{\text{O}}$</td>
<td>0</td>
<td>4</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 3.1: Phosphate glass compositions and associated identifying quantities.

O/P: oxygen to phosphorus ratio.
y: number of oxygen atoms added per $\text{P}_2\text{O}_5$ from network modifiers.
$Q^n$: identifies the number of bridging oxygens (n) per $\text{PO}_4$ tetrahedra.
$\bar{n}^{BO}_P$: number of bridging oxygen (BO) per $\text{PO}_4$ tetrahedra.
$\bar{n}^{NBO}_P$: number of non-bridging oxygen (NBO) per $\text{PO}_4$ tetrahedra.
VU/NBO: valence units per non-bridging oxygen.
Table 3.2: Number of oxygen atoms added per $P_2O_5$ from network modifiers ($y$) and binary meta-, pyro-, and ortho-phosphate compositions for various modifier oxides defined by molar fraction of modifier ($x$).

<table>
<thead>
<tr>
<th>$M^{n+}$</th>
<th>$y$</th>
<th>meta-</th>
<th>pyro-</th>
<th>ortho-</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M^{2+}$</td>
<td>$(M_2O)<em>x (P_2O_5)</em>{1-x}$</td>
<td>$\frac{x}{1-x}$</td>
<td>$x = 1/2$</td>
<td>$x = 2/3$</td>
</tr>
<tr>
<td>$M^{3+}$</td>
<td>$(M_2O_3)<em>x (P_2O_5)</em>{1-x}$</td>
<td>$\frac{3x}{1-x}$</td>
<td>$x = 1/4$</td>
<td>$x = 2/5$</td>
</tr>
<tr>
<td>$M^{4+}$</td>
<td>$(MO)<em>x (P_2O_5)</em>{1-x}$</td>
<td>$\frac{2x}{1-x}$</td>
<td>$x = 1/3$</td>
<td>$x = 1/2$</td>
</tr>
</tbody>
</table>
Table 3.3: Definition of three-region structure model for binary rare-earth phosphate glasses.

<table>
<thead>
<tr>
<th>Region</th>
<th>$\bar{n}<em>{RE}^{NBO}$ vs. $CN</em>{RE}$</th>
<th>$CN_{RE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\bar{n}<em>{RE}^{NBO} &gt; CN</em>{RE}$</td>
<td>Highest Possible</td>
</tr>
<tr>
<td>II</td>
<td>$\bar{n}<em>{RE}^{NBO} = CN</em>{RE}$</td>
<td>$(1+2x)/x$</td>
</tr>
<tr>
<td>III</td>
<td>$\bar{n}<em>{RE}^{NBO} &lt; CN</em>{RE}$</td>
<td>Lowest Possible</td>
</tr>
</tbody>
</table>

$\bar{n}_{RE}^{NBO}$: average number of oxygen available per rare-earth cation.  
$CN_{RE}$: rare-earth coordination number.  
x: molar fraction of RE$_2$O$_3$.  

Figure 3.1: Binary $Q^n$ distribution in binary rare-earth oxide phosphate glasses as given by Equations 3.6, 3.7, and 3.8.
Figure 3.2: Average rare-earth coordination versus mol% RE$_2$O$_3$ for a binary phosphate glass, showing Region I, II, and III behavior for a RE$^{3+}$ that assumes a maximum coordination of 9 and a minimum coordination of 6.

x: molar fraction of RE$_2$O$_3$. 
CHAPTER 4
SYNTHESIS AND EXPERIMENTAL METHODS

4.1. GLASS SYNTHESIS

4.1.1 Melting and Initial Annealing Procedure

Glasses from the cerium aluminophosphate (CAP) and cerium silicophosphate (CSP) glass series were synthesized by melting using the raw materials, crucibles, and furnaces shown in Table 4.1 at InfoSciTex Corporation (Waltham, MA (IST)) and the Pennsylvania State University (University Park, PA (PSU)). The theoretical compositions, melting temperature, and synthesis location for each glass are shown in Table 4.2. Several precautions were taken to mitigate hydration and volatilization of the P$_2$O$_5$ raw material including: preparation of batch materials in a dry nitrogen-purged glove box, lidding the crucible, preheating the furnace to 800 °C before synthesis, and for glasses melted at PSU, overbatching P$_2$O$_5$ by 88.89% in grams of raw material. After pouring the melt into a preheated graphite mold, a stringer was pulled from the crucible for later use in determination of the glass transition temperature ($T_g$). Each glass ingot was initially annealed at the temperatures and times indicated in Table 4.1 and 4.2, with the exception of glass CAP_4. The annealing temperatures for the CAP glasses were based upon glass transition temperatures reported by Karabulut for lanthanum aluminophosphate glasses.$^{24}$
4.1.2 Results

Images of each CAP and CSP composition after melting and initial annealing are given in Figures 4.1, 4.2, and 4.3. Compositions CAP_10, 9, and 8 were colorless while CAP_7 was nearly colorless with only faint yellow coloration. Additionally, the surface of ingot CAP_10 was rough, hazy, and appeared partially crystallized, but did not change with initial annealing. Compositions CSP_1, 2, 3, and 4 were also observed to be colorless, while CSP_5 was nearly colorless. Compositions CAP_6-1 and CSP_9-6 all exhibited an amber-gold coloration.

The yield for the CAP glasses melted with aluminum metaphosphate as the raw material was slightly higher than the CAP glasses melted with aluminum oxide and P_2O_5 overbatching, ~145 g versus ~100 g, as shown in Table 4.2. Additionally, the yield for the CSP glasses steadily decreased with increasing SiO_2 and decreasing Ce_2O_3 content, from ~100 g to ~30 g. This decrease in yield for the CSP glasses corresponded with a significant increase in the melt viscosity, as observed while pouring the melt, despite the increased melting temperature for the high SiO_2 compositions.

4.2 Glass Transition Temperature

4.2.1 Experimental Procedure and Second Annealing

The glass transition temperature (T_g) for each composition was determined using a TA Instruments Quanta SDT 600, simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA/DSC). An alumina pan with lid (AdValue Technology, 99.6%) was used to contain the crushed stringers. Heat flow to and from the samples was measured during heating at 10 °C/minute to 1000 °C under dry nitrogen at
100 mL/min. The $T_g$ was calculated from this data using the slope intercept method, as shown in Figure 4.6 for glass CAP_1. Subsequently, each glass ingot was reannealed for 45 minutes at the annealing temperatures shown in Table 4.1, based upon the measured glass transition temperature.

4.2.2 Results

Glass transition temperatures determined for the CAP and CSP glasses are shown in Table 4.2. Glasses near the cerium metaphosphate composition, CAP_5-1 and CSP_9-7, also exhibited a sharp crystallization peak. Values for $T_x$ are given in Table 4.2, and the crystallization peak for glass CAP_1 is shown in Figure 4.6.

Additionally, images of the CAP and CSP glasses after the second annealing are shown in Figures 4.3, 4.4, and 4.5. Glasses CAP_10 and CSP_1 completely crystallized during annealing. In particular, the surface of CAP_10 became highly textured with visible crystallites and voids, while CSP_1 retained its shape and smooth glassy surface, but became completely opaque. Additionally, glasses CAP_9-6 developed some slight surface haziness during annealing, but no gross crystallization. All other compositions were visually unchanged due to the second annealing except CSP_8 which fractured due to localized adhesion to the setter plate in the annealer.

4.3 SAMPLE PREPARATION

4.3.1 Vacuum Fracture Bars

Bars slightly less than 4 mm square and greater than 35 mm in length were cut from ingots of glasses CAP_9-1 and CSP_9-2 and notched for use in x-ray photoelectron
spectroscopy (XPS) experiments. These fractured bars were then used for determination of density by helium pycnometry.

4.3.2 Polished Plates

Glasses CAP_9-1 and CSP_9-2 were cut and polished into plates 15 mm square and 0.5 mm thick by the Penn State Electro-Optics Center (Freeport, PA). The final polishing slurry was Engis Hypez \(\frac{1}{4}\) \(\mu\)m water-based polycrystalline diamond slurry, strong concentration (0.25(54889)STR-PC). These polished plates were used for the measurement of optical properties and during electron paramagnetic resonance (EPR) experiments.

4.4 DENSITY

4.4.1 Experimental Procedure

The density of each uncrystallized CAP and CSP glass was measured using a QuantaChrome multi pycnometer, equipped with ultra high purity (UHP) helium gas. The pycnometer measured the volume of the glass bars, which combined with the measured mass of the bar, provided the glass density. The instrument was calibrated before the first sample measurement and after the last sample measurement using a standard steel ball bearing of known volume. For each measurement, the pressure difference was measured for when a known quantity of helium flowed from the reference volume into the sample cell occupied by the glass bar. A set of 10 measurements was taken for each sample, and the temperature recorded for each measurement. As the temperature in the room was observed to increase steadily throughout the day, it was
necessary to linearly interpolate a calibration value for each sample according to average measurement temperature as the initial and final calibrations were affected by temperature according to the ideal gas law.

4.4.2 Results

The density and standard deviation for each CAP and CSP glass are given in Table 4.3. A plot of density versus mol% Ce₂O₃ is given in Figure 4.7 and shows that the glass density increases with cerium concentration.

4.5 REFRACTIVE INDEX

4.5.1 Experimental Procedure

The refractive index of each CAP and CSP glass was measured at each of 4 wavelengths (403 nm, 488 nm, 633 nm, and 1541 nm) using a Metricon 2010/m prism coupler. The prism coupler measures the critical angle of reflection for a laser directed into a prism in intimate contact with a polished glass surface using an automated rotary step table and photodetector. Metricon software was used to convert the table position for critical angle of reflection into refractive index based upon the index of the prism at wavelength of measurement. One measurement at each of 4 wavelengths was made at 3 different spots on two samples for a total of 6 measurements per wavelength for each composition.
4.5.2 Results

The refractive index and standard deviation for each CAP and CSP glass are given in Table 4.3. A plot of refractive index at 633 nm versus mol\% Ce\textsubscript{2}O\textsubscript{3} is given in Figure 4.8 and shows that the refractive index increases with cerium concentration.

4.6 OPTICAL TRANSMISSION

4.6.1 Experimental Procedure

UV-VIS spectra were gathered in transmission from polished plates using a Perkin Elmer 950 spectrophotometer equipped with a standard (STD) detector module. Data were gathered at 1 nm steps and 2 nm slit from 200-800 nm.

4.6.2 Results

Glasses CAP\textsubscript{9-8} and CSP\textsubscript{2-4}, which were observed to be colorless to the eye, had sharp ultraviolet absorption edges as shown in Figures 4.9 and 4.10. Alternatively, glasses which appeared amber-gold to the eye, CAP\textsubscript{6-1} and CSP\textsubscript{6-9}, had very broad absorption edges. For glasses CAP\textsubscript{7} and CSP\textsubscript{5}, which were only slightly yellow, the UV absorption edge was intermediate in shape between these two groups.

4.7 Ce\textsuperscript{3+} PHOTOLUMINESCENCE

4.7.1 Experimental Procedure

Emission and excitation spectra were gathered from polished plates of CAP and CSP glasses using a Shimadzu RF-1501 fluorospectrophotometer. Data were gathered from 220-900 nm at a 1 nm step and 10 nm slit width. Emission spectra were gathered at
an excitation wavelength of 280 nm for all samples and excitation spectra were gathered at an emission wavelength of 340 nm for all samples except CAP_7 and CSP_5. For the latter two compositions, excitation spectra were gathered at an emission wavelength of 370 nm and 375 nm respectively.

4.7.2 Results

The excitation and emission spectra for the CAP and CSP glasses are shown in Figures 4.11 and 4.12. Ce$^{3+}$ photoluminescence peaks for CAP_9-8 and CSP_2-4 oversaturated the detector, but appear to have maxima at ~340 nm. For CAP_7, the broad photoluminescence peak occurs at ~370 nm, while for CSP_5, the maximum occurs at ~375 nm with a shoulder at ~330 nm. For the high-cerium compositions, CAP_6-1 and CSP_9-6, there are very low-intensity photoluminescence peaks at ~340 nm and ~415 nm. For all glasses, the excitation spectra indicate a broad absorption band from at least 220 nm to ~300 nm, varying slightly by composition.
Table 4.1: Raw materials, crucibles, and furnaces used for melting CAP and CSP glasses at InfoSciTex Corporation (IST) and the Pennsylvania State University (PSU).

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>IST</th>
<th>PSU</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>SiO₂ (U.S. Silica, Min-U-Sil)</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>AlP₃O₉ (Alfa Aesar 19.4% Al₂O₃)</td>
<td>Al₂O₃ (Alfa Aesar, 99.5%)</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>CeO₂ (Alfa Aesar 99.9%)</td>
<td>CeO₂ (Cerac 99.9%)</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>P₂O₅ (Alfa Aesar, 98% min P₂O₅)</td>
<td>P₂O₅ (Alfa Aesar, 98% min P₂O₅)</td>
</tr>
<tr>
<td>Crucibles</td>
<td>Alumina</td>
<td>CoorsTek (99.5%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AdValue Technology (99.6%)</td>
</tr>
<tr>
<td>Furnaces</td>
<td>Melting</td>
<td>Thermolyne 46200 or 46100</td>
</tr>
<tr>
<td></td>
<td>Initial annealing</td>
<td>5 hours - Thermolyne 600</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 hours - Lindberg Sola Basic</td>
</tr>
<tr>
<td>location</td>
<td>Theoretical Composition (mol%)</td>
<td>( T_m (°C) )</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>CAP_10</td>
<td>IST 75 25</td>
<td>1550</td>
</tr>
<tr>
<td>CAP_9</td>
<td>IST 1.25 75 23.75</td>
<td>1550</td>
</tr>
<tr>
<td>CAP_8</td>
<td>IST 2.5 75 22.5</td>
<td>1550</td>
</tr>
<tr>
<td>CAP_7</td>
<td>IST 5 75 20</td>
<td>1550</td>
</tr>
<tr>
<td>CAP_6</td>
<td>IST 10 75 15</td>
<td>1550</td>
</tr>
<tr>
<td>CAP_5</td>
<td>PSU 15 75 10</td>
<td>1460</td>
</tr>
<tr>
<td>CAP_4</td>
<td>PSU 20 75 5</td>
<td>1430</td>
</tr>
<tr>
<td>CAP_3</td>
<td>PSU 22.5 75 2.5</td>
<td>1415</td>
</tr>
<tr>
<td>CAP_2</td>
<td>PSU 23.75 75 1.25</td>
<td>1408</td>
</tr>
<tr>
<td>CAP_1</td>
<td>PSU 25 75</td>
<td>1400</td>
</tr>
<tr>
<td>CSP_9</td>
<td>PSU 23.75 73.75 2.5</td>
<td>1400</td>
</tr>
<tr>
<td>CSP_8</td>
<td>PSU 22.5 72.5 5</td>
<td>1400</td>
</tr>
<tr>
<td>CSP_7</td>
<td>PSU 20 70 10</td>
<td>1400</td>
</tr>
<tr>
<td>CSP_6</td>
<td>PSU 15 65 20</td>
<td>1465</td>
</tr>
<tr>
<td>CSP_5</td>
<td>PSU 10 60 30</td>
<td>1530</td>
</tr>
<tr>
<td>CSP_4</td>
<td>PSU 5 55 40</td>
<td>1595</td>
</tr>
<tr>
<td>CSP_3</td>
<td>PSU 2.5 52.5 45</td>
<td>1620</td>
</tr>
<tr>
<td>CSP_2</td>
<td>PSU 1.25 51.25 47.5</td>
<td>1650</td>
</tr>
<tr>
<td>CSP_1</td>
<td>PSU 50 50</td>
<td>1650</td>
</tr>
</tbody>
</table>

Table 4.2: Theoretical glass compositions, melting location, maximum melting temperature \( (T_m) \), annealing temperatures \( (T_a) \), measured glass transition temperature \( (T_g) \), crystallization temperature \( (T_x) \), and sample yield for CAP and CSP glasses.
<table>
<thead>
<tr>
<th></th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$n$ (403nm)</th>
<th>$n$ (488nm)</th>
<th>$n$ (632.8nm)</th>
<th>$n$ (1541nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAP_9</td>
<td>2.59 ± 0.02</td>
<td>1.545 ± 0.003</td>
<td>1.538 ± 0.003</td>
<td>1.531 ± 0.003</td>
<td>1.517 ± 0.003</td>
</tr>
<tr>
<td>CAP_8</td>
<td>2.63 ± 0.02</td>
<td>1.545 ± 0.002</td>
<td>1.538 ± 0.002</td>
<td>1.531 ± 0.002</td>
<td>1.517 ± 0.002</td>
</tr>
<tr>
<td>CAP_7</td>
<td>2.67 ± 0.03</td>
<td>1.553 ± 0.002</td>
<td>1.545 ± 0.002</td>
<td>1.537 ± 0.002</td>
<td>1.522 ± 0.002</td>
</tr>
<tr>
<td>CAP_6</td>
<td>2.79 ± 0.02</td>
<td>1.560 ± 0.001</td>
<td>1.552 ± 0.001</td>
<td>1.544 ± 0.001</td>
<td>1.530 ± 0.001</td>
</tr>
<tr>
<td>CAP_5</td>
<td>3.00 ± 0.02</td>
<td>1.580 ± 0.001</td>
<td>1.5706 ± 0.0002</td>
<td>1.5616 ± 0.0002</td>
<td>1.5461 ± 0.0003</td>
</tr>
<tr>
<td>CAP_4</td>
<td>3.08 ± 0.02</td>
<td>1.5866 ± 0.0005</td>
<td>1.5765 ± 0.0003</td>
<td>1.5674 ± 0.0004</td>
<td>1.5521 ± 0.0003</td>
</tr>
<tr>
<td>CAP_3</td>
<td>3.10 ± 0.02</td>
<td>1.590 ± 0.001</td>
<td>1.580 ± 0.001</td>
<td>1.570 ± 0.001</td>
<td>1.5548 ± 0.0003</td>
</tr>
<tr>
<td>CAP_2</td>
<td>3.11 ± 0.03</td>
<td>1.591 ± 0.003</td>
<td>1.581 ± 0.004</td>
<td>1.572 ± 0.004</td>
<td>1.556 ± 0.003</td>
</tr>
<tr>
<td>CAP_1</td>
<td>3.14 ± 0.02</td>
<td>1.594 ± 0.001</td>
<td>1.584 ± 0.002</td>
<td>1.574 ± 0.001</td>
<td>1.559 ± 0.001</td>
</tr>
<tr>
<td>CSP_9</td>
<td>3.08 ± 0.02</td>
<td>1.592 ± 0.001</td>
<td>1.582 ± 0.001</td>
<td>1.572 ± 0.001</td>
<td>1.556 ± 0.001</td>
</tr>
<tr>
<td>CSP_8</td>
<td>3.08 ± 0.02</td>
<td>1.590 ± 0.001</td>
<td>1.580 ± 0.001</td>
<td>1.570 ± 0.001</td>
<td>1.555 ± 0.001</td>
</tr>
<tr>
<td>CSP_7</td>
<td>3.07 ± 0.02</td>
<td>1.5845 ± 0.0005</td>
<td>1.5746 ± 0.0003</td>
<td>1.5652 ± 0.0002</td>
<td>1.5497 ± 0.0002</td>
</tr>
<tr>
<td>CSP_6</td>
<td>2.98 ± 0.01</td>
<td>1.576 ± 0.001</td>
<td>1.5674 ± 0.0003</td>
<td>1.5582 ± 0.0003</td>
<td>1.5430 ± 0.0003</td>
</tr>
<tr>
<td>CSP_5</td>
<td>2.94 ± 0.02</td>
<td>1.5710 ± 0.0005</td>
<td>1.5618 ± 0.0003</td>
<td>1.5533 ± 0.0004</td>
<td>1.5379 ± 0.0005</td>
</tr>
<tr>
<td>CSP_4</td>
<td>2.80 ± 0.05</td>
<td>1.557 ± 0.001</td>
<td>1.550 ± 0.001</td>
<td>1.542 ± 0.001</td>
<td>1.527 ± 0.001</td>
</tr>
<tr>
<td>CSP_3</td>
<td>2.70 ± 0.03</td>
<td>1.549 ± 0.001</td>
<td>1.541 ± 0.001</td>
<td>1.533 ± 0.001</td>
<td>1.519 ± 0.001</td>
</tr>
<tr>
<td>CSP_2</td>
<td>2.58 ± 0.03</td>
<td>1.538 ± 0.001</td>
<td>1.5314 ± 0.0002</td>
<td>1.5239 ± 0.0003</td>
<td>1.509 ± 0.001</td>
</tr>
</tbody>
</table>

Table 4.3: Density and refractive index data for CAP and CSP glasses.
Figure 4.1: Images of glasses CAP_9-1 after melting and initial annealing.
Figure 4.2: Images of glasses CSP_9-2 after melting and initial annealing.
Figure 4.3: CAP_10 and CSP_1 a) after melting and initial annealing, b) after second annealing.
Figure 4.4: Images of glasses CAP_9-1 after second annealing.
Figure 4.5: Images of glasses CSP_9-2 after second annealing.
Figure 4.6: Heat flow versus temperature for glass CAP_1 during simultaneous TGA/DSC measurements showing $T_g$ at 708 °C as determined by the slope intercept method and $T_x$ at 901 °C.
Figure 4.7: Density versus mol% Ce\textsubscript{2}O\textsubscript{3} for CAP and CSP glasses.
Figure 4.8: Refractive index at 633 nm versus mol% Ce$_2$O$_3$ for CAP and CSP glasses.
Figure 4.9: UV-VIS transmission spectra from CAP glasses in the region of the absorption edge.
Figure 4.10: UV-VIS transmission spectra from CSP glasses in the region of the absorption edge.
Figure 4.11: Emission and excitation spectra for Ce$^{3+}$ photoluminescence in CAP glasses.
Figure 4.12: Emission and excitation spectra for Ce$^{3+}$ photoluminescence in CSP glasses.
CHAPTER 5
COMPOSITION AND CHEMICAL STRUCTURE ANALYSIS

X-ray photoelectron spectroscopy (XPS), a surface analytical technique, can be used to examine the bulk composition of glass through the analysis of fracture surfaces created in vacuum. Chemical structure information, including Ce$^{3+}$/Ce$^{4+}$ redox equilibria, is also available through shifts in the binding energy of photoelectron peaks.

5.1 LITERATURE REVIEW

XPS uses monochromatic soft x-rays to excite electrons from the surface region of materials by the photoelectric effect. The kinetic energy (KE) of emitted electrons is measured and used to determine the electron binding energy (BE) according to Equation 5.1 where $h\nu$ is the x-ray photon energy ($h =$ Planck constant, $\nu =$ frequency) and $\phi_s$ is the spectrometer work function. The binding energy of an electron is indicative of the element and energy level of origin, making it possible to determine the composition of a sample surface as the area of the photoelectron peaks are proportional to the elemental concentration. Information about the local chemical environment of an element can also be determined through shifts in the photoelectron binding energy.

\[
KE = h\nu - BE - \phi_s \tag{5.1}
\]

It is possible to distinguish Ce$^{3+}$ and Ce$^{4+}$ through analysis of the photoelectron peaks in the cerium 3d spectrum. Following the work and notations of Romeo and Pfau, 5 pairs of peaks, 10 total, are identified in the Ce 3d region. The 5 peaks from the 3d$_{5/2}$ spin-orbit split doublet are designated as v peaks, while the 5 analogous peaks in the 3d$_{3/2}$ spin-orbit split doublet are designated as u peaks. Of these 10 peaks, two pairs
are assigned to Ce\(^{3+}\) (v\(^o\), u\(^o\), v\(^'\), u\(^'\)), while the remaining three pairs are assigned to Ce\(^{4+}\) (v, u, v\(^''\), u\(^''\), v\(^''''\), u\(^''''\)).\(^{64-67}\) These ten peaks overlap into 3 adjacent regions: the first encompasses four peaks from the 3d\(_{5/2}\) spin-orbit split doublet (v\(^o\), v, v\(^'\), v\(^''\)), the second encompasses the v\(^''''\) peak and four peaks from the 3d\(_{3/2}\) spin-orbit split doublet (v\(^''''\), u\(^o\), u, u\(^'\), u\(^''\)), while the u\(^''''\) peak stands alone. Figure 5.1 shows a simulated Ce 3d XPS spectrum with 50% Ce\(^{4+}\) and 50% Ce\(^{3+}\) by area, and the 5 peaks from each spin-orbit doublet grouped by cerium cation species.

5.2 EXPERIMENTAL PROCEDURE

5.2.1 Data Collection

Samples of each CAP and CSP glass were fractured in vacuum at a pressure < 2.0E-7 torr to provide clean surfaces approximating the bulk composition and structure. A Kratos Analytical Axis Ultra instrument equipped with a monochromatic Al K\(_\alpha\) x-ray source (1486.6 eV) was used to gather XPS spectra at a pass energy of 20 eV. During the acquisition of spectra, a low-energy electron flood gun was directed at the surface to minimize the effects of surface charging.

5.2.2 Compositional Analysis

The composition for each glass was calculated from the XPS spectra for the Ce 3d (880-920 eV), O 1s (533 eV), C 1s (285 eV), P 2p (135 eV), Si 2p (104 eV), and Al 2p (76 eV) regions using CasaXPS software (ver. 2.3.13). All spectra were normalized to the C 1s peak at 285 eV binding energy. A linear background was subtracted from the Ce 3d spectra for each of 3 regions: 3d 5/2, 3d 3/2, and u\(^''''\). For the O 1s, P 2p, and Al 2p
spectra, a single linear background was determined. The entire area under the curve was used during quantification of the atom% composition for the Ce 3d regions, O 1s, P 2p, and Al 2p.

The peak from Ce 4s occurs at a slightly higher binding energy than that from C1s (291 eV) and necessitates peak fitting to separate the two, in order to quantify the atom% carbon present on the vacuum fracture surface. A linear background was used for the entire region and a single synthetic peak (Gaussian/Lorentzian product, 35% Lorentzian (GL(35)) without constraints was used to fit each of the C 1s and Ce 4s peaks. The C 1s and Ce 4s spectrum from CAP_1 with synthetic peak fit is shown in Figure 5.2.

It was also necessary to fit a synthetic peak to Si 2p for compositional quantification due to overlap with the broad Ce 4d peak as shown in Figure 5.3 for CSP_5. A single linear background was used to fit the region encompassing Al 2s (120 eV), Ce 4d (115-106 eV), and Si 2p (104 eV). Individual GL(30) peaks were used to fit the Al 2s and Si 2p peaks while five GL(30) peaks were used to fit the broad Ce 4d spectrum. This was the minimum number required to reproduce the shape of the Ce 4d spectrum without regard for actual photoelectron peaks. The Ce 4d region from CAP_1 was used to determine position, full-width at half-maximum (FWHM), and area constraints for 4 of the Ce 4d peaks relative to the most intense peak Ce 4d peak as shown in Table 5.1.

Atom% compositions were determined for each glass from raw area of the Ce 3d, O 1s, C 1s, P 2p, Si 2p, and Al 2p peaks determined as described above, and weighted by the transmission function for the Kratos spectrometer and relative sensitivity factors (RSF). A mol % composition was determined from the atom% cation composition after
correcting for a layer of adventitious carbon on the fracture surface according to G. C. Smith’s calculation.\textsuperscript{69}

5.2.3 Cerium Oxidation State Quantification

As described in Section 5.2.2 three separate linear backgrounds were subtracted from the Ce 3d spectra for each of 3 regions: 3d 5/2, 3d 3/2, and u.’’’ To limit the number of variables in a 10-peak fit, several constraints on the peak area, position, and FWHM were applied to the GL(30) synthetic peak components, as shown in Table 5.2. These constraints were determined from unconstrained fits to several polished cerium aluminosilicophosphate and cerium aluminophosphate glasses “lightly cleaned” by in-situ etching with 4 keV Ar\textsuperscript{+} ions for Ce\textsuperscript{3+}, and from a powder sample of CeO\textsubscript{2} for Ce\textsuperscript{4+}.

Fitting the Ce 3d spectra was accomplished in three steps. First, the u’’’ peak was fit individually, and values from this fit rather than the CeO\textsubscript{2} standard were used to determine three of the fitting constraints. Then, the maximum area for the u’’’ peak during the 10-peak fit was set as 1.5 times the individual fit. Additionally, the FWHM of the u’’’ peak from the individual fit ± 0.2 eV was used rather than FWHM of 1.8 eV ± 0.2 eV as determined from the CeO\textsubscript{2} standard. Furthermore, the maximum area for the v peak was set as 0.71 times the area of the u’’’ peak from the individual fit based on the area ratio between u’’’ and v from the CeO\textsubscript{2} standard. For the second fit, the Ce 3d spectra was fit for all ten Ce\textsuperscript{3+} and Ce\textsuperscript{4+} peaks using the constraints shown in Table 5.2, with the exception of the position of the Ce\textsuperscript{3+} peaks, which were held relative to the u’ peak without ± 0.1 eV bounds. Finally, for the third fit, the ± 0.1 eV bounds for Ce\textsuperscript{3+}
peak position were added based on position determined in the second fit. The relative position and FWHM for all ten peaks were held to ± 0.1 eV and ± 0.2 eV respectively.

To determine the percentage of cerium cations in the Ce\(^{4+}\) state, the area contributed from peak components attributed to Ce\(^{4+}\) was calculated as a percentage of the total area of all the peak components as shown in Equation 5.2.

\[
Ce^{4+} \% = 100 \times \frac{\text{area}}{u'''' + u'' + u + v'''' + v'' + v + u'}
\]  

(5.2)

5.3 RESULTS

5.3.1 Vacuum Fracture Surface Composition

The atom% compositions of the CAP and CSP glasses as determined from vacuum fracture surfaces after carbon correction are given in Table 5.3. The mol% oxide compositions, along with the theoretical composition, are given in Table 5.4. The compositions of the CAP glasses are reasonably close to the theoretical compositions with the exception of CAP_1, which should have been alumina-free, as seen for the ternary diagram in Figure 5.4. This composition, in addition to all of the CSP glasses, contains ~2 mol% Al\(_2\)O\(_3\) as an impurity picked up from the alumina crucible during melting. Additionally, the loss of P\(_2\)O\(_5\) from the CSP glasses became more significant with decreasing Ce\(_2\)O\(_3\) and increasing SiO\(_2\) as seen in the ternary diagram in Figure 5.5.

5.3.2 Cerium Oxidation State

For both the CAP and CSP series of glasses, the Ce 3d spectra were found to have four main peaks which correspond to the v\(^{0}\), u\(^{0}\), v\(^{'}\), and u\(^{'}\) peaks in Ce\(^{3+}\) spectra, as shown for CAP_1 in Figure 5.6. The contributions from Ce\(^{4+}\) in the Ce 3d spectra
manifested as a small \( u''' \) peak at \( \sim 918 \) eV. During peak fitting, the \( \text{Ce}^{4+} \) peaks (\( v'''', u'''', u, \) and \( v' \)) were always fit, but the \( u''' \) and \( v''' \) peaks were not fit, with an area \( \sim 0 \). After quantification, all CSP and CAP glasses were found to contain \( \leq 5\% \ \text{Ce}^{4+} \). These results are summarized in Table 5.3.

As previously discussed in Section 2.1, there is a preference for \( \text{Ce}^{3+} \) in phosphate glasses that may have local structure origins. Orthorhombic cerium metaphosphate,\(^{22}\) triclinic cerium ultraphosphate,\(^{70}\) and orthorhombic cerium ultraphosphate\(^{71}\) have well-characterized crystal structures where the \( \text{Ce}^{3+} \) cations are coordinated to 8 oxygen nearest neighbors. Additionally, all of the cerium cations in cerium orthophosphate (monazite) are present as 9-coordinated \( \text{Ce}^{3+} \).\(^{72}\) Only the cerium pyrophosphate crystal, known for its limited thermal stability, has cerium present as \( \text{Ce}^{4+} \), where it is coordinated with only 6 nearest oxygen neighbors.\(^{73}\) Thus, the \( 3^+ \) oxidation state may be preferred when cerium assumes a high coordination number in phosphate glasses.
Table 5.1: Ce 4d XPS peak-fitting constraints based on an unconstrained 5 peak fit to CAP_1.
<table>
<thead>
<tr>
<th>Ce&lt;sup&gt;4+&lt;/sup&gt; 3d 5/2</th>
<th>Δ Position (eV)</th>
<th>FWHM (eV)</th>
<th>AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>v</td>
<td>-34.4 ± 0.1</td>
<td>1.2 ± 0.2</td>
<td>max: 0.71u'' *</td>
</tr>
<tr>
<td>v''</td>
<td>-27.8 ± 0.1</td>
<td>4.1 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>v'''</td>
<td>-18.4 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>u</td>
<td>-15.8 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>u''</td>
<td>-9 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>u'''</td>
<td>0</td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Ce&lt;sup&gt;3+&lt;/sup&gt; 3d 5/2</th>
<th>Δ Position (eV)</th>
<th>FWHM (eV)</th>
<th>AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>v''''</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: Ce 3d XPS peak-fitting constraints based on unconstrained fits to CeO<sub>2</sub> for Ce<sup>4+</sup> and argon ion etched cerium aluminosilicophosphate glasses for Ce<sup>3+</sup>.

* : calculated from the initial individual fit for u''.
| Atom% Composition | Ce  | O   | P   | Si  | Al  | Ce^{4+} |%
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
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<td>8.0</td>
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<td>21.4</td>
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<td>21.4</td>
<td>5.0</td>
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<td></td>
</tr>
<tr>
<td>CAP_5</td>
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<td>69.3</td>
<td>21.4</td>
<td>3.3</td>
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<td></td>
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<td>CAP_3</td>
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<td>22.2</td>
<td>1.3</td>
<td>1</td>
<td></td>
</tr>
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<td>23.2</td>
<td>0.9</td>
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<td>22.5</td>
<td>0.1</td>
<td>0.9</td>
<td>3</td>
</tr>
<tr>
<td>CSP_8</td>
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<td>69.3</td>
<td>22.3</td>
<td>0.3</td>
<td>0.8</td>
<td>3</td>
</tr>
<tr>
<td>CSP_7</td>
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<td>69.5</td>
<td>21.9</td>
<td>1.0</td>
<td>0.9</td>
<td>2</td>
</tr>
<tr>
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<td>70.0</td>
<td>20.4</td>
<td>2.9</td>
<td>0.8</td>
<td>3</td>
</tr>
<tr>
<td>CSP_5</td>
<td>5.1</td>
<td>69.9</td>
<td>20.1</td>
<td>4.2</td>
<td>0.7</td>
<td>3</td>
</tr>
<tr>
<td>CSP_4</td>
<td>2.9</td>
<td>69.9</td>
<td>17.5</td>
<td>8.9</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>CSP_3</td>
<td>1.7</td>
<td>70.1</td>
<td>15.9</td>
<td>11.3</td>
<td>1.0</td>
<td>3</td>
</tr>
<tr>
<td>CSP_2</td>
<td>0.9</td>
<td>70.1</td>
<td>14.9</td>
<td>13.1</td>
<td>1.0</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5.3: Atom% composition after carbon correction and Ce^{4+}% measured from vacuum fracture surfaces of CAP and CSP glasses by XPS.
Table 5.4: Theoretical composition versus composition measured from vacuum fracture surfaces of CAP and CSP glasses by XPS.
Figure 5.1: Simulated Ce 3d XPS spectrum with 50% Ce$^{4+}$ and 50% Ce$^{3+}$ by area showing synthetic peak components from Ce$^{3+}$ ($u'$, $u''$, $v'$, and $v''$) and Ce$^{4+}$ ($u'''$, $u''$, $u$, $v'''$, $v''$, and $v$).
Figure 5.2: Synthetic peak fit to Ce 4s and C 1s XPS spectra from CAP_1 after linear background subtraction.
Figure 5.3: Synthetic peak fit to Ce 4d, Al 2s, and Si 2p XPS spectra from CSP_5 after linear background subtraction.
Figure 5.4: Ce$_2$O$_3$-Al$_2$O$_3$-P$_2$O$_5$ ternary diagram showing the theoretical versus XPS-measured compositions for the CAP glasses.
Figure 5.5: Ce$_2$O$_3$-SiO$_2$-P$_2$O$_5$ ternary diagram showing the theoretical versus XPS-measured compositions for the CSP glasses, after renormalizing to exclude Al$_2$O$_3$ impurities.
Figure 5.6: Synthetic peak fit to Ce 3d XPS spectrum from CAP_1 for Ce$^{3+}$ and Ce$^{4+}$ peaks after linear background subtraction.
CHAPTER 6

CERIUM COORDINATION

Extended x-ray absorption fine structure (EXAFS) spectroscopy, a subset of x-ray absorption spectroscopy (XAS), can determine local structure around an element of interest. In particular, both average atomic distance and number of atoms can be determined for the first several coordination shells around a specific element.

6.1 LITERATURE REVIEW

X-ray absorption spectroscopy uses x-rays to stimulate transitions of deep core electrons to excited states using high intensity tunable x-rays available at synchrotron radiation sources. EXAFS is the region of the XAS spectrum starting ~50 eV after the absorption edge where oscillations are due to constructive and destructive interference between outgoing photoelectron waves from the absorbing atom and photoelectron waves backscattered from neighboring atoms. Analysis of this spectral region using a “single-scattering, plane-wave approximation” yields local structure information, average distance and number of nearest neighbors, around the absorbing atom. The maximum range for which structural information can be obtained is determined by the mean free path of the outgoing photoelectron, typically < 6 Å. In ideal crystalline materials, such as metallic copper, it is possible to determine structural information to ~5.5 Å. However, in amorphous materials such as glass, disorder further limits the distance to which it is possible to obtain structural information to ~3 Å.
Ce K-edge EXAFS was chosen for this work due to several advantages over Ce L$_3$-edge EXAFS including an increased range of data, easily over 15 Å$^{-1}$ versus 10 Å$^{-1}$ (limited by the Ce L$_2$-edge), avoidance of problematic double electron excitations, and the ability to gather spectra from thick samples ($\geq$ 0.5 mm) in transmission.\textsuperscript{17} Ce K-edge EXAFS has been used extensively as a local structure probe in CeO$_2$\textsuperscript{75-78} and has been used to characterize diverse materials such as a Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ superconductor\textsuperscript{79} and a Ca$_3$Sc$_2$Si$_3$O$_{12}$ green phosphor for use in white LEDs.\textsuperscript{80} However, only Ce L$_3$-edge EXAFS\textsuperscript{13,14} has been used to study binary cerium phosphate glasses near the metaphosphate composition. To the author’s knowledge, this is the first Ce K-edge EXAFS analysis of cerium phosphate glasses and will compliment other K-edge studies of rare-earth metaphosphate glasses.\textsuperscript{17}

6.2 EXPERIMENTAL PROCEDURE

6.2.1 Standard Sample Preparation

A sample of CeP$_3$O$_9$ for use as the crystalline standard during EXAFS data analysis was synthesized from glass CAP_1. Based on the crystallization temperature, $\sim$900 °C as determined by TGA/DSC and shown in Figure 4.6, a crushed sample of the glass, contained in platinum foil boat (ESPI Metals, 3N5 purity), was heat treated (10 °C/minute to 1000 °C) in a tube furnace under prepurified nitrogen flowing at 100 mL/min. After heat treatment, the crystallized glass was again crushed in a mortar and pestle in preparation for x-ray diffraction (XRD) and EXAFS analysis.

The identity of the crystalline species was confirmed as orthorhombic CeP$_3$O$_9$ by XRD analysis using a PANalytical X'Pert Pro MPD with a PIXcel detector operated in
scanning mode with a PSD length of 3.35 degrees. Excellent agreement for this spectrum with the reference lines from ICSD PDF# 97-041-7805\textsuperscript{81} can be seen in Figure 6.1. Hereafter, this crystallized sample is referred to as CeP$_3$O$_9$.

6.2.2 Sample Thickness

The thickness of glass samples for transmission mode experiments was determined based on the unit edge step condition. The Beer-Lambert Law absorption attenuation is given in Equation 6.1 where $t =$ sample thickness, $\mu =$ attenuation coefficient, $I_o =$ initial intensity, and $I_t =$ transmitted intensity. It can be rewritten as shown in Equation 6.2 where, $(\mu/\rho) =$ mass attenuation coefficient, $x =$ mass thickness = $\rho t$, and $\rho =$ density.\textsuperscript{82}

$$I_t = I_o e^{-\mu t} \quad (6.1)$$

$$\ln \left( \frac{I_o}{I_t} \right) = (\mu/\rho) x \quad (6.2)$$

The attenuation coefficient can be determined as shown in Equation 6.3 for compounds and mixtures, where $\omega_i$ and $(\mu/\rho)_i$ are the weight fraction and mass attenuation coefficient of the $i^{th}$ element.\textsuperscript{82} The weight fraction of each element was calculated from the atom\% compositions measured by XPS and the glass density was taken as 3.0 g/cm$^3$ as the densities had not been measured individually for each composition at the time of the EXAFS experiment.

$$\mu = \rho \sum_i \omega_i (\mu/\rho)_i \quad (6.3)$$

The sample thickness was determined for the unit edge step condition as shown in Equation 6.4 where $\Delta \mu = \mu($edge+25eV$) - \mu($edge-25eV$)$. Values for $\mu/\rho(E)$ were
determined from linear interpolation of $\mu/\rho(40,000 \text{ eV})$ and $\mu/\rho(50,000 \text{ eV})$ given in NISTIR 5632 for O, Ce, Al, Si, and P, as well as $\mu/\rho(40,443 \text{ eV})$ for Ce above and below the K-edge.\footnote{82}

\[ \Delta \mu t = \ln \left( \frac{I_o}{I_t} \right) = 1 \] (6.4)

Values for $\Delta \mu/\rho$ calculated for each CAP and CSP glass are given in Table 6.1 along with the sample thickness determined for the unit edge step condition.

### 6.2.3 Data Collection

The Ce K-edge (40,443 eV) EXAFS spectra were collected in transmission mode at undulator beamline 10-ID-B of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source (APS) at Argonne National Laboratory. The Si(333) reflection was used to reach the energy of the Ce K-edge. The 5\textsuperscript{th} harmonic of the undulator was used to reduce the intensity of unwanted reflections from the monochromator (Si(111), Si(444), etc.). The x-rays from the Si(111) reflection were blocked by a 6 mm aluminum plate while x-rays from the Si(444) and higher reflections were minimized using Pt harmonic rejection mirrors. Argon-filled ion chambers were used for the $I_o$, $I_t$, and $I_{ref}$ detectors. A powder CeO$_2$ sample (Cerac, 99.9\%) was placed between the $I_t$ and $I_{ref}$ detectors and used for absolute energy calibration of each sample spectrum. Spectra were gathered in fast-scanning mode (continuously moving monochromator) with data taken at 2 eV intervals. Ten to twelve scans were collected from each sample and averaged to improve data quality.
6.2.4 Data Processing

Standard methods for the analysis of EXAFS data were applied using the IFEFFIT software packages, ATHENA and ARTEMIS, created by B. Ravel and M. Newville. The EXAFS oscillations ($\chi(k)$) were obtained from the experimentally measured absorption data ($\mu(E)$) using the AUTOBK algorithm, an automated background subtraction algorithm, to perform the calculations shown in Equations 6.5 and 6.6 where $\mu_0(E)$ is the absorption of an isolated atom, $\Delta \mu_0(E_0)$ is the change in single atom absorption at the absorption edge ($E_0$), $h$ is Planck’s constant, $m_e$ is the mass of the electron, and $k$ is the wavenumber of the ejected photoelectron.

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E_0)} \quad (6.5)$$

$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}} \quad (6.6)$$

The EXAFS relationship is shown in Equation 6.7 for the sum over all possible single scattering and significant multiple scattering paths. For single scattering paths, $R_i$, $N_i$, and $\sigma_i^2$ are the distance, coordination number, and Debye-Waller factor for the $i^{th}$ shell of neighboring atoms. $\sigma_i^2$ represents the mean-square variation in $R_i$ due to both static and thermal disorder. $F_i(k)$, $\delta_i(k)$, and $\lambda(k)$ are the backscattering amplitude, phase, and mean-free-path factors, respectively, that are derived from theoretical standards calculated by FEFF. $S_0^2$ is the core-hole or amplitude-reduction factor, which is usually treated empirically. The anharmonicity of the pair-distribution is represented by $C_{3,i}$, though it was determined during fitting that this parameter was not significant.

$$\chi(k) = \sum_i F_i S_0^2 N_i \frac{2R_i}{kR_i^2} e^{-2k^2\sigma_i^2} e^{\frac{2R_i}{\lambda(k)}} \sin \left( 2kR_i + \delta_i(k) - \frac{4}{3} k^3 C_{3,i} \right) \quad (6.7)$$
Using literature values for the crystal structure of CeP$_3$O$_9$,$^{22}$ FEFF was used to calculate the significant scattering paths around cerium. These generated paths were then fit to the experimental data using ARTEMIS. In addition to the structural parameters, a single nonstructural parameter, $e_0$, was varied to correct for the simple estimate of $E_0$ made by FEFF. The value of $S_0^2$ obtained from fitting CeP$_3$O$_9$ was used for the glass samples. The same analysis procedure was used for all samples.

In the fitting process, the Ce $\chi(k)$ data were weighted by $k^2$ and windowed between $2.0 < k < 15.0$ Å$^{-1}$ using a Hanning window with $dk = 1.0$ Å$^{-1}$. The fitting was applied to both the real and imaginary parts of $\chi(R)$ in the region of $1.2 < R < 2.6$ Å.

### 6.3 RESULTS

#### 6.3.1 CeP$_3$O$_9$ Reference

The EXAFS spectrum from the CeP$_3$O$_9$ reference material was used to determine an appropriate fitting procedure for the CAP and CSP glasses as well as an accurate estimate of $S_0^2$ for use in determining the average cerium coordination number.

In the orthorhombic cerium metaphosphate crystal structure, each cerium cation is surrounded by 8 oxygen anions, six of which are located close to the cerium cation (O$_3$: 2.398 Å, O$_1$: 2.411 Å, O$_2$: 2.471 Å) and two at a significantly further distance (O$_2$: 2.733 Å).$^{22}$ Due to the disparity in bond lengths, the cerium coordination polyhedra can be described as 6+2 polyhedra.$^{22}$ These [CeO$_6$]$^{13}$ polyhedra form chains of edge-shared dodecahedra along the c-axis, as seen in Figure 6.2.$^{22}$

For the first oxygen shell, it was only possible to fit the 6 closest oxygen nearest neighbors around cerium. The two oxygens at further distance are likely too disordered
to be detected by EXAFS. In fact, this path cannot be fit independently and significantly increases the uncertainty when included in the fit. Additionally, the average bond length for the first oxygen shell calculated from the fit, 2.42 Å, agrees well with the average Ce-O bond distance for the first six oxygens calculated from the crystal structure, 2.427 Å. Finally, an Eu L₃-edge EXAFS study of the EuP₃O₉ crystal, isostructural with CeP₃O₉, also determined that it was not possible to fit the +2 oxygens around Eu.¹³

Since CeP₃O₉ is being used as a crystalline standard for amorphous samples, it was appropriate to use one single scattering path to fit the first 6 oxygen nearest neighbors. The \( k^2 \)-weighted \( \chi(k) \), imaginary portion of \( \chi(R) \), and magnitude of \( \chi(R) \) for CeP₃O₉ are shown in Figures 6.3. A core-hole factor \( (S_o^2) \) of 1.47 was determined from this fit.

### 6.3.2. CAP and CSP Glasses

The main feature in \( |\chi(R)| \) plots for glasses in the CAP and CSP glass series is a large peak representing the first shell oxygen, as shown in Figure 6.4.c for CAP_2, before phase correction, at 1.8 Å. It is clearly seen from this figure that the first coordination shell is well separated from the second and further shells, justifying its individual analysis. The fit for the first oxygen shell in all glass samples shows good agreement with the data as represented by the \( k^2 \)-weighted \( \chi(k) \), imaginary portion of \( \chi(R) \), and magnitude of \( \chi(R) \) plotted in Figures 6.4 for CAP_2. Quantitative EXAFS fitting results for the first shell oxygen coordination number \( (CN_{Ce}) \), bond distance \( (R_{Ce-O}) \), and Debeye-Waller factor \( (\sigma^2) \) are given in Table 6.2 for all CAP and CSP glasses.
The Debeye-Waller factor ($\sigma^2$), a measure of both thermal and spatial disorder,\textsuperscript{74} is nearly constant across both glass series, $\sim 0.012 \ \text{Å}^2$. However, this is a significant increase over that measured for CeP$_3$O$_9$, $\sim 0.009 \ \text{Å}^2$. Since spectra were gathered from all samples at room temperature, this increase in $\sigma^2$ should be a reflection of increase in spatial disorder in the glasses relative to the CeP$_3$O$_9$ crystal.

In the CAP series, the average cerium coordination number ($\text{CN}_{\text{Ce}}$) increases from $\sim 7.0$ near the cerium metaphosphate composition to $\sim 7.8$ near the aluminum metaphosphate composition though the error is quite large relative to this change, $\sim \pm 0.7$. The average Ce-O bond length shifts ($R_{\text{Ce-O}}$) from $\sim 2.40 \ \text{Å}$ for the high-cerium content CAP glasses, CAP$_{1-6}$, to $\sim 2.42 \ \text{Å}$ for the low-cerium content CAP glasses, CAP$_{7-9}$.

In the CSP series, $\text{CN}_{\text{Ce}}$ increases from $\sim 7.0$ near the cerium metaphosphate composition to $\sim 8.3$ near the silicophosphate endpoint in the series, though this trend is obscured by the large relative error, $\sim \pm 0.7$. The average Ce-O bond length increases from $\sim 2.41 \ \text{Å}$ to $\sim 2.44 \ \text{Å}$ across the CSP compositional series.

6.3.3 Average Cerium Coordination Number

Near the metaphosphate composition (CAP$_{2}$, 24.4 mol\% Ce$_2$O$_3$), the average cerium coordination number ($\sim 7.0$) agrees well with the average Ce-O bond distance (2.41 Å) when compared to the Ce-O bond distance is predicted from effective ionic radii for 7-fold cerium (2.42 Å).\textsuperscript{12} Additionally, the value for $R_{\text{Ce-O}}$ measured for CAP$_{2}$ in this study agrees well with that measured in previous studies of a 23.5 mol\% Ce$_2$O$_3$ metaphosphate glass,\textsuperscript{13-16} as shown in Table 6.3.
Furthermore, the $CN_{Ce}$ measured in this study for a near cerium metaphosphate composition, $\sim 7.0$, shows considerable improvement over that measured in previous studies,$^{13\text{-}16}$ also shown in Table 6.3. The x-ray and neutron diffraction studies cite overlap of the Ce-O correlation with the O-P-O correlation as the reason for underestimation of the average coordination number.$^{15,16}$ The use of CeP$_3$O$_9$ as the crystalline standard for determination of $S_0^2$, as well as other advantages of K-edge EXAFS relative to L$_3$-edge EXAFS, produces a much better estimate of $CN_{Ce}$ directly from the fit. Past L$_3$-edge EXAFS studies, which utilized other rare-earth phosphate crystalline standards, acknowledged that the measured $CN_{Ce}$ was likely underestimated.$^{13,14}$

In both the CAP and CSP series, $R_{Ce-O}$ increases as $CN_{Ce}$ increases, following the expectation for average bond length to increase as average cation coordination increases. However, the divergence between the measured $CN_{Ce}$ and that expected from the measured $R_{Ce-O}$ increases with decreasing Ce$_2$O$_3$ concentration and compositional distance from the cerium metaphosphate endpoint in both the CAP and CSP series. Near the aluminum metaphosphate endpoint, $CN_{Ce} \sim 7.8$, the average Ce-O bond distance calculated from the fit is only 2.42 Å compared to the expected bond length for 8-fold cerium of 2.49 Å.$^{12}$ Similarly, near the silicophosphate endpoint, $CN_{Ce} \sim 8.3$, the $R_{Ce-O}$ calculated from the fit is only 2.44 Å when an average bond length slightly greater than 2.49 Å is expected.$^{12}$

Given the assumptions made during first shell oxygen fitting of the CeP$_3$O$_9$ standard and the larger fractional error for $CN_{Ce}$ compared to $R_{Ce-O}$, it is reasonable to estimate $CN_{Ce}$ from $R_{Ce-O}$ determined during fitting. In fact, for the reasons mentioned
earlier, several studies, both EXAFS and diffraction, have found this to be a more reasonable approach to $CN_{\text{RE}}$ determination.$^{13,15,16}$ Using linear interpolation and the effective ionic radii for $\text{Ce}^{3+}$ and $\text{O}^{2-}(\text{II}),^{12}$ alternative estimates of average cerium coordination for the CAP and CSP glasses are given in Table 6.2 and shown graphically in Figure 6.5 as $CN(\text{R}_{\text{Ce-O}})$.

The plot of $CN(\text{R}_{\text{Ce-O}})$ (average cerium coordination calculated from $\text{R}_{\text{Ce-O}}$) versus composition in Figure 6.5 shows that it is possible to estimate average cerium coordination with an uncertainty small enough to clarify trends with $\text{Ce}_2\text{O}_3$ concentration. In particular, the small shift in $\text{R}_{\text{Ce-O}}$ in the CAP glass series can be correlated to a shift in $CN(\text{R}_{\text{Ce-O}})$ between high-cerium and low-cerium glasses. Likewise, the gradual increase in $CN(\text{R}_{\text{Ce-O}})$ with decreasing $\text{Ce}_2\text{O}_3$ for CSP glasses corresponds to an increase in $\text{R}_{\text{Ce-O}}$. 
<table>
<thead>
<tr>
<th></th>
<th>Δμ/ρ (cm²/g)</th>
<th>t (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAP_9</td>
<td>0.86</td>
<td>3.89</td>
</tr>
<tr>
<td>CAP_8</td>
<td>1.53</td>
<td>2.18</td>
</tr>
<tr>
<td>CAP_7</td>
<td>2.78</td>
<td>1.20</td>
</tr>
<tr>
<td>CAP_6</td>
<td>5.10</td>
<td>0.65</td>
</tr>
<tr>
<td>CAP_5</td>
<td>6.69</td>
<td>0.50</td>
</tr>
<tr>
<td>CAP_4</td>
<td>7.09</td>
<td>0.47</td>
</tr>
<tr>
<td>CAP_3</td>
<td>7.62</td>
<td>0.44</td>
</tr>
<tr>
<td>CAP_2</td>
<td>7.76</td>
<td>0.43</td>
</tr>
<tr>
<td>CAP_1</td>
<td>7.59</td>
<td>0.44</td>
</tr>
<tr>
<td>CSP_9</td>
<td>7.69</td>
<td>0.43</td>
</tr>
<tr>
<td>CSP_8</td>
<td>7.62</td>
<td>0.44</td>
</tr>
<tr>
<td>CSP_7</td>
<td>7.17</td>
<td>0.46</td>
</tr>
<tr>
<td>CSP_6</td>
<td>6.63</td>
<td>0.50</td>
</tr>
<tr>
<td>CSP_5</td>
<td>5.86</td>
<td>0.57</td>
</tr>
<tr>
<td>CSP_4</td>
<td>3.69</td>
<td>0.90</td>
</tr>
<tr>
<td>CSP_3</td>
<td>2.30</td>
<td>1.45</td>
</tr>
<tr>
<td>CSP_2</td>
<td>1.27</td>
<td>2.62</td>
</tr>
</tbody>
</table>

Table 6.1: Difference in mass attenuation coefficient (Δμ/ρ) 25 eV above and below the Ce K-edge (40,433 eV) and glass thickness for the unit edge step condition for CAP and CSP glasses.
<table>
<thead>
<tr>
<th></th>
<th>CN₆Ce</th>
<th>R₆Ce-O (Å)</th>
<th>σ² (Å²)</th>
<th>CN(R₆Ce-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeP₃O₉</td>
<td>6.0 ± 0.5</td>
<td>2.42 ± 0.01</td>
<td>0.009 ± 0.001</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>CAP_9</td>
<td>7.8 ± 0.7</td>
<td>2.42 ± 0.01</td>
<td>0.013 ± 0.001</td>
<td>6.9 ± 0.2</td>
</tr>
<tr>
<td>CAP_8</td>
<td>7.7 ± 0.8</td>
<td>2.42 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.9 ± 0.2</td>
</tr>
<tr>
<td>CAP_7</td>
<td>7.7 ± 0.7</td>
<td>2.42 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>CAP_6</td>
<td>6.9 ± 0.7</td>
<td>2.40 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>CAP_5</td>
<td>6.9 ± 0.7</td>
<td>2.40 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>CAP_4</td>
<td>7.1 ± 0.6</td>
<td>2.40 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.7 ± 0.1</td>
</tr>
<tr>
<td>CAP_3</td>
<td>7.2 ± 0.7</td>
<td>2.41 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.8 ± 0.2</td>
</tr>
<tr>
<td>CAP_2</td>
<td>7.0 ± 0.6</td>
<td>2.41 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.8 ± 0.2</td>
</tr>
<tr>
<td>CAP_1</td>
<td>6.8 ± 0.6</td>
<td>2.40 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>CSP_9</td>
<td>7.0 ± 0.7</td>
<td>2.40 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.8 ± 0.2</td>
</tr>
<tr>
<td>CSP_8</td>
<td>7.2 ± 0.6</td>
<td>2.41 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>6.8 ± 0.1</td>
</tr>
<tr>
<td>CSP_7</td>
<td>7.1 ± 0.5</td>
<td>2.41 ± 0.01</td>
<td>0.011 ± 0.001</td>
<td>6.8 ± 0.1</td>
</tr>
<tr>
<td>CSP_6</td>
<td>7.4 ± 0.7</td>
<td>2.41 ± 0.01</td>
<td>0.011 ± 0.001</td>
<td>6.9 ± 0.1</td>
</tr>
<tr>
<td>CSP_5</td>
<td>7.5 ± 0.7</td>
<td>2.42 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>7.0 ± 0.2</td>
</tr>
<tr>
<td>CSP_4</td>
<td>7.8 ± 0.7</td>
<td>2.43 ± 0.01</td>
<td>0.012 ± 0.001</td>
<td>7.1 ± 0.1</td>
</tr>
<tr>
<td>CSP_3</td>
<td>8.3 ± 0.8</td>
<td>2.43 ± 0.01</td>
<td>0.013 ± 0.001</td>
<td>7.2 ± 0.1</td>
</tr>
<tr>
<td>CSP_2</td>
<td>8.1 ± 0.9</td>
<td>2.44 ± 0.01</td>
<td>0.013 ± 0.002</td>
<td>7.2 ± 0.1</td>
</tr>
</tbody>
</table>

Table 6.2: EXAFS structural parameters for oxygen around Ce and estimate of average cerium coordination from average cerium-oxygen bond distance.

CN₆Ce: average cerium coordination number as determined from EXAFS fitting.
R₆Ce-O: average Ce-O bond distance as determined from EXAFS fitting.
σ²: Debye-Waller Factor as determined from EXAFS fitting.
CN(R₆Ce-O): Estimate of average cerium coordination number from R₆Ce-O using linear interpolation and the effective ionic radii for Ce³⁺ and O²⁻(II).
Table 6.3: $R_{Ce-O}$ and $CN_{Ce}$ values measured for cerium metaphosphate glasses.

$CN_{Ce}$: average cerium coordination number.
$R_{Ce-O}$: average Ce-O bond distance.
Figure 6.1: Comparison of the XRD pattern from crystallized CAP_1 glass and indicator lines from the powder diffraction file for CeP₃O₉ (ICSD PDF #97-041-7805).
Figure 6.2: Ball and stick representation of zigzag chains of [CeO$_8$]$^{13}$ dodecahedra in CeP$_3$O$_9$. Oxygen anions are labeled according to their symmetry-related positions as described by Tong, et.al.$^{22}$
Figure 6.3: Ce K-edge EXAFS spectra for CeP$_3$O$_9$ with the first shell oxygen fit: (a) $k^2$-weighted $\chi(k)$, (b) the imaginary portion of $\chi(R)$, and (c) the magnitude of $\chi(R)$. 
Figure 6.4: Ce K-edge EXAFS spectra for CAP_2 with the first shell oxygen fit: (a) $k^2$-weighted $\chi(k)$, (b) the imaginary portion of $\chi(R)$, and (c) the magnitude of $\chi(R)$. 
Figure 6.5: Average first shell oxygen coordination number calculated from average bond distance (CN(R_{Ce-O})) for aluminophosphate and silicophosphate glasses plotted versus mol% Ce$_2$O$_3$. 
CHAPTER 7

PHOSPHORUS-RELATED RADIATION-INDUCED DEFECTS AND Ce\textsuperscript{3+} PARAMAGNETIC RESONANCE

Electron paramagnetic resonance (EPR) can be used to detect unpaired electrons in glasses. These unpaired spins can be related to intrinsic sites in the glass, such as transition metal and rare-earth cations with unpaired valence electrons. Unpaired spins due to the trapping of electrons or holes during irradiation are also detectable by EPR, making this a useful technique for determining the nature of radiation damage.

7.1 LITERATURE REVIEW

EPR uses microwave radiation to stimulate transitions of unpaired electronic spins between energy levels “split by the application of an external magnetic field (the Zeeman effect).”\textsuperscript{85} These split levels are further split by hyperfine interactions which result from the localization of the unpaired electron on a nuclei with net spin.\textsuperscript{85} In a typical EPR experiment, the microwave frequency is held constant, while the magnetic field intensity is scanned. Absorption of microwave energy as a function of magnetic field is measured as a derivative spectrum and corresponds to electrons transitioning between energy levels.

It is well known that EPR spectra from glasses are similar to that observed from powdered crystalline samples, though due to their amorphous nature, a distribution of electron g-factors and hyperfine coupling A-factors are present.\textsuperscript{85,86} This allows for EPR spectra from glasses to be analyzed in a fashion similar to those from crystalline materials.
7.1.1 EPR Resonance of Ce$^{3+}$

As an ion with a single unpaired electron in the 4f shell (4f$^1$), Ce$^{3+}$ cations are identifiable by EPR, although the broad resonance can only be resolved at low temperatures. For a Ce$^{3+}$ cation with $C_{3h}$ crystal field symmetry, principle g-values of $g_\perp = 2.57$ and $g_\parallel = 0.86$ are calculated. In glasses, the broad cerium resonance occurs at g-values similar to those determined for trigonal axial symmetry. Bishay identified the Ce$^{3+}$ resonance as occurring at $g_\parallel = 3.18$ in barium aluminoborate glasses. However, subsequent analysis of the integral of this as-measured derivative curve by Griscom showed close agreement with the g-values predicted for $C_{3h}$ symmetry.

7.1.2 Radiation-Induced Defects in Phosphate Glasses

Several radiation-induced defects have been identified by EPR in phosphate glasses, occurring at distinct hyperfine splitting values according to localization on the phosphorus cation ($^{31}$P, with a nuclear spin of $\frac{1}{2}$, is naturally 100% abundant). Some of these radiation-induced defects are the result of electron- or hole-trapping at intrinsic defects in phosphate glasses to produce an unpaired spin (P$_1$, P$_2$, P$_3$). Others are the result of electron- or hole-trapping at other sites in the glass (phosphorus oxygen hole center and P$_3$). A summary of these defects is provided below:

1. A pair of resonances with a mean splitting of ~30-50 gauss has been assigned to a phosphorus oxygen hole center (POHC). These resonances are attributed to a hole trapped on the pair of non-bridging oxygens from a Q$^2$ phosphorus, leaving an unpaired spin shared between them. Several absorption bands have been attributed to POHC, including a band at 525-550 nm responsible for magenta
coloration, and another at 380-440 nm which was found to vary in wavelength with alkali content. Additional bands at 570 nm, 510 nm, 400 nm, and 240 nm were identified in phosphorus-doped silicate glasses, while the band at 400 nm was specifically attributed to a low-temperature form of POHC where the unpaired spin is localized on one oxygen instead of two.

2. The EPR resonance from the P₄ defect is characterized by a central resonance with step shoulders at a splitting of ~300 gauss. This defect is analogous to the phosphinyl radical (PO₂⁻) and has been described as a Q³ P³⁺ with a non-bridging oxygen vacancy, an intrinsic defect, that subsequently traps an electron entirely on a p-orbital and breaks a bridging oxygen bond. An absorption band at 260 nm in phosphorus-doped silicate glasses was attributed to this defect.

3. A pair of resonances with a mean splitting of ~660-770 gauss, observed in high-alkali phosphate glasses, is denoted the P₃ defect. It has been attributed to a “P₁ or P₂ center that is sharing part of its spin with a nearby alkali.”

4. The P₁ defect, with EPR resonances characterized by a hyperfine splitting of ~850-950 gauss, is analogous to the phosphoryl radical (PO₃²⁻). It is attributed to trapping of a hole on the non-bridging oxygen vacancy of a Q³ P³⁺, also an intrinsic defect, and is considered to be the phosphorus analog of the silicon E’ center. In phosphorus-doped silicate glasses, an absorption band at 1570 nm was found to correlate with the P₁ defect.

5. Finally, the P₂ defect, identified by EPR resonances with a mean splitting of ~1200 gauss, is considered to be the analog of the phosphoranyl radical (PO₄⁴⁻). The precursor site for this defect is a Q⁴ phosphorus, an intrinsic defect, which
traps an electron on the P$^{5+}$. The P$_2$ defect was found to correlate with an absorption band at 270 nm in phosphorus-doped silicate glasses.$^{88}$

The defects observed after irradiation of phosphate glasses are highly dependant on composition. ν-P$_2$O$_5$ and many binary phosphate glasses with low alkali content exhibit peaks from P$_1$, P$_2$, and POHC defects.$^{86}$ In a 90 SiO$_2$-10 P$_2$O$_5$ glass extensively studied by Griscom, et.al., P$_1$, P$_2$, P$_4$, and POHC defects were identified in the irradiated glass.$^{88}$ While high-alkali binary phosphate glasses have been found to have only P$_3$ and POHC defects.$^{86}$

For many aluminophosphate glasses, often only P$_1$ and POHC are observed, such as in sodium aluminophosphate,$^{84}$ sodium-calcium aluminophosphate,$^{95}$ lithium aluminophosphate,$^{96,97}$ and calcium aluminophosphate glasses.$^{98}$ However, other studies of sodium-, calcium-, strontium-, and magnesium-aluminophosphate glasses have detected P$_1$, POHC, and P$_2$ defects.$^{99,100}$

7.2 EXPERIMENTAL PROCEDURE AND THEORY

7.2.1 Data Collection

EPR spectra were gathered using a Bruker EMX x-band EPR spectrometer equipped with an ER041 XG microwave bridge and operated using WinEPR software. Spectra were gathered from irradiated and unirradiated samples at liquid nitrogen temperatures using an analysis dewar for the CAP glasses and flowing nitrogen vapor for the CSP glasses.
7.2.2 EPR Theory

The conditions for resonance under a strong external field for axial symmetry and nuclear hyperfine interaction have been given by Bleaney using first- and second-order perturbation theory.\(^{101}\) Excluding nuclear electric quadrupole interaction, the resonance conditions can be written as follows in Equation 7.1, for the transition \((M_S, M_I) \rightarrow (M_S-1, M_I)\) where collinear axes of symmetry are assumed for the \(g\) and \(A\) tensors, \(\parallel\) and \(\perp\) indicate components parallel and perpendicular to the axis of symmetry, \(h =\) Planck’s constant, \(\nu =\) frequency, \(g = g\)-tensor, \(\beta =\) Bohr magneton, \(\theta =\) angle between the symmetry axis and applied magnetic field \((H)\), \(A =\) hyperfine coupling tensor, \(I =\) nuclear spin, \(M_I =\) nuclear magnetic quantum number, \(S =\) electron spin = \(\frac{1}{2}\), \(M_S =\) electron magnetic quantum number, and \(H_o = h\nu/g\beta\), the resonance condition in the absence of hyperfine splitting.

\[
H_{res} = H_o - \frac{AM_{II}}{g\beta} - \frac{A_{I}^{2}(A_{I}^{2} + A_{II}^{2})}{4A_{II}^{2}g^{2}\beta^{2}H_{o}}\left\{I(I + 1) - M_{I}^{2}\right\}
\]

\[
- \frac{(A_{II}^{2} - A_{I}^{2})^{2}}{2A_{II}^{2}g^{2}\beta^{2}H_{o}}\left(\frac{g_{I}g_{II}}{g_{II}}\right)^{2}\sin^{2}\theta\cos^{2}\theta M_{I}^{2} \tag{7.1.a}
\]

\[
g^{2} = g_{I}^{2}\sin^{2}\theta + g_{II}^{2}\cos^{2}\theta \tag{7.1.b}
\]

\[
A_{II}^{2} = A_{I}^{2}\sin^{2}\theta + A_{II}^{2}\cos^{2}\theta \tag{7.1.c}
\]

The quantities \(A_{II}\) and \(A_{I}\) can be related to the s-character (isotropic) and p-character (anisotropic or axial) of the unpaired spin by Equation 7.2, where \(a = \) isotropic hyperfine coupling and \(b = \) anisotropic hyperfine coupling.\(^{102}\)

\[
A_{II} = a + 2b \tag{7.2.a}
\]

\[
A_{I} = a - b \tag{7.2.b}
\]
In turn, the localization of the unpaired spin on the nuclei can be given as $C_s^2 + C_p^2$, defined in Equation 7.3, where $C_s^2 = \text{fraction s-character}$, $C_p^2 = \text{fraction p-character}$, $a_o = \text{isotropic hyperfine parameter}$, and $b_o = \text{axial hyperfine parameter}$. Values of $a_o$ and $b_o$ for $^{31}\text{P}$ are given as 474.79 mT and 13.088 mT respectively.

$$C_s^2 = a / a_o \quad \text{(7.3.a)}$$

$$C_p^2 = b / b_o \quad \text{(7.3.b)}$$

Due to the large hyperfine splitting in $^{31}\text{P}$-associated defects in glasses, second order effects are significant and manifest in the measured EPR spectra by shifting the characteristic resonances to a lower field. This shift is also responsible for the asymmetric width of the observed resonances. An idealized EPR absorption spectrum for a resonance with large hyperfine splitting is given in Figure 7.1 to provide clarification of the following equations. From Equation 7.1, the magnetic field resonances for a generic $^{31}\text{P}$ defect with $I = \frac{1}{2}$ and $g \approx g_\parallel \approx g_\perp$ were determined for the extreme values, $\parallel$ and $\perp$ conditions, where $\theta = 0^\circ$ and $90^\circ$ as shown in Equation 7.4.

$$H_\parallel^+ = H_o + \frac{A_\parallel}{2g\beta} - \frac{A_{\perp}^2}{4g^2\beta^2H_o} \quad \text{(7.4.a)}$$

$$H_\parallel^- = H_o - \frac{A_\parallel}{2g\beta} - \frac{A_{\perp}^2}{4g^2\beta^2H_o} \quad \text{(7.4.b)}$$

$$H_\perp^+ = H_o + \frac{A_\perp}{2g\beta} - \frac{A_\parallel^2 + A_{\perp}^2}{8g^2\beta^2H_o} \quad \text{(7.4.c)}$$

$$H_\perp^- = H_o - \frac{A_\perp}{2g\beta} - \frac{A_\parallel^2 + A_{\perp}^2}{8g^2\beta^2H_o} \quad \text{(7.4.d)}$$
It follows that the width of the high-field resonance and the low-field resonance can be defined as shown in Equation 7.5.

\[
\Delta^+ = \frac{A_\parallel - A_\perp}{2g\beta} + \frac{A_\parallel^2 - A_\perp^2}{8g^2\beta^2H_o} \tag{7.5.a}
\]

\[
\Delta^- = \frac{A_\parallel - A_\perp}{2g\beta} - \frac{A_\parallel^2 - A_\perp^2}{8g^2\beta^2H_o} \tag{7.5.b}
\]

The average width of the high- and low-field resonances is the same with or without second order effects as shown in Equation 7.6.

\[
\Delta = \frac{\Delta^+ + \Delta^-}{2} = \frac{A_\parallel - A_\perp}{2g\beta} \tag{7.6}
\]

7.2.3 Data Processing

To determine hyperfine splitting parameters for radiation-induced defects, the measured derivative spectra were first integrated and then the broad Ce$^{3+}$ resonance was subtracted using a spline background. Gaussian peaks were then fit to the hyperfine resonances and the resultant peak position and width were used to calculate the hyperfine splitting parameters. Background subtraction and peak fitting were accomplished using OriginPro 8.5.

Calculations were performed with $A_\parallel$ and $A_\perp$ given in magnetic field units assuming isotropic g-values where $g \approx g_\parallel \approx g_\perp \approx g_s$, and $g_s$ is the g-value for an isolated electron, 2.0023. This assumption is supported by previous measurements of the g-values for these defects, where $g_\parallel \approx g_\perp \approx g_s$. Thus, the average width ($\Delta_{\text{avg}}$) of corresponding hyperfine pairs was set as $(A_\parallel - A_\perp)/2$ and the average separation of the hyperfine pairs ($\Delta H_{\text{avg}}$) was set as $(A_\parallel + A_\perp)/2$, which when combined with Equation 7.2
yield the relationships as given in Equation 7.7, where a and b are also given in magnetic field units.

\[ \Delta_{\text{avg}} = \frac{3b}{2} \quad (7.7.a) \]

\[ \Delta H_{\text{avg}} = \frac{2a + b}{2} \quad (7.7.b) \]

After determination of a and b, \( C_S^2 \) and \( C_P^2 \) were determined using Equation 7.3 and the localization on the \( ^{31}P \) nucleus, \( n \), calculated. Additionally, \( A_\parallel \) and \( A_\perp \) were determined from \( a \) and \( b \), using Equation 7.2.

For comparison purposes, sample spectra were scaled using Equation 7.8, where \( I_o = \) measured intensity, \( P = \) microwave power, \( G = \) receiver gain, \( S = \) number scans, \( V = \) volume sample (as determined from sample mass and density), and normalized to \( I(100 \text{ gauss}) = 0 \).

\[ I = \frac{I_o}{\sqrt{P \times G \times V \times S}} \quad (7.8) \]

 Additionally, spline backgrounds fit to as-measured EPR derivative spectra were used to determine \( I_{\text{max}} \), \( g_\parallel \), and \( g_\perp \) for the \( \text{Ce}^{3+} \) resonance. This provided a smooth curve to locate intensity maxima and minima, mitigating the effect of noise in the as-measured spectra.

7.3 RESULTS

EPR derivative spectra from gamma-irradiated CAP glasses are shown in Figure 7.2, and from CSP glasses in Figure 7.3. A broad resonance from \( \text{Ce}^{3+} \) was present in the CAP and CSP glasses, \( P_1 \) and \( P_2 \) radiation-induced defects in CAP_9-7 and CSP_2-4, and POHC radiation-induced defects in CSP_2-4. These resonances are discussed in detail in
Sections 7.3.1, 7.3.2, and 7.3.3 respectively. In addition to these resonances, a single resonance at $g \approx 4.23$, observed in the low Ce$_2$O$_3$ samples, was attributed to Fe$^{3+}$ impurities, and is noted on Figures 7.2 and 7.3. Finally, two resonance features in both CAP_9-7 and CSP_2-4 which were not immediately identifiable are discussed in Section 7.3.4.

### 7.3.1 Ce$^{3+}$ Resonance

In accordance with previous studies, axial symmetry was assumed for Ce$^{3+}$ in the CAP and CSP glasses. Values for $g_\parallel$ and $g_\perp$ as determined from spline background fits are shown in Table 7.1. It should be noted that resonances from radiation-induced defects overlap with $g_\perp$ from Ce$^{3+}$, adding uncertainty to the estimate of this value for glasses CAP_9-7 and CSP_2-4. Values of $g_\perp$ (2.5-3.1) and $g_\parallel$ (0.85-1.00) for the Ce$^{3+}$ resonance in the CAP and CSP glasses agree well with values for a Ce$^{3+}$ cation with $C_{3h}$ crystal field symmetry ($g_\perp = 2.57$ and $g_\parallel = 0.86$).

As shown in Figure 7.4 for the CAP glasses, $g_\perp$ for Ce$^{3+}$ decreases initially with increasing mol% Ce$_2$O$_3$ for CAP_9-6, is constant for CAP_6-4, and then increases slightly for CAP_4-1. Additionally, the maximum intensity of the Ce$^{3+}$ resonance generally increases with Ce$_2$O$_3$ concentration, but not monotonically. For the CSP glasses, $g_\perp$ for Ce$^{3+}$ increases slightly from CSP_2-3, then decreases with increasing Ce$_2$O$_3$ concentration, as shown in Figure 7.5. The Ce$^{3+}$ resonance intensity increases with Ce$_2$O$_3$ concentration for CSP_2-6, then decreases slightly for CSP_6-9. For both the CAP and CSP glasses, trends in $g_\parallel$ for Ce$^{3+}$ are not definitive.
7.3.2 Phosphorus-Related Defect Resonances

For the CAP glasses, radiation-induced paramagnetic defect sites related to phosphorus are only detected in glasses CAP_9, CAP_8, and CAP_7, and identified as P₁ and P₂ type defects based upon their mean splitting of ~910 gauss and ~1260 gauss respectively. Plots of these resonances are shown after subtraction of the Ce³⁺ resonance using a spline background in Figure 7.6. It is seen that the intensity of these resonances decrease with increasing Ce₂O₃ content.

For the CSP glasses, phosphorus-related radiation-induced defects are only detected in glasses CSP_2-4. In addition to P₁ and P₂ defects with mean splittings of ~870 gauss and ~1170 gauss respectively, the POHC defect was also identified, with a mean splitting of ~50 gauss. These resonances are shown after subtraction of the Ce³⁺ resonance in Figure 7.7 and 7.8. As with the CAP glasses, the intensity of the radiation-induced defect resonances decreases with increasing Ce₂O₃ content.

7.3.3 P₁ and P₂ Hyperfine Splitting Parameter Identification

The spectra from CAP_9 and CSP_2 were used to determine the hyperfine splitting parameters for the P₁ and P₂ defects as the resonances were most intense in these samples. Due to the overlap between P₁ and P₂ defect resonances, it was necessary to integrate the measured derivative spectra and perform a Gaussian peak fit to determine the average width (Δavg) and separation (ΔHavg) of the resonances. The EPR absorption spectra after Ce³⁺ resonance subtraction are shown in Figure 7.9 for CAP_9 and Figure 7.10 for CSP_2, along with the Gaussian peak fit. For CAP_9, four Gaussian peaks were used for the fit, one each for the upper and lower P₁ and P₂ resonances. The central
resonance at $g \approx 1.997$ and shoulder on the low-field side of the upper-field resonance of P$_1$ in the integrated spectrum were not fit. Eight Gaussian peaks were used to fit CSP$_2$, one each for the upper and lower P$_1$, P$_2$, and POHC resonances, and two for the unknown resonance at $g \approx 1.904$. Values for the hyperfine splitting parameters were determined from the average width ($\Delta_{\text{avg}}$) and separation ($\Delta H_{\text{avg}}$) of these Gaussian peaks as described in Section 7.2.3 and are given in Table 7.2. Hyperfine splitting parameters determined for P$_1$ and P$_2$ defects in CAP$_9$ and CSP$_2$ compare favorably with literature values as shown in Table 7.3, supporting this identification.

It was not possible to use this method to fit hyperfine parameters for the POHC defect in CSP$_2$ due to the coincidence of the resonance at $g \approx 2.0007$ with the high-field POHC resonance.

7.3.4 Other Resonance Features

Other resonance features were also present in glasses CAP$_9$-7 and CSP$_2$-4. In CAP$_9$, a single resonance is present at $g \approx 1.997$, possibly due to free electrons at the fracture surfaces created during sample preparation, along with a feature that may be a positive step shoulder at $g \approx 1.924$. While in CSP$_2$, an intense single resonance at $g \approx 2.0007$ overlaps with the high-field POHC resonance. This resonance is likely due to the Si E’ center, but positive identification was not possible as $g_1$, $g_2$, and $g_3$ values were not resolved. Additionally, in CSP$_2$, there is a feature which may be a resonance centered $g \approx 1.904$, or a positive step shoulder at $g \approx 1.932$. 
Table 7.1: $g_\perp$ and $g_\parallel$ values for the Ce$^{3+}$ paramagnetic resonance in CAP and CSP glasses.

<table>
<thead>
<tr>
<th></th>
<th>$g_\perp$</th>
<th>$g_\parallel$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAP_9</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>CAP_8</td>
<td>2.80</td>
<td>0.96</td>
</tr>
<tr>
<td>CAP_7</td>
<td>2.73</td>
<td>0.93</td>
</tr>
<tr>
<td>CAP_6</td>
<td>2.55</td>
<td>0.93</td>
</tr>
<tr>
<td>CAP_5</td>
<td>2.55</td>
<td>0.94</td>
</tr>
<tr>
<td>CAP_4</td>
<td>2.55</td>
<td>0.92</td>
</tr>
<tr>
<td>CAP_3</td>
<td>2.61</td>
<td>0.91</td>
</tr>
<tr>
<td>CAP_2</td>
<td>2.61</td>
<td>0.90</td>
</tr>
<tr>
<td>CAP_1</td>
<td>2.60</td>
<td>0.93</td>
</tr>
<tr>
<td>CSP_9</td>
<td>2.56</td>
<td>0.92</td>
</tr>
<tr>
<td>CSP_8</td>
<td>2.55</td>
<td>0.97</td>
</tr>
<tr>
<td>CSP_7</td>
<td>2.62</td>
<td>0.93</td>
</tr>
<tr>
<td>CSP_6</td>
<td>2.68</td>
<td>0.94</td>
</tr>
<tr>
<td>CSP_5</td>
<td>2.80</td>
<td>0.92</td>
</tr>
<tr>
<td>CSP_4</td>
<td>2.98</td>
<td>1.00</td>
</tr>
<tr>
<td>CSP_3</td>
<td>3.02</td>
<td>0.96</td>
</tr>
<tr>
<td>CSP_2</td>
<td>2.98</td>
<td>0.84</td>
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</table>
Table 7.2: Hyperfine splitting parameters for P1 and P2 defects in glasses CAP_9 and CSP_2.

<table>
<thead>
<tr>
<th></th>
<th>ΔHavg (G)</th>
<th>Δavg (G)</th>
<th>a (G)</th>
<th>b (G)</th>
<th>Cₛ²</th>
<th>Cₚ²</th>
<th>n</th>
<th>A∥ (G)</th>
<th>A⊥ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₁</td>
<td>CAP_9</td>
<td>1256.7</td>
<td>124.7</td>
<td>1215</td>
<td>83</td>
<td>0.26</td>
<td>0.64</td>
<td>0.89</td>
<td>1381.4</td>
</tr>
<tr>
<td></td>
<td>CSP_2</td>
<td>1168.6</td>
<td>136.9</td>
<td>1123</td>
<td>91</td>
<td>0.24</td>
<td>0.70</td>
<td>0.93</td>
<td>1305.6</td>
</tr>
<tr>
<td>P₂</td>
<td>CAP_9</td>
<td>908.0</td>
<td>97.8</td>
<td>875</td>
<td>65</td>
<td>0.18</td>
<td>0.50</td>
<td>0.68</td>
<td>1005.8</td>
</tr>
<tr>
<td></td>
<td>CSP_2</td>
<td>866.5</td>
<td>96.1</td>
<td>834</td>
<td>64</td>
<td>0.18</td>
<td>0.49</td>
<td>0.67</td>
<td>962.6</td>
</tr>
</tbody>
</table>

ΔHavg: average separation of hyperfine pairs.
Δavg: average width of hyperfine pairs.
a: isotropic hyperfine coupling.
b: anisotropic hyperfine coupling.
Cₛ²: fractional s-character.
Cₚ²: fractional p-character.
n: localization of the unpaired spin on the ³¹P nuclei.
A∥: parallel component of the hyperfine coupling tensor.
A⊥: perpendicular component of the hyperfine coupling tensor.
Table 7.3: Comparison of hyperfine parameters for P₁ and P₂ defects.

<table>
<thead>
<tr>
<th></th>
<th>a (G)</th>
<th>b (G)</th>
<th>Cₛ²</th>
<th>Cₚ²</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂</td>
<td>CAP 9</td>
<td>1215</td>
<td>83</td>
<td>0.26</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>CSP 2</td>
<td>1123</td>
<td>91</td>
<td>0.24</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>Lenahan et. al.¹⁰⁴</td>
<td>1200</td>
<td>80</td>
<td>0.25</td>
<td>0.61</td>
</tr>
<tr>
<td>P₁</td>
<td>CAP 9</td>
<td>875</td>
<td>65</td>
<td>0.18</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>CSP 2</td>
<td>834</td>
<td>64</td>
<td>0.18</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>Lenahan et. al.¹⁰⁴</td>
<td>853</td>
<td>68</td>
<td>0.18</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>Weeks, Bray⁸⁶</td>
<td>950</td>
<td>70</td>
<td>0.24</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>Griscom et. al.⁸⁸</td>
<td>910</td>
<td>60</td>
<td>0.23</td>
<td>0.50</td>
</tr>
</tbody>
</table>

a: isotropic hyperfine coupling.
b: anisotropic hyperfine coupling.
Cₛ²: fractional s-character.
Cₚ²: fractional p-character.
n: localization of the unpaired spin on the ³¹P nuclei.
Figure 7.1: Sketch of an idealized EPR absorption spectrum for an axially symmetric defect with large hyperfine splitting, $I = \frac{1}{2}$ and $S = \frac{1}{2}$. 
Figure 7.2: Scaled derivative EPR spectra for CAP glasses. The Fe$^{3+}$ impurity resonance is noted as well as the broad Ce$^{3+}$ resonance.
Figure 7.3: Scaled derivative EPR spectra for CSP glasses. The Fe$^{3+}$ impurity resonance is noted as well as the broad Ce$^{3+}$ resonance.
Figure 7.4: Intensity and g-values versus Ce$_2$O$_3$ concentration for Ce$^{3+}$ resonance in CAP glasses.
Figure 7.5: Intensity and $g_\perp$ values versus Ce$_2$O$_3$ concentration for Ce$^{3+}$ resonance in CSP glasses.
Figure 7.6: EPR derivative spectra for glasses CAP_9-7, after subtraction of Ce$^{3+}$ resonance, showing resonances from P$_1$ and P$_2$ defects, and g-values for the unknown resonance and central resonance.
Figure 7.7: EPR derivative spectra for glasses CSP_2-4 after subtraction of Ce$^{3+}$ resonance showing resonances from P$_1$ and P$_2$ defects, and g-values for the unknown resonance.
Figure 7.8: EPR derivative spectrum for glass CSP_2 showing the resonance pair from POHC as well as the g-value for the resonance attributed to Si E’ centers.
Figure 7.9: Gaussian peak fit to EPR absorption spectrum from CAP_9 after subtraction of Ce$^{3+}$ resonance by spline background.
Figure 7.10: Gaussian peak fit to EPR absorption spectrum from CSP_2 after subtraction of Ce$^{3+}$ resonance by spline background.
CHAPTER 8

CERIUM CLUSTERING

The models for rare-earth phosphate and rare-earth aluminophosphate glasses discussed in Section 3.3 and 3.4 were expanded to estimate average cerium cluster size. As cerium clusters were not directly measured by Ce K-edge EXAFS, the chain fragment cluster model provides an additional parameter to correlate with property trends beyond the simple presence or absence of clustering. For the purposes of this discussion, average cerium coordination (CN\textsubscript{Ce}) is set to average cerium coordination calculated from R\textsubscript{Ce-O} (CN(R\textsubscript{Ce-O})) as discussed previously.

8.1 CHAIN FRAGMENT CLUSTER MODEL

The chains of edge-shared cerium dodecahedra in the CeP\textsubscript{3}O\textsubscript{9} crystal, previously shown in Figure 6.2, were used as a model for how clustering might occur in these glasses, by sharing of two oxygen anions between pairs of cerium cations. Thus, clusters calculated by this method are actually chain segments, or fragments, composed of two types of cerium: chain-end and mid-chain. Specifically, a two-cerium cluster is composed of two chain-end cerium cations, and a three-cerium cluster is composed of two chain-end cerium cations and one mid-chain cerium cation. Schematics of a two-cerium, and three-cerium cluster are shown in Figure 8.1.

Using this model, the atom fraction of oxygen required by isolated cerium (c\textsubscript{O}\textsuperscript{Ce}) is shown in Equation 8.1, where c\textsubscript{Ce} is the atom fraction of cerium and CN\textsubscript{Ce} is the average cerium coordination.
Comparison of the oxygen requirements for chain-end, mid-chain, and isolated cerium shows that regardless of cerium coordination, edge-sharing of oxygen between cerium cations effectively decreases the cerium coordination by one. Thus, the atom fraction of oxygen required by chain-end \((c_{Ce}^{ce})\) and mid-chain cerium \((c_{Ce}^{mc})\) can be calculated using Equations 8.2 and 8.3.

\[
c_{Ce}^{ce} = \left( \frac{CN_{Ce} - 1}{2} \right) c_{Ce} \quad (8.2)
\]

\[
c_{Ce}^{mc} = \left( \frac{CN_{Ce} - 2}{2} \right) c_{Ce} \quad (8.3)
\]

To solve for a binary distribution of cerium sites, the atom fraction of oxygen available to cerium was set equal to the atom fraction of oxygen required by cerium. Two different idealized binary distributions were calculated, the first, a combination of isolated and chain-end cerium for cluster sizes between one and two, and the second, a combination of mid-chain and chain-end cerium, for cluster sizes between two and \(\infty\) (as is the case for the CeP3O9 crystal).

### 8.1.1 Isolated and Two-Cerium Cluster Distribution

For a binary distribution of isolated cerium and chain-end cerium, the atom fraction of oxygen for cerium \((c_{Ce}^{ce})\) is calculated as shown in Equation 8.4 where \(x\) is the fraction of chain-end cerium.

\[
c_{Ce}^{ce} = (1 - x)c_{Ce}^{ice} + xc_{Ce}^{ce} = \frac{c_{Ce}^{ce}}{2}(CN_{Ce} - x) \quad (8.4)
\]
The atomic fraction of oxygen for cerium \( c^\text{Ce}_O \) is related to the NBO available per cerium cation \( \bar{n}_{\text{Ce}}^{\text{NBO}} \) as shown in Equation 8.5.

\[
\bar{n}_{\text{Ce}}^{\text{NBO}} = \frac{2c^\text{Ce}_O}{c_{\text{Ce}}} = \frac{2(c_O - 2C_p) - C_AlCN_{Al}}{c_{\text{Ce}}} \quad (8.5)
\]

Thus, the fraction of chain-end cerium \( x \) in a binary distribution of isolated and chain-end cerium is calculated from the NBO available per cerium cation as shown in Equation 8.6.

\[
x = CN_{\text{Ce}} - \bar{n}_{\text{Ce}}^{\text{NBO}} \quad (8.6)
\]

For any binary distribution, the average cerium cluster size \( n_{\text{Ce}} \) is calculated as the total number of cerium cations divided by the number of cerium clusters. Therefore, in any distribution of isolated and two-cerium clusters, a chain-end cerium is half of a two-cerium cluster, and an isolated cerium is a one-cerium cluster. Using the binary distribution calculated from Equation 8.6, an average cluster size can be calculated as shown in Equation 8.7 for isolated and chain-end cerium.

\[
n_{\text{Ce}} = \frac{1}{(1-x) + x/2} \quad (8.7)
\]

### 8.1.2 Two-Cerium and Larger Clusters

Similar to the calculations in Section 8.1.1 for cluster sizes between one and two, a binary distribution of mid-chain and chain-end cerium can be calculated to predict cluster sizes greater than two. Equation 8.8 shows the atom fraction oxygen for cerium where \( y \) is the fraction of mid-chain cerium.

\[
c^\text{Ce}_O = (1-y)c^\text{Ce}_O + yc^m_{\text{Ce}} = \frac{c^\text{Ce}_O}{2}(CN_{\text{Ce}} - 1-y) \quad (8.8)
\]
Substitution of the relationship between $c_{Ce}^{O}$ and $\bar{n}_{Ce}^{NBO}$ given in Equation 8.5 yields the definition for fraction of mid-chain cerium ($y$) in a binary distribution of chain-end and mid-chain cerium as shown in Equation 8.9.

$$y = CN_{Ce} - 1 - \bar{n}_{Ce}^{NBO} \tag{8.9}$$

For a distribution of chain-end and mid-chain cerium, the number of clusters is equal to half the number of chain-end cerium. Thus, the average cluster size can be calculated as shown in Equation 8.10.

$$n_{Ce} = \frac{1}{(1 - y)/2} = \frac{2}{1 - y} \tag{8.10}$$

8.1.3 Extension to Silicophosphate Glasses

This model for estimation of average cluster size, as well as Equation 3.11 for fraction of NBO’s shared between rare-earth cations ($f_s$) and Equation 3.12 for average number of rare-earth next nearest neighbors ($\bar{n}_{RE}^{RE}$), can also be applied to cerium silicophosphate glasses with alumina impurities, once the definition for $\bar{n}_{Ce}^{NBO}$ is extended to include silicon as shown in Equation 8.11.

$$\bar{n}_{Ce}^{NBO} = \frac{2(c_O - 2c_p) - c_{AL}CN_{AL} - c_{Si}CN_{Si}}{c_{Ce}} \tag{8.11}$$

8.2 ALUMINUM AND SILICON COORDINATION

In order to estimate the cerium cluster size as accurately as possible in the aluminophosphate and silicophosphate glasses, nuclear magnetic resonance (NMR) spectroscopy was used to determine the proportion of both aluminum and silicon present
in tetrahedral, five-fold, and octahedral coordination sites. $^{27}$Al magic angle spinning (MAS) NMR spectra were gathered from glasses CAP_9-5 and $^{29}$Si Carr–Purcell–Meiboom–Gill (CPMG) MAS NMR spectra were gathered from glasses CSP_2-6. It was not possible to analyze the high-cerium CAP and CSP compositions due to increased paramagnetic broadening from cerium, as well as the lower concentration of the NMR-active species. The procedure for the $^{27}$Al MAS NMR and $^{29}$Si CPMG MAS NMR experiments is given in the Appendix.\textsuperscript{105}

As shown in Figures 8.2 and 8.3, octahedral aluminum (~20 ppm) is the predominant coordination for CAP_9-7, while the proportion of tetrahedral (~38 ppm), five-fold (~3 ppm), and octahedral coordinate aluminum are roughly equal for CAP_6-5. The percentage of aluminum present in each coordination, and the average aluminum coordination (CN$_{Al}$), are shown in Table 8.1 and Figure 8.4.

For the CSP glasses analyzed, CSP_2-6, the majority of the silicon cations are tetrahedrally coordinated (~120 ppm), as shown in Figures 8.5 and 8.6. However, five-fold (~165 ppm) and octahedral (~220 ppm) silicon were also detected in glasses CSP_2-4. Only tetrahedral and octahedral silicon were detected in glasses CSP_5-6. As Ce$_2$O$_3$ content increased, the fraction of octahedrally coordinated silicon increased, as well as the fraction of five-fold silicon, for the low-cerium compositions. The percentage of silicon present in each coordination, and average silicon coordination (CN$_{Si}$), are given in Table 8.2 and Figure 8.7.
8.3 ESTIMATION OF CERIUM CLUSTERING

8.3.1 Cerium Aluminophosphate Glasses

As aluminum speciation data was not available for glasses CAP_4-1, an average coordination of 5 was assumed, based on the average coordination of CAP_6 (4.95) and CAP_5 (5.05). To estimate whether cerium clustering would occur in the CAP glasses, Equations 3.11-13 were used to determine the fraction of oxygen shared between cerium cations ($f_s$), average number of cerium next-nearest neighbors around cerium ($\bar{n}_{Ce}^{Ce}$), and the average number of NBO available per cerium ($\bar{n}_{Ce}^{NBO}$) respectively. These results are shown in Table 8.3 alongside average cation coordination determined by EXAFS and NMR.

It is readily seen that $CN_{Ce} < \bar{n}_{Ce}^{NBO}$ for compositions CAP_9-7, indicating isolated cerium cations as reflected by the negative values for $f_s$ and $\bar{n}_{Ce}^{Ce}$. However, for glasses CAP_6-1, with higher concentrations of cerium, clustering is indicated by $CN_{Ce} > \bar{n}_{Ce}^{NBO}$ and positive values for $f_s$ and $\bar{n}_{Ce}^{Ce}$. Thus, a shift from isolated-cerium to clustered-cerium is predicted in the CAP glasses between 7 mol% and 14 mol% Ce$_2$O$_3$. This is analogous to a shift from Region I to Region III behavior in binary rare-earth phosphate glasses. In this glass series, no evidence for Region II behavior was seen, where $CN_{Ce} = \bar{n}_{Ce}^{NBO}$ over an extended compositional range.

This shift from isolated cerium to clustered cerium correlates with a shift in average cerium coordination from ~7.0 to ~6.7, as well as a shift in average aluminum coordination from ~5.4 to ~5.0, and a shift in aluminum coordination distribution from predominantly six-fold to an near-equal distribution of 4-, 5-, and 6-coordinate aluminum.
Using the chain fragment cluster model, the estimated fraction of cerium present as isolated, chain-end, or mid-chain cerium is shown in Table 8.3, along with average cerium cluster size, calculated using the appropriate equations from Section 8.1. For glasses CAP_6-2, cluster size increases with increasing cerium concentration, but remains less than a two-cerium cluster on average. Alternatively, for glass CAP_1, the average cerium cluster size calculated is nearly three.

It is useful to compare these results from the CAP glasses to two series of lanthanum aluminophosphate (LAP) glasses synthesized by Karabulut et al. containing 25 mol% P₂O₅ (LAP I) and 30 mol% P₂O₅ (LAP II). Cerium and lanthanum are expected to incorporate into aluminophosphate glasses in a similar fashion due to their similar ionic radius, 1.143 Å for Ce³⁺(VIII) versus 1.160 Å for La³⁺(VIII). In fact, both cations have isostructural metaphosphate crystal structures, and similar CN_RE at the glass metaphosphate composition, ~6.8 for Ce versus ~7.0 for La.

As seen from the average aluminum coordination’s plotted in Figure 8.8, there was a change in the slope of the decreasing CN_Al trend for the LAP I glasses between 15 and 20 mol% Al₂O₃. This change was not as significant as the shift in aluminum coordination observed in the CAP glasses. Additionally, series LAP II did not show a change in CN_Al trend with composition.

Further comparison can be made between the CAP and LAP glasses by using parameter f_s, fraction of oxygen shared between rare-earth cations, to predict rare-earth clustering. Martin’s method for calculating f_s for LAP I and LAP II glasses using a CN_La of 7.2 and 7.5 respectively was followed. As indicated by positive f_s values in Figure 8.9, clustering is expected for CAP and LAP I glasses with less than 17.5 mol% Al₂O₃,
and for all LAP II glasses. These predictions correlate with the shift in $CN_{\text{Al}}$ trend for CAP and LAP I glasses, and the lack of a change in trend for the LAP II glasses.

Additionally, very close agreement is seen between the $f_s$ values for the CAP and LAP I glasses, as might be expected for two rare-earth aluminophosphate glasses with approximately the same mol% $P_2O_5$. The only exception is CAP_1, which has a much higher $f_s$ value than the other LAP I and CAP glasses near 24 mol% $RE_2O_3$.

The chain fragment cluster model was also used to estimate lanthanum cluster size for LAP I and LAP II glasses. The trends in estimated cluster size can be seen graphically in Figure 8.10 for the CAP, LAP I, and LAP II glasses. For all three series, the average rare-earth cluster size increases with decreasing $Al_2O_3$ concentration. Additionally, it should be noted that the proposed chain fragment cluster model is incapable of estimating a cluster size for the lanthanum phosphate glass in series LAP II with 30 mol% $La_2O_3$ when a $CN_{\text{La}}$ of 7.5 is assumed. For this composition, $\bar{n}^{RE}_{RE} = 2.2$, indicating that a cluster model where a rare-earth cation can have three edge-sharing next nearest neighbors may be necessary, or that face-sharing clusters should be considered for a cluster size prediction model, particularly when $RE_2O_3 > 25$ mol%.

The high estimated cluster size for CAP_1 correlates with the high $f_s$ value previously mentioned. Though CAP_1 did not contain the greatest amount of cerium, it did contain the least at% oxygen of all the CAP glasses. This difference may be due to incorporation of alumina from the crucible rather than from the batch as in the other CAP glasses.
8.3.2 Cerium Silicophosphate Glasses

Coordination for the impurity fraction of aluminum in the CSP glasses was assumed to be 100% octahedral. Additionally, as silicon speciation data was not available for CSP_7-9, an average coordination of 4.5 was assumed, based on the average coordination of CSP_6 (4.46) and CSP_5 (4.54). To estimate whether cerium clustering would occur in the CSP glasses, Equations 3.11, 3.12, and 8.11 were used to determine \( f_s \), \( \bar{n}_{Ce} \), and \( \bar{n}_{Ce}^{NBO} \). These results are shown in Table 8.3 alongside average cation coordination determined by EXAFS and NMR.

It is readily seen that \( \text{CN}_{Ce} < \bar{n}_{Ce}^{NBO} \) for compositions CAP_2-5, indicating isolated cerium cations as reflected by the negative values for \( f_s \) and \( \bar{n}_{Ce} \). However, for glasses CAP_6-9, with higher concentrations of cerium, clustering is indicated by \( \text{CN}_{Ce} > \bar{n}_{Ce}^{NBO} \) and positive values for \( f_s \) and \( \bar{n}_{Ce} \). Thus, a shift from isolated-cerium to clustered-cerium, is predicted in the CSP glasses between 15 mol% and 18 mol% Ce\(_2\)O\(_3\). This is analogous to a shift from Region I to Region III behavior in binary rare-earth phosphate glasses. Similar to the CAP series, no evidence for Region II behavior was seen, where \( \text{CN}_{Ce} = \bar{n}_{Ce}^{NBO} \) over an extended compositional range.

Using appropriate equations for the chain fragment model for cerium cluster size given in Section 8.1, and the revised definition for \( \bar{n}_{Ce}^{NBO} \) in Equation 8.11, the average cerium cluster size in the CSP glasses was estimated, as shown in Table 8.3. In all cases, the average cluster size was between one and two, and increased with increasing cerium concentration, as shown in Figure 8.11.
8.4 PROPERTY TRENDS WITH CERIUM CLUSTERING

8.4.1 Refractive Index and Density

It was readily seen in Table 4.3, and Figures 4.7 and 4.8 that both the refractive index and density increase with increasing cerium concentration in the CAP and CSP glasses. Given the significantly greater mass of cerium relative to the other ions in the glasses, this increase in density is unsurprising. Likewise, as a large cation with many electrons, it is expected that increasing cerium concentrations would increase the refractive index due to the increased electron density in the glass. The linear relationship between refractive index and density shown in Figure 8.12 illustrates the strong dependence both properties have on cerium concentration. Additionally, it is seen that CAP_1, the glass with the highest estimated average cerium cluster size, but not the highest cerium content, was measured to have both the highest refractive index and density. The average estimated cerium cluster size in CAP_1 was ~3.0, much higher than the average cluster size of ~1.8 in CAP_2, the glass with the highest cerium concentration. This suggests that cluster size may influence both the refractive index and density independently of cerium concentration.

8.4.2 Visible Coloration

As discussed in Section 2.3, both Ce^{3+} and Ce^{4+} have intrinsic absorption bands in the ultraviolet portion of the visible spectrum. Thus, pure Ce^{3+} materials such as CeP_{3}O_{9} and pure Ce^{4+} materials such as CeO_{2} are colorless.\textsuperscript{22,108} However, the oxidation state of cerium in the CAP and CSP glasses is mixed, with the maximum percentage of Ce^{4+}
measured at \( \sim 5\% \). This mixed oxidation state raises the possibility of intervalence charge transfer and associated optical absorption bands.

Intervalence charge transfer, or the transfer of a valence electron from one cation to another, is possible in materials with a cation able to adopt two different oxidation states.\(^{109}\) Intervalence charge transfer is well known in iron compounds containing \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \), as well as slightly reduced \( \text{TiO}_2 \) which contains \( \text{Ti}^{3+} \) in addition to \( \text{Ti}^{4+} \).\(^{109,110}\) In fact, a visible absorption band at 540 nm has been measured in mixed valence cerium oxisulfide (\( \text{Ce}_4\text{O}_4\text{S}_3 \)) that is attributed to intervalence transitions of the cerium cation.\(^{111}\)

It is therefore suggested that the additional absorption near the UV edge in the high-cerium glasses, responsible for amber-gold coloration, is due to intervalence charge transfer. The low-cerium glasses remain clear, despite a mixed oxidation state, as the cerium cations are not in close enough proximity for electron transfer to occur. However, with the onset of clustering and the possibility for \( \text{Ce}^{4+}-\text{O}-\text{Ce}^{3+} \) linkages, intervalence charge transfer can occur, resulting in an additional visible absorption.

### 8.4.3 \( \text{Ce}^{3+} \) Photoluminescence

As previously shown in Figures 4.11 and 4.12, the low-cerium compositions (\( \text{CAP}_9, \text{CAP}_8, \text{CSP}_2, \text{CSP}_3 \) and \( \text{CSP}_4 \)) have intense \( \text{Ce}^{3+} \) photoluminescence peaks at \( \sim 340 \) nm which oversaturated the detector. Glasses \( \text{CAP}_7 \) and \( \text{CSP}_5 \) have less intense photoluminescence peaks, with a maxima at \( \sim 370 \) nm. Alternatively, the high-cerium compositions, \( \text{CAP}_6-1 \) and \( \text{CSP}_6-9 \), have two very low intensity photoluminescence peaks at \( \sim 340 \) nm and \( \sim 415 \) nm. This behavior correlates very well with the prediction of clustering in these glasses, such that the lowest cerium
compositions would be expected to have intense photoluminescence from the high number of isolated cerium cations.

For the CAP glasses, the photoluminescence initially increases from CAP_9 to CAP_8 as evidenced by the broader peak, attributable to a higher number of isolated cerium cations. Then for CAP_7, the photoluminescence intensity decreases, as it is possible that even though clustering is not predicted, some cerium clusters could be present and quenching photoluminescence. For the CSP glasses, the Ce$^{3+}$ photoluminescence peak from CSP_3 was slightly narrower than that from CSP_2, which does not follow the trend seen in the CAP glasses, indicating an additional structural influence. However, CSP_4 exhibits the broadest photoluminescence peak, in keeping with the trend of increasing cerium photoluminescence with increasing number of isolated cerium cations. Glass CSP_5 is similar to glass CAP_7 in that it is predicted to have isolated cerium cations but has a lower photoluminescence intensity than the next-lowest cerium content glass in the series, indicating that clusters may be present and quenching photoluminescence.

For the high-cerium compositions, with a significant fraction of cerium present in clusters, the photoluminescence is highly quenched. However, the quenching of photoluminescence is attributed to the inherent disorder present in the glass, rather than energy transfer between the cerium cations. By using the equations given by Quimby, it is possible to estimate the Ce$^{3+}$-Ce$^{3+}$ separation for energy transfer ($R_{\text{Ce}^{3+}}$), and the probability for energy transfer in a random distribution of ions ($p_{\text{Ce}^{3+}}$) using the Ce$^{3+}$ excited state lifetime, as well as the average Ce-Ce separation ($R_{p=0.5}$) for a random distribution of ions.$^{112}$ As the photoluminescence lifetime of Ce$^{3+}$ was not measured in
the CAP and CSP glasses, the average value of 26 ns was used, based on measurements in other phosphate glasses.\textsuperscript{113-115}

At a Ce\textsuperscript{3+} photoluminescence lifetime of 26 ns, a Ce\textsuperscript{3+}-Ce\textsuperscript{3+} separation of 2.25 Å is required for energy transfer and concentration quenching. As seen in Table 8.4, the average random cerium-cerium separation (R<sub>p=0.5</sub>) is much greater than this, reaching a minimum of 3.23 Å for CAP_2 which has the highest mol% Ce\textsubscript{2}O\textsubscript{3}. Accordingly, the probability for charge transfer is only 23% for the high-cerium glasses, which is insufficient to explain the high degree of quenching seen in the glasses predicted to have clustered cerium. It is also unlikely that the mere presence of clusters is responsible for quenching Ce\textsuperscript{3+} luminescence. The average Ce-Ce distance expected in a cerium cluster, calculated from the CeP\textsubscript{3}O\textsubscript{9} crystal, is much greater than the Ce\textsuperscript{3+}-Ce\textsuperscript{3+} distance for energy transfer, 4.29 Å versus 2.25 Å.\textsuperscript{22}

It is proposed that the high degree of quenching when clusters are present is due to disorder based upon observations of luminescence in crystalline CeP\textsubscript{3}O\textsubscript{9} and the well-known requirement for efficient scintillators to have a high degree of crystalline lattice perfection.\textsuperscript{117} As reported by Ternane et. al. (and Tong et. al.), CeP\textsubscript{3}O\textsubscript{9} exhibits an excitation maxima at 300 nm (280 nm) and two emission maxima at 307 nm (305 nm) and 323 nm (320 nm) which correspond to transitions from the excited state to the \textsuperscript{2}F\textsubscript{5/2} and \textsuperscript{2}F\textsubscript{7/2} ground states.\textsuperscript{22,116} A Ce\textsuperscript{3+} luminescence lifetime of 9 ns (14 ns) was reported, which corresponds to a 1.89 Å (2.03 Å) Ce\textsuperscript{3+}-Ce\textsuperscript{3+} separation for energy transfer, which is a significantly shorter distance than in cerium-containing phosphate glasses due to the shorter relaxation time.\textsuperscript{22,116}
Crystalline CeP₃O₉ has infinite chains of CeO₈ edge-shared dodecahedra, a very ordered and clustered structure. The high-cerium CAP and CSP glasses are highly disordered, proposed to contain clusters as a distribution of chain fragments, as well as alumina and silica. Thus, it is proposed that disorder of isolated cerium cations is insufficient to quench Ce³⁺ photoluminescence in glasses but disorder of cerium in close proximity, i.e. clustering, quenches the photoluminescence significantly.

Additionally, for the high-cerium compositions, the integrated intensity (after background subtraction and Gaussian peak fitting using OriginPro 8.5) of the ~340 nm photoluminescence peak was found to decrease with increasing Ce₂O₃ in both the CAP and CSP series as shown in Figure 8.13. However, no trend with composition was found for the ~415 nm peak. The presence of an additional Ce³⁺ photoluminescence peak at ~415 nm in the high-cerium glasses, and at ~370 nm in glasses CAP_7 and CSP_5 indicates that there are multiple cerium environments contributing to photoluminescence. These sites would be distinct from the peak at ~340 nm which is very intense in the low-cerium glasses.

8.4.4 Ce³⁺ Electron Paramagnetic Resonance

There is a break in the Ce³⁺ gµ-value trend with mol% Ce₂O₃ for the CAP glasses which can be attributed to a change from isolated cerium to clustered cerium. As shown in Figure 7.4, there is a strong decrease in gµ-value for the Ce³⁺ resonance in glasses CAP_9-6 with increasing mol% Ce₂O₃. For glasses CAP_6-4, the gµ-value is constant and then increases slightly for glasses CAP_3-1. This drastic change in behavior
coincides with the predicted shift from isolated cerium to clustered cerium between 7-14 mol% Ce₂O₃ in the CAP glasses.

For the CSP glasses there is no similar break in the trend of Ce³⁺ g⊥-value with mol% Ce₂O₃ that corresponds to the shift from isolated to clustered cerium, as seen in Figure 7.5. Instead, there is a roughly monotonic decrease in g⊥-value with increasing mol% Ce₂O₃, with the exception of CSP_2, that is similar to the decrease in average cerium coordination number with increasing mol% Ce₂O₃.

Additionally, the Ce³⁺ resonance intensity increases with mol% Ce₂O₃ in CAP glasses with two exceptions. Between CAP_7 and CAP_6, the Ce³⁺ resonance intensity does not increase, and the Ce³⁺ resonance intensity for CAP_1 is slightly lower than CAP_2. These two compositions correlate to the shift from isolated cerium to clustered cerium and from average cluster size less than two to greater than two cerium cations respectively. Thus, it is possible that Ce³⁺ resonance intensity is influenced by both Ce³⁺ concentration and local cerium structure. A change in slope of Ce³⁺ resonance intensity versus cerium concentration was observed by Bishay in barium aluminoborate glasses, suggesting the “possibility of a change in the structural role of Ce³⁺ at high concentrations.”

The trend in Ce³⁺ resonance intensity for the CSP glasses also corresponds to the predicted presence or absence of clustering, but not in the same manner as the CAP glasses. As seen in Figure 7.5, the Ce³⁺ resonance intensity increases for glasses CSP_2-6, and subsequently decreases for glasses CSP_6-9. These two differing trends for the CSP glasses coincide with the switch from isolated to clustered-cerium between 15 mol% and 18 mol% Ce₂O₃.
Table 8.1: Quantification of aluminum coordination in CAP glasses by $^{27}$Al MAS NMR.

<table>
<thead>
<tr>
<th>CAP</th>
<th>% CN = 4</th>
<th>% CN = 5</th>
<th>% CN = 6</th>
<th>CN$_{Al}$</th>
</tr>
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<tbody>
<tr>
<td>9</td>
<td>15</td>
<td>24</td>
<td>61</td>
<td>5.46</td>
</tr>
<tr>
<td>8</td>
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<tr>
<td>7</td>
<td>17</td>
<td>26</td>
<td>57</td>
<td>5.40</td>
</tr>
<tr>
<td>6</td>
<td>38</td>
<td>29</td>
<td>33</td>
<td>4.95</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>31</td>
<td>37</td>
<td>5.05</td>
</tr>
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### Table 8.2: Quantification of silicon coordination in CSP glasses by $^{29}\text{Si}$ CPMG MAS NMR.

<table>
<thead>
<tr>
<th></th>
<th>% CN = 4</th>
<th>% CN = 5</th>
<th>% CN = 6</th>
<th>CN$_{\text{Si}}$</th>
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</thead>
<tbody>
<tr>
<td>CSP_2</td>
<td>82</td>
<td>4</td>
<td>14</td>
<td>4.32</td>
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<tr>
<td>CSP_3</td>
<td>78</td>
<td>7</td>
<td>15</td>
<td>4.37</td>
</tr>
<tr>
<td>CSP_4</td>
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<td>18</td>
<td>4.46</td>
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<tr>
<td>CSP_5</td>
<td>73</td>
<td></td>
<td>27</td>
<td>4.54</td>
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<tr>
<td>CSP_6</td>
<td>77</td>
<td></td>
<td>23</td>
<td>4.46</td>
</tr>
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Table 8.3: Average cation coordination, parameters for estimation of cerium clustering, binary cerium site distributions, and average cerium cluster size calculated from the chain fragment cluster model.

<table>
<thead>
<tr>
<th></th>
<th>CN$_{Ce}$</th>
<th>CN$_{Al}$</th>
<th>CN$_{Si}$</th>
<th>$\bar{n}^{NBO}_{Ce}$</th>
<th>$f_s$</th>
<th>$\bar{n}^{Ce}_{Ce}$</th>
<th>Fraction</th>
<th>Average cluster size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>isolated</td>
<td></td>
<td>chain-end</td>
<td>mid-chain</td>
<td></td>
</tr>
<tr>
<td>CAP 9</td>
<td>6.92</td>
<td>5.46</td>
<td></td>
<td>16.52</td>
<td>-1.39</td>
<td>-9.60</td>
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<td></td>
</tr>
<tr>
<td>CAP 8</td>
<td>6.92</td>
<td>5.44</td>
<td></td>
<td>11.42</td>
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<td>-4.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAP 7</td>
<td>6.97</td>
<td>5.40</td>
<td></td>
<td>10.24</td>
<td>-0.47</td>
<td>-3.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAP 6</td>
<td>6.67</td>
<td>4.95</td>
<td></td>
<td>6.55</td>
<td>0.02</td>
<td>0.12</td>
<td>0.88</td>
<td>0.12</td>
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<tr>
<td>CAP 5</td>
<td>6.68</td>
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<td>0.09</td>
<td>0.62</td>
<td>0.38</td>
<td>0.62</td>
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<tr>
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<td>5</td>
<td></td>
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<td>0.10</td>
<td>0.65</td>
<td>0.35</td>
<td>0.65</td>
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<td>6.78</td>
<td>5</td>
<td></td>
<td>5.91</td>
<td>0.13</td>
<td>0.87</td>
<td>0.13</td>
<td>0.87</td>
</tr>
<tr>
<td>CAP 2</td>
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<td>5</td>
<td></td>
<td>5.94</td>
<td>0.13</td>
<td>0.86</td>
<td>0.14</td>
<td>0.86</td>
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<td>1.32</td>
<td>0.68</td>
<td>0.32</td>
</tr>
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<td>6</td>
<td>4.5</td>
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<td>0.93</td>
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<td>0.93</td>
</tr>
<tr>
<td>CSP 8</td>
<td>6.78</td>
<td>6</td>
<td>4.5</td>
<td>5.98</td>
<td>0.12</td>
<td>0.80</td>
<td>0.20</td>
<td>0.80</td>
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<tr>
<td>CSP 7</td>
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<td>6</td>
<td>4.5</td>
<td>6.14</td>
<td>0.10</td>
<td>0.69</td>
<td>0.31</td>
<td>0.69</td>
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<td>CSP 6</td>
<td>6.92</td>
<td>6</td>
<td>4.46</td>
<td>6.83</td>
<td>0.01</td>
<td>0.09</td>
<td>0.91</td>
<td>0.09</td>
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<td>CSP 5</td>
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<td>4.54</td>
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<td>CSP 4</td>
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<td>-1.57</td>
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<tr>
<td>CSP 3</td>
<td>7.20</td>
<td>6</td>
<td>4.37</td>
<td>12.43</td>
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<td>-5.23</td>
<td></td>
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</tr>
<tr>
<td>CSP 2</td>
<td>7.24</td>
<td>6</td>
<td>4.32</td>
<td>19.05</td>
<td>-1.63</td>
<td>-11.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$n^{NBO}_{Ce}$: average number of NBO available per cerium.
$f_s$: fraction of oxygen shared between cerium cations.
$n^{Ce}_{Ce}$: average number of cerium next nearest neighbors around cerium.
<table>
<thead>
<tr>
<th></th>
<th>$N_{\text{Ce}}$ (at/cm³)</th>
<th>$R_{p=0.5}$ (Å)</th>
<th>$p_{\text{Ce}^{3+}}$</th>
</tr>
</thead>
<tbody>
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<td>CAP_9</td>
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<td>CAP_8</td>
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</tr>
<tr>
<td>CAP_5</td>
<td>4.05E+21</td>
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<td>0.19</td>
</tr>
<tr>
<td>CAP_4</td>
<td>4.42E+21</td>
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<td>0.21</td>
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<td>CAP_3</td>
<td>4.80E+21</td>
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<td>0.23</td>
</tr>
<tr>
<td>CAP_2</td>
<td>4.89E+21</td>
<td>3.23</td>
<td>0.23</td>
</tr>
<tr>
<td>CAP_1</td>
<td>4.83E+21</td>
<td>3.25</td>
<td>0.23</td>
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<tr>
<td>CSP_9</td>
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<td>0.23</td>
</tr>
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<td>0.19</td>
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<td>CSP_5</td>
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<td>3.62</td>
<td>0.17</td>
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<td>4.29</td>
<td>0.10</td>
</tr>
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<td>CSP_3</td>
<td>1.26E+21</td>
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<td>0.06</td>
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<td>CSP_2</td>
<td>6.95E+20</td>
<td>6.20</td>
<td>0.03</td>
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Table 8.4: Cerium concentration (atoms/cm³), average cerium-cerium distance in a random distribution ($R_{p=0.5}$), and probability for $\text{Ce}^{3+}$-$\text{Ce}^{3+}$ energy transfer ($p_{\text{Ce}^{3+}}$) for CAP and CSP glasses.
Figure 8.1: Schematic representation of two-cerium and three-cerium clusters used in the chain fragment cluster model.
Figure 8.2: $^{27}$Al MAS NMR spectra from CAP_9-7 showing the predominance of octahedral aluminum (~20 ppm), as well as peaks from 5-fold and tetrahedral aluminum at ~3 ppm and ~38 ppm respectively.
Figure 8.3: $^{27}$Al MAS NMR spectra from CAP_6-5 showing the near equivalent distribution of octahedral, 5-fold, and tetrahedral sites.
Figure 8.4: Aluminum speciation for CAP glasses as a function of mol% Ce$_2$O$_3$. 
Figure 8.5: $^{29}$Si CPMG MAS NMR spectra from CSP_2-4 showing peaks from tetrahedral silicon (∼120 ppm), 5-fold silicon (∼165 ppm), and octahedral silicon (∼220 ppm).
Figure 8.6: $^{29}$Si CPMG MAS NMR spectra from CSP_5-6 showing peaks from tetrahedral and octahedral silicon.
Figure 8.7: Silicon speciation for CSP glasses as a function of mol% Ce$_2$O$_3$. 
Figure 8.8: Average aluminum coordination as determined by $^{27}$Al MAS NMR for CAP, LAP I, and LAP II glasses versus mol% Al$_2$O$_3$. 
Figure 8.9: Fraction of oxygen shared between rare-earth cations ($f_s$) for CAP, LAP I, and LAP II glasses versus mol% $\text{Al}_2\text{O}_3$. 
Figure 8.10: Cluster size as estimated from the chain fragment model for CAP, LAP I, and LAP II glasses versus mol% Al$_2$O$_3$. 
Figure 8.11: Cluster size as estimated from the chain fragment model for CSP glasses versus mol% Ce$_2$O$_3$. 
Figure 8.12: Refractive versus density for CAP and CSP glasses.
Figure 8.13: Integrated intensity of Ce$^{3+}$ photoluminescence peak at ~340 nm versus mol% Ce$_2$O$_3$ for high-cerium CAP and CSP glasses.
CHAPTER 9
RADIATION DAMAGE RESISTANCE

Radiation damage resistance in the CAP and CSP glasses was assessed after a 2 Mrad gamma dose at the Penn State Radiation Science and Engineering Center using a Gammacell 220 Excel (MDS Nordion) with a $^{60}$Co source. Radiation-induced optical absorption was measured by UV-VIS spectroscopy and radiation-induced phosphorus-related defect resonances were measured by EPR.

9.1 RADIATION-INDUCED PARAMAGNETIC DEFECTS

9.1.1 Cerium Aluminophosphate Glasses

P$_1$ and P$_2$ defects were detected in the low-cerium aluminophosphate glasses, with hyperfine splitting parameters similar to those reported in previous studies, as shown in Figure 7.6 and Table 7.3. These low-cerium glasses, CAP$_{7-9}$, were also predicted to have isolated cerium cations. Only the resonance from Ce$^{3+}$ is detected in glasses CAP$_{6-1}$, which were predicted to have clustered cerium. Clustering is predicted to occur in these cerium aluminophosphate glasses due to a lack of NBO’s available from phosphorus for bonding to cerium cations. In order to satisfy coordination requirements, large cerium cations must share oxygen, or cluster, after all NBO’s from PO$_4$ tetrahedra have been exhausted. Thus, it follows that once clustering is occurring in these glasses, all PO$_4$ tetrahedra must have a cerium close enough in the vicinity to prevent the formation of radiation-induced defects. A decrease in the intensity of P$_1$ and P$_2$ defect resonances would be expected with increasing cerium content below the threshold for
clustering as more of the defect precursor sites have a cerium in the vicinity to act as preferential electron- or hole-trap. In fact, Karapetyan et.al., found that the addition of cerium to a highly reduced zinc phosphate glass reduced the intensity of the P1 doublet.\textsuperscript{92} Schematics for the P1 and P2 defect precursors, without and with cerium in the vicinity, are shown in Figures 9.1 and 9.2.\textsuperscript{118}

While P1 and P2 defects have been observed simultaneously in other studies of aluminophosphate glasses,\textsuperscript{99,100} the POHC defect site is also identified with significant intensity in aluminophosphate glasses.\textsuperscript{94-100} The lack of POHC defects in the CAP glasses is not surprising upon considering the local structure in these glasses. While a predominance of Q\textsuperscript{2} phosphate tetrahedra is expected for these near-metaphosphate glasses, the Ce\textsuperscript{3+} cations and Al\textsuperscript{3+} cations would bond to their NBO’s, the precursor site for POHC defects. Though \( \bar{n}_{Ce}^{NBO} > CN_{Ce} \) for the low-cerium glasses, indicating that there is an excess of non-bridging oxygens over cation bonding requirements, it is reasonable that most, if not all, of the Q\textsuperscript{2} phosphate tetrahedra in these glasses have at least one NBO bonded to an Al\textsuperscript{3+} or Ce\textsuperscript{3+} cation. Thus, these sites would be unavailable to trap a hole to form the POHC defect. Schematics for the Q\textsuperscript{2} tetrahedra without and with cerium and aluminum in the vicinity are shown in Figure 9.3.\textsuperscript{118}

\textit{9.1.2 Cerium Silicophosphate Glasses}

P1, P2, and POHC defects were detected in the low-cerium CSP glasses, CSP_2-4, as shown in Figure 7.7 and 7.8, and Table 7.3. As described in Section 9.1.1, the presence, and decrease in intensity, of the P1 and P2 defects is correlated to the increasing probability of cerium in close proximity to the defect precursor sites with increasing
cerium concentration. Alternatively, POHC defects were detected in the low-cerium CSP glasses, though not in the low-cerium CAP glasses. This difference can be explained by a model of preferential intermediate range bonding in silicophosphate glasses.

Similar to the Al-NBO-P linkages discussed in Section 3.4, two Si-NBO-P linkages are possible which satisfy, or nearly satisfy, the NBO’s charge requirements, as shown in Table 9.1. Octahedrally coordinated Si$^{4+}$ cations provide 2/3 VU to each of their coordinate oxygens and are capable of fully satisfying the charge requirements of NBO’s from a Q$^1$ phosphorus, as in the SiP$_2$O$_7$ crystal.$^{119}$ Additionally, 5-fold Si$^{4+}$ cations, with 0.8 VU per oxygen, nearly satisfy the charge requirements for Q$^0$ NBO’s, with 0.25 VU from phosphorus. However, there is no tetrahedral silicon and phosphorus combination which satisfies NBO charge requirements. Thus, preferential intermediate-range bonding, similar to that proposed for sodium silicophosphate glasses,$^{26}$ is expected: SiO$_2$-like regions composed of silicate tetrahedra, SiP$_2$O$_7$-like regions incorporating silicon octahedra and Q$^1$ phosphate tetrahedra, and cerium ultraphosphate-like regions which also incorporate the impurity aluminum. It is in these cerium ultraphosphate-like regions that the POHC defects are expected to occur. When $\bar{n}_{Ce}^{NBO} > CN_{Ce}$ in these regions, Q$^2$ phosphate tetrahedra would be present without either cerium or aluminum bonded to their NBO’s and available to trap holes.

Additionally, an intense resonance at g$\approx$2.0007 overlaps with the high-field POHC resonance. This resonance is likely due to the Si E’ center, but positive identification was not possible as the $g_1$, $g_2$, and $g_3$ values were not resolved. As SiO$_2$-like regions are predicted for the CSP glasses, these Si E’ defects are predicted to occur in those regions of the glass. At high-cerium concentrations, it is reasonable to expect
that the limited cerium solubility in SiO$_2$ is sufficient to inhibit hole-trapping on bridging oxygen vacancies to form Si E’ centers.$^{85}$

Finally, it is of note that phosphate-related defect resonances were only detected in CSP$_{2-4}$, though glasses CSP$_{2-5}$ were predicted to have only isolated cerium cations. While simplistic models for cerium clustering and intermediate range segregation were able to explain the presence or absence of radiation-induced defects in the other CAP and CSP glasses, this inconsistency indicates that there are limitations to those models.

9.1.3 Unknown Defect Resonance

As shown in the integrated EPR derivative spectrum for CAP$_9$ in Figure 7.9, there was a small shoulder at $g \sim 1.924$ which was not fit during calculation of hyperfine splitting parameters. A much more intense shoulder, which required two Gaussian peaks during fitting, is seen at a similar location for the integrated EPR derivative spectrum from CSP$_2$ in Figure 7.10. The latter feature could be identified as an additional resonance centered at $g \sim 1.903$ or a step shoulder at $g \sim 1.932$.

Further comparison of the Gaussian peak fits for CAP$_9$ and CSP$_2$ shows that the low-field fit for CAP$_9$ follows the measured data much closer than the low-field fit for CSP$_2$. This suggests that there is a low-field component to the unidentified resonance, coincident with the low-field resonances for the P$_1$ and P$_2$ defects. In CAP$_9$, this resonance is of low-intensity and does not perturb the Gaussian peak fit significantly. However, in CSP$_2$, the resonance is of significant intensity and results in a poorer fit to the data, while still yielding P$_1$ and P$_2$ hyperfine splitting parameters close to the literature values. Constraining the width and amplitude of the P$_1$ and P$_2$ peak pairs using
the ratios from CAP_9 was unable to produce a viable fit in CSP_2 when two additional peaks were added to correspond to the low-field components of the unknown high-field resonance.

Using the average position of the unknown high-field resonance peak and the low-field component to the P₁ defect, a splitting of ~700 Gauss is estimated for the unknown resonance. To the author’s knowledge, this splitting does not correspond to any reported phosphorus-related defects. However, given the high hygroscopicity of the P₂O₅ raw material, there is a reasonable possibility for hydroxyl units in both the CAP and CSP glasses. The splitting between the two unknown high-field components is ~80 Gauss, which is similar in splitting to H(I) and H(II) radiation-induced defects in silica glass at 70-74 gauss and 112-120 gauss respectively. If the radiation-induced defect site was located at a phosphorus hydroxyl site, its paramagnetic resonance would exhibit hyperfine splitting from both phosphorus and hydrogen, resulting in 4 peaks. Thus, it is possible that the unknown resonance is actually the high-field component of two pairs of resonances from a radiation-induced phosphorus-related hydroxyl defect.

9.2 RADIATION-INDUCED OPTICAL ABSORPTION

After gamma irradiation, those glasses which were initially colorless or nearly so, CAP_9-7 and CSP_2-5, were observed to have an amber-gold color similar to the initial color of CAP_6-1 and CSP_9-6. These low-cerium glasses, where isolated cerium cations were predicted, also exhibited a drastic change in the shape of their UV absorption edges after irradiation as shown in Figures 9.4 and 9.5. By comparison, the change in UV absorption edge was minimal for the high-cerium glasses. The UV
absorption edge for these glasses, predicted to have clustered cerium cations, only shifted a few nanometers after irradiation, as seen in Figures 9.4 and 9.5 for the CAP and CSP glasses, respectively.

Radiation-induced absorption spectra were calculated by subtracting the transmission spectra after irradiation from that prior to irradiation. The induced absorption for both CAP and CSP glasses peaked at 320-335 nm for the low-cerium glasses and shifted to longer wavelengths for the high-cerium glasses, ~365 nm as shown in Figures 9.6 and 9.7.

Absorption bands were measured for the P₁ and P₂ defects at 1570 nm and 270 nm by Griscom in phosphorus-doped silicate glasses. In addition to these IR and UV absorption bands, several visible absorption bands attributed to POHC defects have been measured at 240 nm, 570 nm, 510 nm, and 400 nm in phosphorus-doped silicate glasses, as well as between 525-550 nm in several phosphate glasses.

It is readily seen from examination of the difference spectra in Figures 9.6 and 9.7 that none of the aforementioned absorption bands correspond with the measured radiation-induced absorption. The UV absorption bands from POHC and P₂ defects are obscured by the intrinsic absorption of the CAP and CSP glasses. Additionally, the IR absorption band from the P₁ defect was not detected, as IR absorption spectra were not measured in these experiments. Finally, though the POHC defect was detected by EPR in the lowest-cerium silicophosphate glasses, radiation-induced absorption bands were not measured in the 510-570 nm region. These bands are responsible for the magenta or purple coloration in irradiated phosphate glasses, but no explanation is available for the presence of the defect but lack of induced absorption bands in the CSP glasses.
Instead, the radiation-induced absorption measured in low-cerium glasses, between 320-335 nm, compares well with that measured by Alers in a study of Ce-Ba-phosphate glasses, 320-340 nm. The induced absorption bands for the high-cerium content glasses also occur close to this value, between 350-365 nm. Examination of the intensity and wavelength of the radiation-induced optical absorption shows a ‘break’, or change in slope for each trend with cerium concentration. For the CAP glasses, this occurs between compositions CAP_7 and CAP_6, as shown in Figure 9.8. Similarly, this shift occurs between compositions CSP_5 and CSP_6 as shown in Figure 9.9. These are the compositions between which a shift from isolated to clustered cerium is predicted in each glass series. Thus, the radiation-induced absorption is influenced by the local structure of cerium in the glass.

The visible color observed for the irradiated CAP_9-6 and CSP_2-5 glasses is not unlike that observed from glasses predicted to have clustered cerium. Thus, it is possible that this absorption is associated with a radiation-induced change in the local electronic structure of cerium, rather than phosphorus-related defects, which were only found in the low-cerium content glasses. This change may be similar to the intervalence electron transfer which is responsible for coloration of the high-cerium glasses, where clustering is predicted.

Finally, the slight change in optical absorption with irradiation, and its subsequent attribution to changes in the local electronic structure of cerium, provides evidence for the method of cerium-induced radiation damage resistance where cerium acts as a preferential electron- or hole-trap and either changes oxidation state or forms Ce$^{3+}$ and Ce$^{4+}$e$^-$. 
Table 9.1: Aluminum and silicon coordination’s matched to phosphate tetrahedra
according to satisfaction of charge on non-bridging oxygen anions by valence unit
notation.

<table>
<thead>
<tr>
<th></th>
<th>VU/O</th>
<th>Q(^n) match</th>
<th>Phosphate Network Connectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCN = 4</td>
<td>0.75</td>
<td>Q(^6)</td>
<td>AlPO(_4) – an SiO(_2) analog</td>
</tr>
<tr>
<td>AlCN = 5</td>
<td>0.6</td>
<td>Q(^4)</td>
<td>Near match to 1.33 VU from Q(^4)</td>
</tr>
<tr>
<td>AlCN = 6</td>
<td>0.5</td>
<td>Q(^2)</td>
<td>AlP(_3)O(_9) – metaphosphate crystal</td>
</tr>
<tr>
<td>SiCN = 4</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiCN = 5</td>
<td>0.8</td>
<td>Q(^6)</td>
<td>Near match to 1.25 VU from Q(^6)</td>
</tr>
<tr>
<td>SiCN = 6</td>
<td>0.67</td>
<td>Q(^4)</td>
<td>SiP(_2)O(_7) – diphosphate crystal</td>
</tr>
</tbody>
</table>
Figure 9.1: Materials Studio 5.5 schematic\textsuperscript{118} of a Q\textsuperscript{3} phosphate tetrahedra with an NBO vacancy, the precursor to the P\textsubscript{1} defect, without and with cerium in the vicinity.

Purple sphere: phosphorus.
Red sphere: oxygen.
Yellow sphere: cerium.
Figure 9.2: Materials Studio 5.5 schematic\textsuperscript{118} of a $Q^4$ phosphate tetrahedra, precursor to the $P_2$ defect, without and with cerium in the vicinity.

Purple sphere: phosphorus.
Red sphere: oxygen.
Yellow sphere: cerium.
Figure 9.3: Materials Studio 5.5 schematic\textsuperscript{118} of a Q\textsuperscript{2} phosphate tetrahedra, the POHC defect precursor, without and with cerium and aluminum in the vicinity.

Purple sphere: phosphorus.
Red sphere: oxygen.
Blue sphere: aluminum.
Yellow sphere: cerium.
Figure 9.4: UV-VIS transmission spectra from CAP glasses in the region of the absorption edge before and after gamma irradiation.
Figure 9.5: UV-VIS transmission spectra from CSP glasses in the region of the absorption edge before and after gamma irradiation.
Figure 9.6: Change in transmission following gamma irradiation for CAP glasses.
Figure 9.7: Change in transmission following gamma irradiation for CSP glasses.
Figure 9.8: Intensity and wavelength of maximum intensity for radiation-induced absorption versus cerium content in CAP glasses.
Figure 9.9: Intensity and wavelength of maximum intensity for radiation-induced absorption versus cerium content in CSP glasses.
CHAPTER 10

SUMMARY

This study has expanded the range of phosphate glass compositions where the coordination of cerium has been studied, from binary glasses near the metaphosphate composition to a series of aluminophosphate and silicophosphate glasses. It is expected that the coordination of cerium will be predictive of the behavior of the other large lanthanides (La, Pr, Nd) in similar compositional series.

Additionally, a chain fragment cluster model for estimating rare-earth cluster size has been introduced, building from earlier models for rare-earth phosphate and rare-earth aluminophosphate glasses. This model is applicable binary phosphate, aluminophosphate, silicophosphate, and aluminosilicophosphate glasses containing up to 25 mol% of RE$_2$O$_3$, where RE is a large lanthanide cation.

The primary impact of this work, however, was to examine the structure-property relationships in two series of cerium phosphate glasses, particularly with respect to the influence of cerium clustering, or the sharing of oxygen between cerium cations. Cerium clustering was predicted in the aluminophosphate series above 14 mol% Ce$_2$O$_3$ and above 18 mol% Ce$_2$O$_3$ in the silicophosphate series. Many measured properties were observed to correlate with the presence or absence of clustering, cluster size, or other concomitant structural changes.

Visible coloration of the cerium aluminophosphate and silicophosphate glasses was found to depend on the presence or absence of cerium clusters. Those glasses predicted to have isolated cerium cations were colorless and had a sharp UV absorption
edge. Alternatively, the glasses predicted to have cerium clusters exhibited amber-gold coloration due to an additional absorption from intervalence charge transfer, which is possible when Ce$^{3+}$-O-Ce$^{4+}$ bonding occurs.

The trend of increasing density and refractive index with cerium concentration was also found to be influenced by the presence of large cerium clusters. The cerium aluminophosphate glass with the largest estimated average cluster size was measured to have both the highest density and refractive index, despite not having the highest mol% Ce$_2$O$_3$.

Ce$^{3+}$ photoluminescence intensity was also found to depend on the presence or absence of cerium clusters. For glasses predicted to have isolated cerium cations, intense photoluminescence at ~340 nm was measured. However, the additional disorder introduced by a distribution of cerium cluster sizes was sufficient to quench Ce$^{3+}$ photoluminescence in the glasses predicted to have clustered cerium cations.

Additionally, the intensity of the Ce$^{3+}$ paramagnetic resonance peak was influenced by the average cluster size in the cerium aluminophosphate and silicophosphate glasses. Both the onset of clustering and shift to a cluster size greater than two coincided with a slight decrease in the trend of increasing Ce$^{3+}$ resonance intensity with mol% Ce$_2$O$_3$ in the cerium aluminophosphate glasses. In the cerium silicophosphate glasses, the Ce$^{3+}$ resonance intensity increased with mol% Ce$_2$O$_3$ for the glasses with isolated cerium cations and decreased with mol% Ce$_2$O$_3$ for the glasses containing cerium clusters.

Radiation damage resistance was identified in the high-cerium aluminophosphate and silicophosphate glasses through the absence of radiation-induced phosphorus-related
paramagnetic defects. This resistance is attributed to a structural implication of clustering, rather than the presence of clustered cerium itself. Specifically, cerium will be in close proximity to defect precursor sites at the concentrations required for clustering in the aluminophosphate and silicophosphate glasses and is thus able to prevent localization of electrons and holes on those sites.

Finally, radiation-induced optical absorption was measured for both the low-cerium and high-cerium aluminophosphate and silicophosphate glasses. The trends in intensity and wavelength of this visible absorption were different for glasses predicted to have isolated or clustered cerium on average. As radiation-induced absorption was detectable for both glasses with and without radiation-induced defect sites, and the resulting coloration was similar to that of the high-cerium glasses, this absorption is attributed to a change in the local electronic structure of cerium which is similar to valence electron transfer. The presence of an induced absorption, attributed to cerium, provides evidence for the method for cerium-induced radiation damage resistance where cerium acts as a preferential electron- or hole-trap and either changes oxidation state or forms $\text{Ce}^{3+}$ and $\text{Ce}^{4+}e^-$. 

Additional structural information could be obtained about network-forming cations (Al, P, and Si) through two-dimensional cross-polarization magic angle spinning (CPMAS) NMR experiments. Specifically, the data from a $^{27}\text{Al}/^{31}\text{P}$ 2D CPMAS NMR experiment could be used to analyze the connectivity between aluminum and phosphorus cations in the cerium aluminophosphate glasses and look for trends with aluminum coordination and phosphorus Q-speciation. Additionally, the data from $^{29}\text{Si}/^{31}\text{P}$ 2D CPMAS NMR experiments would look for similar trends between silicon coordination,
silicon Q-speciation, and phosphorus Q-speciation in cerium silicophosphate glasses that could provide evidence for preferential intermediate range bonding. Specifically, a lack of connectivity between Q⁴ silicon and phosphorus would provide evidence for silica-like regions in the silicophosphate glasses, while connectivity between Q⁶ silicon and Q¹ phosphorus would provide evidence for SiP₂O⁷-like regions in the glass.

Future work is needed to investigate the possibility of colorless high-cerium phosphate glasses which are also resistant to radiation damage. Clear glasses could be synthesized with 100% Ce³⁺ by melting under a reducing atmosphere or addition of a reducing agent such as ammonium phosphate. A similar investigation of radiation damage would utilize EPR to detect radiation-induced defects and UV-VIS spectroscopy to measure induced-absorption bands. This would ascertain whether only a polyvalent cation is required for protection against radiation damage, or if a polyvalent cation must be present in mixed oxidation states for radiation damage resistance.
APPENDIX

27Al MAS NMR EXPERIMENTAL PROCEDURE\textsuperscript{105}

27Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were conducted at a magnetic field strength of 11.7 T utilizing a Varian/Chemagnetics Infinity 500 instrument interfaced to a 3.2 mm double resonance NMR probe with a 27Al transmitter frequency of 130.253 MHz. A total of 4096-100000 transients were acquired and averaged using a 27Al radiofrequency pulse of 2.5 \( \mu \)s for a tip angle of \( \pi/10 \), a pulse delay of 1 s, a spinning rate of 17 kHz. The chemical shifts were referenced to an aqueous 1 M AlCl\(_3\) standard. Spectra were processed with 150 Hz of line broadening and peaks were integrated with NUTS NMR processing software (Acorn, Inc.) to quantify the contributions to each aluminum coordination.

29Si CPMG MAS NMR EXPERIMENTAL PROCEDURE\textsuperscript{105}

29Si Carr–Purcell–Meiboom–Gill (CPMG) MAS NMR experiments were conducted at a magnetic field strength of 9.4 T on a home-built spectrometer with a Tecmag pulse program interfaced to a 4.0 mm double resonance NMR probe at a 29Si transmitter frequency of 79.463 MHz. Experimental conditions included the acquisition of a total of 1500 transients, a \( \pi/2 \) pulse of 4 \( \mu \)s, a pulse delay of 60 s, and a spinning speed of 10 kHz. A total of 128 points were acquired during 16 echoes. Tau values were: \( \tau_1 = 5093.25 \), \( \mu \)s \( \tau_2 = 70 \), \( \mu \)s, and \( \tau_3 = \mu \)s. Chemical shifts were referenced to TMS and a secondary standard tetrakis. All spectra were processed in NUTS NMR processing software (Acorn Inc.) to quantify the contributions to each silicon coordination.
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81. Orthorhombic CeP3O9, PDF #97-041-7805, Inorganic Crystal Structure Database, FIZ Karlsruhe, Eggenstein-Leopoldshafen, Germany.


105. NMR spectra were gathered and analyzed by Ms. Kelly Murphy, a graduate student in the Chemistry Department at the Pennsylvania State University.


118. Schematics of P₁, P₂, and POHC defects were taken from Materials Studio 5.5 visualizations of MD simulations created by Leopold Kokou and Jincheng Du at the University of North Texas.

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PUBLICATIONS


SELECTED PRESENTATIONS


