RARE EARTH COORDINATION ENVIRONMENTS IN ULTRAPHOSPHATE GLASSES

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Abstract Rare earth phosphate glasses with molar compositions $x\text{RE}_2\text{O}_3$ ($1-x$) P_2O_5 ($0 \leq x \leq 0.30$) were prepared and characterized by extended x-ray absorption fine structure (EXAFS) spectroscopy and by high-energy x-ray diffraction (XRD) analyses. The analyses indicate that the average coordination number (CN) of the RE^{3+} ions depends on composition: ultraphosphate glasses with less than ~15 mole% RE_2O_3 have average RE CN's of 8–9 and CN decreases to ~6 with increasing RE_2O_3 content to 25 mole%. The compositional dependence of RE CN can be understood with a simple model in which the formation of structurally isolated RE–polyhedra is favored in ultraphosphate glasses. Glass properties, including refractive index and glass transition temperature, are sensitive to changes in glass structure.

Introduction

Structural information about the local coordination environments of rare earth (RE) ions in phosphate glasses is interesting because of the use of these materials in lasers and optoelectronic components¹. Binary rare earth phosphate glasses can be made with over 25 mole% RE_2O_3 and these glasses possess interesting luminescent and magnetic properties. There have been a number of studies on the structure of binary rare earth phosphate glasses, including Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and neutron and x-ray diffraction^{2,3,4,5}. Because of the volatility of P_2O_5 from phosphate-rich melts, most of these investigations involved only glasses with compositions close to the RE metaphosphates (25 mole% RE_2O_3). Studies of the structures of RE ultraphosphate (<25 mole% RE_2O_3) glasses are much more limited⁶. Such studies are warranted, however, because of the useful laser⁷ and ferroelastic⁸ properties of ultraphosphate crystals (REPO_4).

We have recently reported EXAFS⁹ and high-energy x-ray diffraction (XRD)¹⁰ analyses of rare earth ultraphosphate glasses. These studies indicate that the coordination environments of RE ions depend on the glass composition.

Experimental Procedures

Ultraphosphate glasses were prepared from mixtures of vacuum-purified P_2O_5 and La_2O_3 , $NdPO_4$, $GdPO_4$, and $ErPO_4$ handled in an argon dry-box and sealed in flame-dried silica ampoules to prevent P_2O_5 volatilization. The samples were heated to 1000–1100°C, depending on composition, for twenty minutes until a homogeneous liquid was formed. The ampoules were then transferred to the dry-box before separating the RE-glasses. Glasses with more than 20 mole% RE_2O_3 were prepared by melting oxide mixtures in covered silica crucibles at 1250°C for thirty minutes. Glass compositions were determined using analytical electron microscopy. The analyzed RE/P ratios were in close agreement with the batched compositions and the glasses contain up to ~6 mole% SiO_2 . Refractive indices were measured using comparative index oils and are accurate to ± 0.002 . Glass transition temperatures (T_g) were measured by differential scanning calorimetry, heating at 10°C/min in an inert atmosphere after first cooling samples through the glass transformation range at -10°C/min to fix the thermal history; the T_g 's are reproducible to $\pm 4^\circ C$.

Room-temperature L_{III} -edge EXAFS spectra were collected at the Stanford Synchrotron Radiation Laboratory using a half-tuned Si(220) double-crystal monochromator. Samples were prepared and analyzed using procedures described elsewhere⁹⁻¹¹. The X-ray diffraction experiments were performed on the BW5 wiggler beamline at the DORIS III synchrotron (Hamburg/Germany), as described by Hoppe *et al*¹⁰.

Results and Discussion

FIGURE 1 shows the refractive indices of several series of RE-phosphate glasses. In general, the refractive index increases with increasing RE_2O_3 contents, although for each series, increasing RE_2O_3 between about 15 and 25 mole% has less of an effect on n .

FIGURE 2 shows the glass transition temperatures of the Nd and Gd-phosphate glasses as well as the T_g 's reported for a series of Li-ultraphosphate glasses¹², plotted against the oxygen-to-phosphorus ratio, determined from the respective glass compositions. Each series, including the Li-ultraphosphates, reveals a minimum in T_g at O/P $\approx$ 2.6–2.7 (~7 mole% RE_2O_3). Similar results have been reported for the La-glasses.¹³

FIGURE 1: Refractive indices of La-, Nd-, and Gd-phosphate glasses.

FIGURE 2: Glass transition temperatures for Nd- and Gd-phosphate glasses and for a set of Li-phosphate glasses reported by Hudgens and Martin¹².

FIGURE 3 shows the Nd and Er coordination numbers determined from the EXAFS experiments⁹ and from high-resolution x-ray diffraction analyses of La-phosphate glasses¹⁰ and Nd-phosphate glasses⁵. There are ~8–9 oxygens coordinating the RE ions in glasses containing less than ~15 mol% RE₂O₃. The RE CN decreases to ~6 for glasses with >25 mole% RE₂O₃.

FIGURE 3: Coordination numbers determined from the EXAFS spectra⁹ from Nd- (○) and Er- (△) phosphate glasses and XRD analyses of La10- (□) and N5d- (●) phosphate glasses. The solid line is calculated from equation 1.

Hoppe et al. have proposed that the structures and properties of ultraphosphate glasses are dependent on the number of terminal oxygens available to coordinate the modifier ions^{3,14}. For glasses with the stoichiometry $x(M_{2v}O) - (1-x)P_2O_5$, where M is a metal modifier and v is the valence of the modifier ion, the number of terminal oxygens per modifying ion is $M_{TO} = v(1/x)$. This equation can be re-written for $xRE_2O_3 - (1-x)P_2O_5$ glasses to determine the dependence of the number of terminal oxygens per RE³⁺ ion on the mole fraction (x) of RE₂O₃:

$$TO/RE^{3+} = (1+2x)/x \quad (1)$$

There are at least two structurally sensitive compositional ranges¹⁴ that are defined by the RE coordination number (CN_{RE}) and the number of terminal oxygens (TO/RE^{3+}). When $TO/RE^{3+} > CN_{RE}$, there are sufficient terminal oxygens to form

isolated RE coordination polyhedra within the phosphate network, as are found in crystalline $\text{NdP}_5\text{O}_{14}$ and $\text{ErP}_5\text{O}_{14}$.^{15,16} When $\text{TO}/\text{RE}^{3+} < \text{CN}_{\text{RE}}$, there are not enough terminal oxygens available to satisfy the coordination requirements of *isolated* RE ions and so these ions must share the available terminal oxygens through RE–O–RE linkages.

The EXAFS and XRD results indicate that there is a decrease in the RE coordination number (and a reduction in the average RE–O bond length^{9,10}) with increasing RE_2O_3 (FIGURE 3). According to equation (1), *isolated* eight-coordinated RE^{3+} ions, like those found in the RE_5O_{14} crystals, can exist in $x\text{RE}_2\text{O}_3 \cdot (1-x)\text{P}_2\text{O}_5$ glasses when $x \leq 0.167$. *Isolated* RE–polyhedra can also exist in glasses with greater RE_2O_3 contents only if the average RE coordination number decreases. The solid line in FIGURE 3 is the predicted dependence according to equation 1. Note that for coordination numbers and compositions to the left of (and below) the line, isolated polyhedra are expected to be present. Clustered RE–polyhedra sharing common oxygens will result for CN/composition combinations to the right of (and above) the line. The decrease in RE CN between ~15 and 25 mole% RE_2O_3 and thus avoids the formation of RE–clusters in glasses with increasing RE_2O_3 . Note that equation 1 predicts that when RE_2O_3 exceeds 25 mole%, CN must fall below six in order for the RE–polyhedra to remain isolated. It is unlikely that these large ions possess coordination numbers under six, and so RE–clusters are expected to be present in glasses with RE_2O_3 contents >25 mole%.

Breaks in the compositional dependence of the refractive index near ~15 mole% and 25 mole% RE_2O_3 (FIGURE 1) are consistent with this structural model and indicate the range over which the average RE CN decreases to avoid clustering. The minimum in T_g , near 7 mole% RE_2O_3 (O/P~2.7), occurs outside of this compositional range. High-energy x-ray diffraction analyses of La–ultraphosphate glasses¹⁰ indicate a possible change in ordering between La–polyhedra and P–tetrahedra near 7 mole% La_2O_3 . The presence of a T_g minimum at a similar O/P ratio for the Li–ultraphosphate glass series indicates that this minimum depends on the phosphate network and is less sensitive to the nature of the modifying ions.

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