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EFFICIENCIES OF Ce DOPED ALKALINE EARTH LITHIUM
SILICATE GLASSES

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CORRELATION of XANES FEATURES with the SCINTILLATION EFFICIENCIES of Ce DOPED ALKALINE EARTH LITHIUM SILICATE GLASSES

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ABSTRACT

Cerium activated glasses of composition $20\text{Li}_2\text{O}\cdot 15\text{MO}\cdot 64.4\text{SiO}_2\cdot 0.6\text{Ce}_2\text{O}_3$ (where M is Mg, Ca, Sr, or Ba) exhibit scintillation efficiencies that vary by more than a factor of 2.5 with the alkaline earth. Previous work has suggested a correlation between the microstructure of these glasses and scintillation efficiency. Measurements of the Ce L_{III} x-ray absorption edge in the Mg, Ca and Sr glasses display a feature near the absorption edge that is suggestive of the presence of Ce^{4+} . The area of this peak is, in fact, correlated with the scintillation efficiency of the glass. The amount of Ce^{4+} indicated by the intensity of this feature is, however, too high to be a permanent population. We suspect that the feature is a transient phenomenon related to creation of Ce^{4+} and trapped electrons due to photoionization by the x-ray beam.

INTRODUCTION

Cerium-activated, lithium-silicate glasses are widely used as thermal neutron detectors because of their versatility, robustness and low cost. The glasses convert the energy of the neutrons to visible light pulses that may be counted. This process, scintillation, is generally thought to be composed of three steps: ionization, energy transfer, and luminescence. If defects are present, they can trap the excitations, altering the scintillation output. These features have been discussed previously.¹⁻⁴ The presence of magnesium in these glasses increases scintillation efficiency,⁵ but as previously observed¹ the effect drops by a factor greater than 2.5 with substitution through the series of alkaline earths (Fig. 1).

Figure 1. Scintillation efficiency of alkaline earth glasses as a percentage of that of NaI.

scintillation light from Ce^{3+} . The observation that the glasses are clear and colorless is

Data on scintillation lifetime and thermoluminescence suggested the following explanation: 1) energy transport is greatest in the Mg-containing glass, 2) trap densities are highest in the Ba-containing glass, and 3) the Ca- and Sr-containing glasses are intermediate in transport and trap density. Fluorometry, front-face fluorescence and UV-Vis spectroscopy provided no evidence for changes in the activator (Ce^{3+}), nor for the presence of Ce^{4+} , nor for problems with scintillation light exiting the material. [In this paper, the notation Ce(III) will refer to the valence state and Ce^{3+} will refer to the actual ion or ions. Although it is theoretically possible for Ce^{4+} to be a scintillation center, this ion absorbs light strongly over a range of frequencies that includes the Ce^{3+} fluorescence. Therefore the presence of Ce^{4+} is believed to reduce the scintillation efficiency of a glass by absorbing

consistent with the lack of evidence for Ce^{4+} .]

Atomic force microscopy (AFM) measurements of the polished and etched glass surfaces revealed significant differences in microstructure for the different glasses. Features consistent with crystalline inclusions were observed in the Mg and Ca containing glasses. Phase separation was also observed in the Sr and Ba glasses, but neither phase appeared crystalline. These observations provide a possible explanation for the increased energy transport (hence increased scintillation efficiency) for the Mg and Ca glasses. Electrons and holes are expected to be more mobile in crystalline phases. If the crystallites nucleate at Ce ions, elevated transport efficiency in these glasses would be expected, with the glass with the larger crystal size having the greatest energy transfer rate.

In this paper, we report an investigation of the x-ray absorption fine structure (XAFS) of the Ce L_{III} edge of the Mg, Ca and Sr glasses. The x-ray absorption near edge structure (XANES) for Ce^{3+} and Ce^{4+} is quite different, suggesting a method of detecting the presence of Ce^{4+} ions in the glass. Although Ce^{4+} was not detected in the previous experiments, its concentration is expected to be extremely low (less than 10% of the total Ce, or less than 0.06 mol% in the glass). The difference in the XANES for the two ions is sufficient to provide a detection limit for Ce^{4+} of at least 1% of the total Ce.

EXPERIMENTAL

Glasses of the composition $20\text{Li}_2\text{O} \cdot 15\text{MO} \cdot 64.4\text{SiO}_2 \cdot 0.6\text{Ce}_2\text{O}_3$ (where M is Mg, Ca, Sr, or Ba) were prepared as described previously¹. The materials were melted in a reducing atmosphere to minimize Ce^{4+} . The glass containing 15 mol% MgO will be referred to as the Mg glass, and glasses with other alkaline earths will be referred to similarly.

Scintillation efficiency. The glass samples (as poured shards approximately $2 \times 2 \times 0.5 \text{ cm}^3$) were mounted in an integrating hemisphere at the end of a photomultiplier tube.⁶ Each sample was surrounded by immersion oil to reduce the effects of internal reflection and sample-to-sample geometry effects. A ^{137}Ce gamma ray source was used to excite the sample. A Compton backscattering coincidence method was used to ensure that only those scintillation events that deposit a given amount of energy are counted.

X-ray Absorption Spectroscopy. Absorption spectra of the Mg, Ca and Sr glasses and Ce reference compounds were recorded at room temperature on Beamline 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). (Analyses of the L_{III} edge of Ce in the Ba glass was complicated by the presence of the Ba L_{II} edge at approximately 5625 eV. The extended fine structure from the Ba edge made the uncertainty in the analysis of the Ce XANES too great for inclusion.) The synchrotron radiation for this line is generated in the storage ring using an 1.8 Tesla, four period wiggler. Double Si(220) crystals and a 0.5 mm entrance slit were used for monochromatization of the beam. The resolution was approximately 0.5 eV at the Ce L_3 absorption edge (5723 eV). Spectra were obtained by monitoring the fluorescence using a Lytle detector.⁷ Small errors in the energy scale were corrected by reference to the Fe K edge from an Fe foil and to a Ce^{3+} acetate reference. The latter was run periodically during the experiments.

RESULTS

Scintillation efficiency.

The gamma-ray-induced scintillation efficiency for the series of glasses is shown in Figure 1 as a percentage of that for crystalline NaI. As observed previously¹, the amount of light produced varies significantly (greater than a factor of 2.5) as the alkaline earth is varied.

X-ray absorption near edge structure. The x-ray absorption structure near the Ce L_{III} edge is shown in Fig 2 for Ce(III) acetate [$Ce(C_2H_3O_2)_3$], Ce(IV) hydroxide [$Ce(OH)_4$], and for the series of glasses. The difference between the Ce(III) and Ce(IV) edges is quite striking, and has been observed for CeF_3 and CeF_4 as well.⁸

Figure 2. Ce L_{III} XANES for the series of alkaline earth glasses and for two reference compounds.

presence of a single white line in the glass spectra and from the proximity of the glass spectra edges to the Ce(III) reference edge. However, the alignment of the shoulder at 5739 eV in the glass spectra with the second major peak in the Ce(IV) reference suggests the presence of Ce^{4+} .

To estimate the amount of Ce^{4+} present in the glasses, the spectra were normalized to the step edge and then fit using a combination of Voigt peaks and a cumulative step function. A Voigt peak, the convolution of Lorentzian and Gaussian lineshapes, accounts for both the natural lineshape (Lorentzian) and the detector function (Gaussian). The method of Puerta and Martin¹⁷ was used to approximate the Voigt peaks. Transitions to the continuum were represented by a cumulative Gaussian step function. The widths of the step function and the Gaussian components of the pseudo-Voigt peaks were set to the same value but allowed to vary together to reflect a consistent instrument response. Best fits were found for a Gaussian width of 1.80 ± 0.03 eV, consistent with the observed resolution of approximately 0.5 eV. The Lorentzian widths of the pseudo-Voigt peaks were allowed to vary to reflect differences in the natural (lifetime) linewidths.

The Ce(III) standard best fit is shown in Fig. 3. Solid squares indicate data points, and the solid line through them is the fit. The Ce(IV) standard fit is shown in Fig. 4. The four features corresponding to the four Voigt peaks have been observed previously and reproduced by various calculations.⁹⁻¹¹ The peak at 5739 eV is believed to cause the shoulder in the glass spectra.

The Ce(III) spectrum displays a single large white line due to excitation of an electron from the $2p_{3/2}$ core level to empty 5d bands. The Ce(IV) XANES shows two strong absorption peaks. A theoretical treatment that includes multiple scattering effects and many body final states suggests that these are 2p to 5d transitions with two different final state configurations, $4f^0$ and $4f^1L$ (the latter designates hybridization of the Ce 4f orbitals with O 2p ligand orbitals).⁹ Such hybridization of cation and anion wavefunctions has been shown to be significant in insulating Ce(IV) compounds, which have been the subject of much investigation and discussion.⁸⁻¹⁶ The Ce L_{III} XANES for the glass samples indicate that they contain predominantly Ce^{3+} . This may be inferred from the