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EFFICIENCY OF SCINTILLATING GLASSES

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RELATIONSHIP BETWEEN MICROSTRUCTURE AND EFFICIENCY OF SCINTILLATING GLASSES

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ABSTRACT

Prior work has shown that there is a correlation between trap densities and scintillation efficiency of cerium-activated, lithium-aluminosilicate glasses. Raman spectroscopy has strongly suggested that phase separation may be playing an important role in governing the scintillation efficiency. In this study, we relate the thermoluminescence glow-curve data and microstructural analysis for a compositional series. The thermoluminescence data provide information about the traps in the neighborhood of the activator (Ce^{3+}). The microscopy and crystallization of the glasses provide direct evidence of activator partitioning.

INTRODUCTION

Cerium-activated, lithium-silicate glasses constitute an important and interesting system of scintillators. They are widely used as thermal neutron detectors. Small changes in composition can have dramatic changes in scintillation efficiency. For example, adding magnesium to these glasses increases scintillation efficiency¹. It is also known, that substituting calcium for magnesium decreases the scintillation efficiency. The change of network modifier from one alkaline earth to another would not be expected to cause a major change in the glass structure since there is no change in valence and only a small change in ionic radii. Yet, the substitution does have a dramatic effect on scintillation efficiency.

The conventional model for scintillation involves three consecutive processes: ionization, energy transfer, and luminescence. Ionization, the generation of electrons and holes in the matrix, is the result of interactions between the ionizing radiation and the matrix. The subsequent motion of these electrons and holes through the matrix to an activator (Ce^{3+} in this case) constitutes the energy-transfer process. At the activator, the excitations recombine to produce luminescence. During the energy-transfer stage, the excitations can be trapped at charged defects in the matrix. This trapping will act to prevent or delay the excitation of and eventual recombination at the activator.

By examining light-generating mechanisms in a simple compositional series, it should be possible to discern if scintillation in cerium-activated glasses is dominated by any one of the three processes described above. Because the glasses are all chemically very similar (mostly silica), the initial conversion of the ionizing radiation in the matrix can be expected not to vary significantly. Changes in charge transport or electron and hole mobility through the matrix to the activator will be indicated by changes in time or energy dependent phenomena, such as scintillation lifetime and thermoluminescence. Direct excitation of fluorescence from the Ce^{3+} in the glass will indicate changes in the activator and its immediate environment. Examining the UV-Vis absorption of the glasses will indicate problems with scintillation light leaving the material.

EXPERIMENTAL

Glasses of the composition $20\text{Li}_2\text{O} \cdot 15\text{AO} \cdot 64.4\text{SiO}_2 \cdot 0.6\text{Ce}_2\text{O}_3$ (where A is Mg, Ca, Sr, or Ba) were prepared. These glasses were studied via scintillation efficiency, scintillation lifetime, front-

face fluorescence, UV-Vis transmission, Raman spectroscopy, thermoluminescence, and atomic-force microscopy (AFM). The scintillation lifetime provides information on the mechanisms by which energy is transferred to the activator (Ce^{3+}). Raman spectroscopy provides information on the overall glass structure, giving the most information on the degree of disorder of the silica network². Front-face fluorescence, fluorometry, and UV-Vis absorption measurements provide indirect and direct evidence as to the relative energies of the Ce^{3+} states and the relationship of these electronic states to other energy levels of the glass matrix (i. e., the UV band edge and Ce^{4+} states). Thermoluminescence measurements provide information about the depth and number of traps in the region of a few mean paths from the Ce^{3+} activator. Microstructural analyses are necessary to ensure that the data from other measurements are not misleading due to the presence of multiple phases.

High-purity raw materials^a were dry mixed, melted in platinum crucibles at 1370 to 1380 °C in a reducing atmosphere, and cooled by pouring onto a water-cooled, platinum-coated nickel plate. Using of a reducing atmosphere minimizes Ce^{4+} , which will absorb light emitted by the Ce^{3+} . Samples from these melts were annealed and polished into 1 x 1 x 0.25 to 0.5-cm pieces. Each sample was annealed and polished on both large faces and one edge. All of the samples of a single composition came from the same glass melt.

Scintillation efficiency. The cut, polished, and annealed samples were mounted in an integrating hemisphere at the end of a photomultiplier tube³. 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.

Scintillation lifetime. Samples were excited with 100-ps pulsed 20-keV X-rays generated by an optically-excited X-ray tube. The scintillation was measured with a microchannel photomultiplier tube feeding a standard time-to-amplitude convertor arrangement. The scintillation lifetime spectra were fit to multiple decaying exponentials.

Raman Spectroscopy. The cut, polished, and annealed samples were mounted with the large faces horizontal and the polished edge facing the spectrometer. Argon-ion laser light (514.5 nm) was passed through the sample. A mirror above the sample reflected transmitted laser light back through the sample. Spectra were gathered from 50 cm^{-1} through 1450 cm^{-1} in 1.0 cm^{-1} increments with a 2.5-sec integration time.

UV-Vis Spectroscopy. To obtain thin enough samples to measure meaningful absorption spectra, fibers of the glasses were drawn under reducing conditions. These fibers were held between two fused silica flats with immersion oil. Spectra were measured on a Cary 3 spectrometer.

Thermoluminescence. The thermoluminescence samples were cut to an approximately 0.3 x 0.3 x 0.05-cm size to minimize the effects of thermal gradients in the sample. Low-temperature thermoluminescence measurements were performed by cooling the sample to approximately -150 °C and then exposing it to UV selected lines from an Argon-ion laser to expose the sample to approximately 77 mJ of UV radiant energy⁴. The UV photoionizes the Ce^{3+} , sending an electron (or hole) into the matrix where it can then be trapped by charged defects in the glass matrix. The

^a Magnesium oxalate - Johnson Matthey Puratronic
Barium carbonate - Electronic Space Products International
Calcium carbonate - EM [FO-Optipure]
Strontium carbonate - Johnson Matthey Puratronic
Silicon dioxide - EM [FO-Optipure]
Cerium acetate - Johnson Matthey REacton
Lithium carbonate - Noah Technologies

sample is then allowed to warm, in vacuum, to room temperature. This takes approximately one hour.

After the low-temperature experiments were completed, it was found that consistently reproducible amplitude data could only be achieved if the sample was fully annealed (for at least 1 h at 400 °C) before the experiment. This anneal depopulated all of the traps and avoided the problem of partially-filled deep traps filling shallower traps between consecutive thermoluminescence measurements. This anneal was performed for the high-temperature thermoluminescence measurements. The excitation time was chosen to expose the sample to approximately 1/2 the UV radiant energy used for the low-temperature thermoluminescence experiments. This exposure level was chosen to avoid detector saturation. High-temperature thermoluminescence measurements were performed in a Harshaw Model 2000-A TLD reader between 90 °C and 270 °C with a model 2080 Glow Curve Analyzer.

Front-face fluorescence. The samples were mounted in a blackened holder at the center of a 6-in integrating sphere. These were excited with 324-nm radiation from a HeCd laser arranged such that the exciting light just grazes the front face of the sample. Optics between the exit port of the integrating sphere and the spectrometer slit match the aperture of the spectrometer. Using an integrating sphere removes effects due to dispersion in the sample. The blackening of the sample holder reduces the effect of the fluorescence into the sample.

Fluorometry. The samples were examined in front-face mode in a SPEX Fluorolog-2 fluorometer. The excitation wavelength was scanned from 190 to 400 nm. The excitation wavelength was 420 nm. Single scans with an integration time of 1 sec were taken. The samples were mounted such that the excitation beam was normal to the large face.

Microscopy. Samples were etched using a 2% nitric acid, 2% hydrofluoric acid solution for 25 sec. After etching, the sample was washed with deionized water and dried with pressurized fluorocarbon. AFM measurements were performed with a Digital Instruments Nanoscope III scanning-probe microscope using a 0.12N/m tip. Parameters were set to optimize the image quality.

RESULTS AND DISCUSSION

Scintillation efficiency. The gamma-ray-induced scintillation efficiency is shown in Figure 1 as a percentage of that for NaI. It is seen that the amount of light produced varies by more than a factor of 2.5. This is a large effect. A change this large should be reflected as large changes in other, energy-transfer-related phenomena in the glasses.

Scintillation lifetime. The scintillation lifetime abundances are shown in Figure 2. The scintillation-light decay curves were best fit with three lifetime components: a fast component of 5 to 10 ns, a moderate component of 45 to 60 ns and a slow component of >400 ns. The abundance is the total amount of light arising from a given lifetime component. (For the long component, it is the amount of light that is released within 2 μ sec.) The abundance of the two slower components varies with alkaline earth; the abundance of the fastest component is essentially constant.

The slower components are expected to be controlled by thermal detrapping of excitations from charged defects in the glass matrix surrounding the Ce^{3+} . Shallow traps would delay the recombination for short time; deep traps delay the recombination for longer periods of time. The decrease in abundance of the two slower components with alkaline-earth atomic number could be consistent with a model in which overlap of the higher lying Ce^{3+} states with the UV-band edge allows for increased nonradiative decay. The nearly constant abundance of the fast component is unexplained.

Raman Spectroscopy. The Raman data normalized to the 1070- to 1090- cm^{-1} Si-O stretching

band are shown in Figure 3. The differences between the spectra are small, with the exception of the Mg-containing glass, for which this band is broadened. Brawer and White² showed that, in alkali silicates and alkaline-earth silicates, the width of this line represents the degree of disorder in the SiO_4 network.

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

Taken alone, a distinct increase in the number of traps should imply a distinct decrease in the scintillation efficiency, but an increase in thermoluminescence. Likewise, a distinct increase in excitation mobility in the neighborhood of the Ce^{3+} ion should imply a distinct increase in both scintillation efficiency and thermoluminescence. Thus, these two possibilities for affecting scintillation efficiency act differently for scintillation efficiency and thermoluminescence. The low-temperature and high-temperature thermoluminescence data are shown in Figures 4 and 5, respectively.

The low-temperature data are shown scaled to the peak maximum. Heating rates were nonlinear; sample-to-sample heating rates were not identical, but were nearly the same. The heating rate will affect the sharpness of the luminescence peaks and may cause slight changes in the centroid of a given peak. In light of these considerations, these data are interpreted to be essentially identical. (The sharp peaks in the low-temperature thermoluminescence data are the result of light leaks due to inadvertent exposure and do not represent data.)

The high-temperature data are shown with absolute intensities. These data show the peaks for the Mg-, Sr-, and Ba-containing glasses to be at approximately the same temperature. This implies that these represent very similar structural defects. The peak for the Ca-containing glass is shifted to a higher temperature, implying that the defect forming the trap is somewhat more highly charged.

UV-Vis Absorption. The UV-Vis absorption spectra in Figure 6 show several features. The peak near 350 nm is the lowest 4f-5d transition of Ce^{3+} ; the peaks at shorter wavelengths represent transitions from the ground state to higher-lying d states. The feature near 200 nm is the tail of the UV absorption edge and is consistent with the literature.⁵ (The decrease in absorption for shorter wavelengths is an experimental artifact.) The UV absorption edge moves towards longer wavelength as the alkaline-earth atomic number increases; the absorption associated with the higher lying cerium levels is unchanged. This is consistent with the slight changes in the fluorescence spectra; however, it does not explain the large variation in scintillation efficiency for the series.

Thermoluminescence. Separate thermoluminescent experiments were performed at high and low temperatures. In the experiments, the sample is exposed to UV excitation at the lowest temperature of each experiment. The UV excitation photoionizes the Ce^{3+} ion; the electron or hole can migrate through the matrix and be caught on a trap. On heating, the trapped excitation is released and migrates back to an activator ion on which it recombines, generating the luminescence. Thus, thermoluminescence gives us a probe of two aspects of the matrix surrounding the Ce^{3+} ion. First, it contains information about the depth and number of traps. Second, it contains data about the transport of the excitation from the ion to the trap and back.

A difference in amplitudes indicates a difference in numbers of traps, or mobilities of excitations, or some combination thereof.

Front-face fluorescence. The front-face fluorescence spectra, normalized to unit amplitude at the fluorescence peak maximum, are shown in Figure 7. The spectrum maximum move to longer wavelengths as the alkaline earth atomic number is increased. This is a small effect and gives little guidance as to the cause of the large change in scintillation efficiency. This effect may be attributable to absorption by the glass matrix as the UV-band edge decreases for higher-atomic-weight alkaline earths.

Figure 2. Abundances of lifetime components for the alkaline-earth series. The lifetime, in nanoseconds, is just above the abundance bar.

Figure 3. Raman spectra for the alkaline-earth series. Spectra are normalized such that the 1070/1090 cm^{-1} peak has unit amplitude. Curves are offset for clarity.

Figure 4. Low-temperature thermoluminescent curves for the alkaline-earth series.

Figure 5. High-temperature thermoluminescence curves for the alkaline-earth series.

Fluorometry. The fluorometry spectra in Figure 8 show several features. The peak near 360 nm is direct excitation of the main 4f-5d absorption of Ce^{3+} ; the peak at about 270 nm represents transitions to the higher-lying Ce^{3+} states. The increase in fluorescence for the Ba-containing glass

at wavelengths below 250 nm is real and is the result of the intersection of UV band-edge states with the Ce^{3+} 5d states. There are small differences between the fluorescence excitation spectra for the series, but none sufficient to provide an explanation for the large difference in scintillation efficiency for the various glasses.

Figure 6. UV-vis absorption spectra for the alkaline-earth series.

Figure 7. Front-face fluorescence spectra. Spectra are normalized to unit peak amplitude.

Figure 8. Fluorometry spectra for the alkaline-earth series.

Figure 9. AFM micrograph of $20\text{Li}_2\text{O} \cdot 15\text{MgO} \cdot 64.4\text{SiO}_2 \cdot 0.6\text{Ce}_2\text{O}_3$ sample. Vertical scale is $0.150 \mu\text{m}$.

Microscopy. The AFM measurements give significant information about the extent of phase separation in this series of glasses. Phase separation can confuse the interpretation of the scintillation-efficiency issue by mixing different phenomena in different phases. It could also be a primary cause of the differences in scintillation efficiency by affecting energy-transfer mechanisms.

The AFM data show a distinct difference in the nature of the phase separation in the compositions.

The Mg-containing sample (Figure 9) has glass-immiscibility phase separation on a 0.05- μm scale with 0.5- μm crystals. The relief associated with glass-glass features is small indicating a small difference in etch rate between the two components.

The Ca-containing sample appears similar to that of the Mg-containing glass with glass-immiscibility phase separation on a 0.05- μm scale but with 0.1- μm crystals. The glass-glass features show little relief, as well.

The Sr-containing sample (Figure 10) shows distinctly different phase separation. The gross phase separation has a scale factor on the order of 1.0 μm and shows considerable relief, indicating a significant difference in stability between the two phases. There is no obvious indication of crystallinity in either phase and no indication of finer-scaled structures.

The Ba-containing sample (Figure 11) shows no gross features; on a 500-nm scale, phase separation of two components with very different surface energies and very different stabilities is seen as evidenced by the etching behavior.

Figure 10. AFM micrograph of $20\text{Li}_2\text{O} \cdot 15\text{SrO} \cdot 64.4\text{SiO}_2 \cdot 0.6\text{Ce}_2\text{O}_3$ sample. Vertical scale is 0.150 μm .

Figure 11. AFM micrograph of $20\text{Li}_2\text{O} \cdot 15\text{BaO} \cdot 64.4\text{SiO}_2 \cdot 0.6\text{Ce}_2\text{O}_3$ sample. Vertical scale is 0.07 μm .

SUMMARY

It is clear that the scintillation efficiency dramatically changes with the alkaline earth in an otherwise identical compositional series. This variation reflects significant variation in the energy-transfer mechanisms or trap density in the neighborhood of the Ce^{3+} ion in this glass series. The small variation in the relative proportions of the moderate and the slow components of the scintillation lifetime shows that the difference in scintillation efficiency cannot be attributed entirely to a difference in number and location of traps in the glass matrix. The slight relative increase in slow component in the Ba-containing glass suggests that, in this glass, more traps or more-effective traps may be present.

The fast component of the scintillation lifetime appears to be independent of the material composition and may be intrinsic to the matrix or unrelated to the activator. The front-face fluorescence, fluorometry, and UV-vis absorption data show that changes in the UV cutoff is insufficient to explain the large variation in scintillation efficiency. Nor does it appear that the energy levels of the Ce^{3+} have been affected by the matrix in a significant way.

The high-temperature thermoluminescence data show that the combination of number of traps and energy-transfer efficiency is greatest in the Mg-containing and the Ba-containing glasses. Taken together, the thermoluminescence data show that the trap energies do not appear to differ substantively for the glass series. A reasonable hypothesis consistent with these data and the luminescence lifetime data is that the glasses fall into three categories: 1) the Mg-containing glass for which the energy transport is greatest, 2) the Ba-containing glass for which the trap densities are increased, and 3) the Ca- and Sr-containing glasses, which have neither the increased transport nor the increased trap density. This hypothesis would address only the neighborhood of the Ce^{3+} ion.

The Raman data show that the SiO_4 backbone is more disrupted in the magnesium glass than in the other glasses. The lack of significant variation between the other glasses does not offer an explanation of the large variation in scintillation efficiency.

The AFM data on etched samples tie the hypothesis together with the other data. The Mg-containing glass contains regular 500-nm inclusions consistent with crystallization. The bulk of the material appears to be made up of two chemically similar immiscible glasses. The Ca-containing glass is similar to that of the Mg-containing glass except the crystals are much smaller. The Sr- and Ba-containing glasses also showed phase separation. The differences in the morphology and etch rates of the two phases show a fundamental difference between the Sr- and Ba-based glasses.

If it is assumed that the crystallization in the Mg- and Ca-containing glasses is nucleated on the Ce ions, then the increased electron and hole mobility in crystalline phases, compared to that of amorphous material, would explain the apparent improvement in energy transport. This is strong support for the hypothesis with the modification that the Ca-containing falls into the same category as the Mg-containing glass, the difference being that the crystal size is sufficiently reduced that the effect of increase in transport efficiency is masked.

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