Radiation Effects on the Photoluminescence of Rare-earth Doped Pyrochlore Powders


Abstract—This work examined the sensitivity of the luminescence spectra of europium-doped lanthanum zirconate to different types and amounts of radiation exposure. For the samples and radiation sources used in this work (X-rays and protons), changes in the photoluminescence of europium-doped lanthanum zirconate were minimal. However, when the phosphor was paired with an alternate luminescent material, which had a differing radiation response, relative changes in the photoluminescence of the two materials were correlated to the radiation exposure.

Index Terms—photoluminescence, proton irradiation, pyrochlore phosphors, radiation effects, X-ray irradiation

I. INTRODUCTION

Various phosphors have been used as radiation detectors and dosimeters for a range of applications. Specifically, phosphors have been utilized as scintillation detectors and storage phosphors. Scintillation detectors use phosphors to convert incident X-ray or gamma-ray radiation into UV or visible light. The light emitted is immediately captured by a photodetector, typically a photomultiplier tube, and is analyzed for dosimetry [1-2]. Unlike scintillation technology, which detects incident radiation at the time of exposure, storage phosphors are able to maintain radiation information several days after the initial exposure. Storage phosphors, whose matrix materials are generally salts, have been used for several decades as dosimeters in space and medical applications [3-5]. When exposed to ionizing radiation, storage phosphors trap electrons and holes at defect sites. Trapped electrons and holes recombine to emit light when stimulated optically or thermally, also referred to as Optically or Thermally Stimulated Luminescence (OSL or TSL). Emission from the recombination of electron-hole pairs can be correlated to the dose of the incident radiation. Current storage phosphor technology includes detection for X-rays, gamma-rays, neutrons and thermal neutrons. There have been various other studies investigating the radiation effects on ceramic phosphors. For example, Hollerman et al. reported degradation of photoluminescence during proton irradiation of rare earth oxides, including yttrium aluminum garnet (YAG) phosphor powders [6]. Kaczmarek et al. studied the effects of proton and gamma exposure on the absorption coefficients of various oxide compounds, including YAG phosphors [7]. Despite the history of phosphor powders and their use as detectors, little is known about how radiation affects the photoluminescence spectra of phosphor materials.

The effects of radiation on the luminescence of europium-doped lanthanum zirconate (LZO) are reported in this work. Rare-earth doped ceramic oxides are effectively inert under various ambient conditions, including high temperatures, humidity and oxidizing environments. Consequently, any radiation-induced defects are less likely to anneal in ceramic oxides. Europium-doped LZO has a photoluminescence spectrum that is highly affected by the state of the crystalline structure surrounding the activator. Damage to the crystalline structure from radiation-induced defects has the potential to change the photoluminescence of europium-doped LZO.

europium-doped LZO powders were fabricated using a combustion synthesis method and irradiated to quantify the sensitivity of the photoluminescence to different types and amounts of radiation. Two different sample sets were created in order to understand the radiation response of LZO by itself and the radiation response of LZO when another luminescent material is present. Lanthanum zirconate samples were exposed to ionizing and non-ionizing radiation. Changes in the photoluminescence spectra, including shifts in peaks or changes in intensity, were compared before and after radiation exposure to quantify the radiation responses of these two material systems.

Exposure to either ionizing or non-ionizing radiation did not produce shifts in the wavelengths of the photoluminescence peaks. Changes in intensity were found for LZO-only samples exposed to ionizing and non-ionizing radiation. However, the changes in intensity were relatively small and inconsistent from run to run. Unexpected and promising results were found after exposure to energetic protons of samples with a secondary luminescent material. Changes in the differing responses of the two photoluminescence spectra were compared and correlated with increased proton exposure.

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II. EXPERIMENTAL DETAILS

A. Eu-doped Lanthanum Zirconate

Lanthanum zirconate (LZO) is a pyrochloric compound. When doped with rare-earth ions, LZO luminesces. Pyrochlores have a chemical form of $A_2B_2O_7$, where $La^{3+}$ or trivalent europium occupy the A site and $Zr^{4+}$ occupies the B site. Pyrochlores, specifically rare earth zirconates ($A_2Zr_2O_7$), have complex crystal structures that lend themselves to a variety of physical and chemical properties, including stability in extreme environments. Pyrochlores have been used as high-temperature thermographic phosphors for their intense light emission and high-temperature stability [8]. Pyrochlores have been used to insulate vulnerable mechanical components from prolonged exposure to extreme temperatures because of their high thermal expansion coefficient, high melting point and low thermal conductivity [9].

The trivalent rare-earth ion $Eu^{3+}$ is used as an activator in lanthanum zirconate powders. Trivalent europium substitutes readily for the $La^{3+}$ ion site in the pyrochlore crystalline structure (Fig. 1a), where a concentration of 5% (percent replacement of La) was used in order to maximize emission intensity. The $Eu^{3+}$ activator produces emission in the red spectral region with various bands corresponding to optical transitions within the 4f orbital. Fig. 2b provides a representative example of phosphor photoluminescence under UV excitation. The sharp $Eu^{3+}$ emission lines provide information regarding the state of the crystalline structure surrounding the activator. For example, relative peak intensities between the magnetic and electric dipole transitions indicate the probabilities of these transitions and are highly affected by the geometrical symmetry surrounding the europium ion [10]. Splitting within the various electric and magnetic dipole transitions is highly affected by the state of the host lattice material.

Emission lines are denoted by the Russel Sauner’s Term Symbol, $^2S_1/2_L_J$, which defines transitions by their quantum numbers and characterizes the various electronic transitions within the $Eu^{3+}$ ion. Optical transitions occur from the $^5D_{0} \rightarrow ^7F_J$ ($J = 0, 1, 2$ and $3$) states and are present between 560 and 680 nm. The emission spectrum for a single representative sample of europium-doped lanthanum zirconate is shown in Fig. 1b. Emission bands between 610 and 635 nm are caused by electric dipole transitions from the $^5D_0^0 \rightarrow ^7F_2$ electronic states. The sharp emission bands between 580-610 nm and 635-660 nm are the magnetic dipole transitions from the $^5D_0^0 \rightarrow ^7F_1$ and the $^5D_0^0 \rightarrow ^7F_3$ states, respectively.

B. Sample Preparation

In order to understand radiation effects on lanthanum zirconate independent from other materials, a sample set was created by mounting the phosphor on an aluminum substrate without the use of a binder. The non-binder-assisted technique is advantageous as there are no adverse darkening affects and radiation-induced damage observed will not be obscured by any possible binder interactions. Powders are inherently difficult to securely mount onto a substrate using a non-binder technique. Non-binder-assisted samples were prepared by pressing the powder into a gap fabricated in an aluminum substrate (Fig. 2a). The aluminum substrate is approximately 0.5 - 1.0 mm thick and 1 cm$^2$ in area with a hole 2 mm in diameter, drilled approximately 25 µm into the face of the substrate.

Cyanoacrylate, a common glue, was used in this work initially as a binder. It is common for phosphor powders to be mounted using a binder or glue for ease of application onto a substrate. Cyanoacrylate luminesces within the spectral range of $Eu^{3+}$, when excited under UV at 395 nm. Comparing results from LZO-only and binder-assisted LZO samples yields an understanding of how a secondary luminescent material may affect the radiation response of europium-doped LZO’s...
Photoluminescence. The preparation of binder-assisted samples is considerably simplified compared to the non-binder-assisted samples. Binder-assisted samples were fabricated by applying a small amount of LZO powders on a thin aluminum substrate using cyanoacrylate. The spectral emission of binder-assisted contain an additional peak near 647 nm associated with the magnetic dipole transition of europium. The secondary luminescent peak is not associated with magnetic dipole transition, but with the cyanoacrylate emission. Emission from cyanoacrylate was confirmed by comparing photoluminescence spectra for cyanoacrylate-only, LZO-cyanoacrylate and LZO-only mounted on an aluminum substrates. The 647 nm peak was present for all cases which cyanoacrylate was used in the sample. Whereas, the photoluminescence of the LZO-only sample contained no peaks at 647 nm, which would be indicative of magnetic dipole transitions within the europium ion (Fig. 3).

The use of a binder is advantageous for adhering powders onto a substrate such that there is no material loss; however, binders can have undesirable consequences as mentioned earlier. Hollerman et al. showed that a yttrium aluminum garnet (YAG) powder mounted on an aluminum substrate using a polysiloxane binder darkened due to release of carbon after exposure to energetic protons [6]. Darkening from a binder has the disadvantage of possible luminescence intensity degradation. Such consequences are considered in this work and implications of darkening are discussed in further detail in the experimental results section.

**C. Photoluminescence Measurements**

Photoluminescence spectra measurements were taken pre- and post-irradiation. After a baseline measurement, each sample was exposed to increasing amounts of radiation, and photoluminescence spectra were taken between each step stress. Emission spectra measurements were compared to the baseline in order to understand and quantify the dose dependencies of all radiation-induced changes.

Radiation-induced changes in the photoluminescence were quantified by monitoring the photoluminescence intensity and the characteristic shape of the emission curve. Changes in absolute intensity measurements for exposure experiments are quantified by monitoring maximum intensities. The maximum intensity for the emission spectrum at a given exposure is normalized by the pre-irradiation maximum intensity for the data set. Error bars, which are reported along with changes in maximum intensities, are estimates of uncertainty for intensity measurements of a single sample and were obtained by characterizing the same sample multiple times.

Variability testing for intensity measurements was performed by taking five separate measurements on three different samples. To obtain a single variability measurement a fresh sample was placed into an optically black (dark) box, the emission spectrum was measured and the sample was removed. This process was repeated five times for each non-binder-assisted sample. Error bars are defined as the relative standard deviation at the maximum intensity which is calculated using the set of spectra from the worst-case sample (sample with the highest intensity variability). Fig. 4 depicts un-normalized emission spectra for the worst-case non-binder-assisted sample. The maximum intensity is indicated by the vertical bar and, for the europium-doped LZO fabricated for this work, always occurs near 630 nm.

Changes within the characteristic shape of the emission spectra include any shifts of the peak wavelengths in the spectra, any missing peaks, and additional peaks or changes in relative peak intensities after exposure. Intensity measurements are inherently variable; consequently, it is advantageous for radiation-induced effects to manifest themselves through changes in the characteristic shape of the photoluminescence. Changes in the shape of the emission spectra are monitored by comparing pre- and post-irradiation normalized photoluminescence spectra.

Samples were placed in an optically black (dark) box where they were excited using a Xenon lamp and monochromator. Photoluminescence measurements were taken using a spectrometer. Samples were exposed to 10-keV X-rays using an ARACOR Model 4100 irradiator. Additionally, samples were exposed to 1 MeV protons in one of the following facilities: the Pellettron accelerator or the High Voltage Engineering AN-2000 Van de Graaff accelerator, both of which are located at Vanderbilt University.

**III. EXPERIMENTAL RESULTS**

Neither proton or X-ray irradiation (10-keV X-ray or 1 MeV proton) of non-binder-assisted samples yielded any changes in the characteristic shape of the emission spectra. However, intensity changes were found after X-ray irradiation. The
absolute intensity of LZO:Eu 5% samples exposed to X-ray doses greater than 500 krad(SiO$_2$) showed a slight decrease from the baseline, seen in Fig. 5a. However, decreases in intensity were relatively small, approximately 10% from the pre-irradiation value. Inconclusive results were found for intensity measurements of non-binder-assisted samples exposed up to 1x10$^{16}$ 1-MeV proton fluence at the Pelletron facility, as shown in Fig. 5b.

Binder-assisted samples were exposed to 1-MeV protons in the Van de Graaff facility. Samples exposed to 1 MeV protons were found to have a correlation between changes in peak intensities of the europium electric dipole and the cyanoacrylate peaks. The integral normalized emission spectra at various exposures, ranging from 10$^{14}$ to 10$^{16}$ protons-cm$^{-2}$, are shown in Fig. 6a. The two $^5$D$_{0}$-$^7$F$_{2}$ electric dipole peaks between 610 and 630 nm will be referred to as peaks “1” and “2”, respectively. The cyanoacrylate emission, located at approximately 647 nm, will be referred to as peak “3”. Relative peak intensities were computed by fitting the integral normalized peaks with gaussians using a nonlinear least squares method. The relative peak intensity between the two electric dipole peaks remains constant with increasing fluence, as expected from the non-binder-assisted sample exposure results. However, the relative peak intensity for peaks 1 to 3 decreases with increasing fluence. Relative peak intensities versus total fluence for the ratios of peaks 1 to 3 (black data set) and peaks 1 to 2 (blue data set) are shown in Fig. 6b. The ratio of peaks 1 to 3 decreases by about 60% for samples exposed to 10$^{16}$ protons-cm$^{-2}$ compared to the baseline.

In addition to the unexpected response to energetic protons, binder-assisted samples also demonstrated darkening of the phosphors after exposure. As cited by Hollerman et al., darkening is caused by the release of carbon from the binder after proton irradiation [6]. The darkening is unlikely to be the source of changes in the relative peak intensities between the europium and cyanoacrylate peaks. If darkening were the source of the changes seen, it would be expected to yield an equivalent decrease over the entire spectra. Changes in relative peak intensities could be due to various complicated interactions between the energetic protons, cyanoacrylate and lanthanum zirconate. However, the cyanoacrylate emission may also provide an integrated reference such that changes in the intensity of europium-doped lanthanum zirconate can be measured.

IV. CONCLUSIONS

Photoluminescence measurements, specifically absolute intensity and characteristic shape of the spectra, were monitored before and after exposures for two sample preparations and exposure types. Photoluminescence intensity measurements are highly variable from run to run. Therefore, general changes in post-exposure intensity measurements were reported along with estimates of the absolute intensity’s uncertainty for all non-binder-assisted sample sets.
Data from non-binder-assisted samples showed no changes within the characteristic shape of the emission spectra post exposure. Changes were found within the maximum intensity measurements after X-ray exposures of non-binder-assisted samples. However, decreases found in maximum intensity measurements, amounting to approximately 10% from the baseline, did not occur until a high total dose of 500 krad(SiO₂). Changes in maximum intensities for non-binder-assisted samples exposed to 1 MeV protons were highly variable from run to run and yielded no discernable trend. Binder-assisted samples exposed to 1 MeV protons exhibited a systematic decrease of relative peak intensity between the phosphor and cyanoacrylate peaks with increasing fluence.

Quantifying radiation-induced changes in the photoluminescence for a single material is an exceptionally difficult task. The results from the LZO-only samples indicate that the luminescence of europium-doped lanthanum zirconate alone is not particularly sensitive to radiation, at least for the radiation sources considered here. When cyanoacrylate was present, changes in the relative intensities of the luminescence of the LZO and the binder were measured.

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REFERENCES