Cerium Oxidation State in LSO:Ce Scintillators

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***Abstract*—Trivalent cerium ions form the luminescence centers in several important families of scintillation materials including the rare earth oxyorthosilicates, pyrosilicates, and aluminates. When comparing the experimentally determined scintillation properties of cerium-doped scintillators to theoretical models of scintillation mechanisms, there is often speculation regarding the fraction of the total cerium that exists in the radiative trivalent charge state (Ce^{3+}) rather than the nonradiative tetravalent state (Ce^{4+}). Until now, however, no technique has been developed to quantitatively measure both Ce^{3+} and Ce^{4+} in single crystal scintillators . We report here for the first time direct measurements of Ce^{3+} and Ce^{4+} in Lu_2SiO_5:Ce single crystals. Synchrotron radiation was used to measure the X-ray absorption on the M_4 and M_5 edges of Ce, and the results were compared to model samples of Ce^{3+} (Ce_2O_3) and Ce^{4+} (CeO_2) which provided clear signatures of the two charge states. The spectra were obtained with a high-resolution superconducting tunnel junction spectrometer on beamline 4.0.2 at the Advanced Light Source synchrotron at Lawrence Berkeley National Laboratory. The results clearly show 100% Ce^{3+}, independent of light yield and sample coloration. Therefore, energy migration to the luminescence centers appears to be the determining factor in the scintillation efficiency of these samples, rather than variations in the Ce^{3+}/Ce^{4+} ratio.**

***Index Terms*—Cerium, oxidation state, scintillation detectors, scintillation mechanism, X-ray absorption spectoscropy.**

I. Introduction

As cerium-doped scintillators have increased in significance, considerable effort has gone into the characterization of the host material properties and the investigation of scintillation mechanisms that include the excitation and emission of the Ce luminescence centers. Although Ce can exist in either the trivalent (Ce^{3+}) or tetravalent (Ce^{4+}) state, it is well understood that only trivalent Ce gives rise to luminescence emission. In order to compare experimentally determined scintillation characteristics with models of the scintillation mechanism, one usually needs to know the fraction of total Ce in the crystal that exists in the trivalent state. Optimization of the crystal growth process also relies heavily on knowledge of the Ce charge state.

The relative populations of Ce^{3+} and Ce^{4+} in a scintillator are often estimated from analyses of the total Ce and the Ce^{3+} since a direct measurement of Ce^{4+} has been elusive. The total Ce can be measured by various techniques including glow discharge mass spectroscopy, inductively coupled plasma mass spectroscopy, and X-ray fluorescence. However, in our experience, the results usually have uncertainties in excess of 20% and often times much greater due, at least in part, to the lack of reliable calibration standards in the matrix of interest. Ce^{3+} can be observed by UV-visible spectroscopy, but it is difficult to determine the concentration quantitatively with good precision again due to the lack of good calibration standards. Since Ce^{4+} is not optically active, it cannot be observed directly.

X-ray absorption spectroscopy (XAS) can be used to precisely determine the electronic energy levels of elements, including small shifts in these levels due to the oxidation state of the ion. A highly monochromatic X-ray beam is scanned in energy through the region of the electron binding energy and the resulting absorption is measured. Rather than measure absorption via attenuation of the incident beam, quantities that are directly proportional to absorption are more commonly utilized. Concentrated compounds such as the $Ce_2^{3+}O_3$ and $Ce^{4+}O_2$ model compounds in the current study are best measured via the total electron yield (TEY) where photoelectrons and Auger electrons emitted by the sample are measured by a channeltron. Dilute samples such as the Ce-doped scintillator crystals studied here are best measured via the partial fluorescence yield (PFY) where a high resolution detector selects fluorescence only from the element of interest and thus provides much improved sensitivity.

II. Experimental

Single crystal boules of Ce-doped Lu_2SiO_5 (LSO:Ce) were grown from the melt via the Czochralski technique in inductively heated iridium crucibles [1]. The Lu_2O_3, SiO_2, and CeO_2 starting materials were at least 99.99% pure. Crystal growth was initiated with seed crystals, and was controlled via an automated system that used the derivative of the crystal weight as the process variable. Samples with dimensions of 3 mm $\times$ 4 mm $\times$ 1 mm were cut with a diamond saw.

Prior to measurement of the scintillation light yield, the samples were stored in the dark for at least 24 h to eliminate the thermoluminescence emission that is stored upon exposure to white light. The scintillation light yield was measured by placing the crystal directly onto a Hamamatsu R877 photomultiplier tube. The crystal was covered with a loose fitting Teflon cap to enhance the light collection efficiency. A 10 μCi ^{137}Cs source was located $\sim$15 mm from the crystal surface. The natural background spectrum from the Lu^{176} beta decay was minimal due to the small sample size and was not subtracted. The light output was reproducible to within $\pm$5%.

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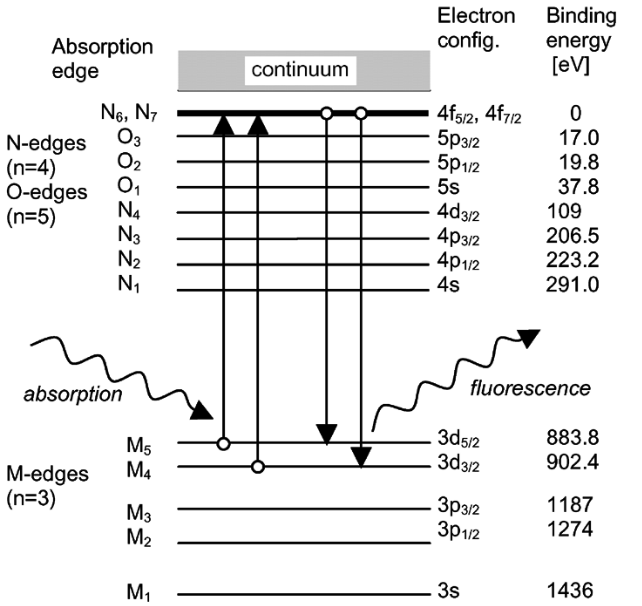

Fig. 1. Energy levels of cerium. The M_4 and M_5 absorption edges shift as a function of oxidation state. The binding energies of these levels are shown for metallic cerium [4]. The vertical upward arrows indicate absorption while the vertical downward arrows indicate fluorescence emission.

X-ray absorption spectra on the Ce M_4 and M_5-edges were taken at beam line 4.0.2 of the Advanced Light Source synchrotron at Lawrence Berkeley National Laboratory [2]. The synchrotron provides a flux of $\sim 10^{12}$ photons/s, and the beamline monochromator has an energy resolution of $\sim$0.15 eV at a slit setting of 20 μm/20 μm. This is well below the natural line width of the X-ray absorption features. The two absorption edges at $\sim$884 and $\sim$902 eV correspond to dipole-allowed transitions between the Ce $3d_{3/2}$ and the $3d_{5/2}$ core levels and the 4f valence band as shown in Fig. 1.

The $Ce_2^{3+}O_3$ and $Ce^{4+}O_2$ model compounds were obtained from commercial suppliers in powder form. Since $Ce_2^{3+}O_3$ oxidizes in air, this sample was stored in argon with the exception of a few minutes air exposure during grinding and loading into the vacuum chamber. No special precautions were needed for the $Ce^{4+}O_2$ sample. The model compounds were measured by TEY with a channeltron electron multiplier.

Absorption spectra of Ce dopants in LSO:Ce single crystals were measured by partial fluorescence yield using a superconducting tunnel junction spectrometer and gating on the Ce M fluorescence [3]. The detector was a nine-element array of Nb-Al-AlOx-Al-Nb tunnel junctions cooled to 0.1 K by a two-stage adiabatic demagnetization refrigerator and provided $\sim$15 eV resolution to isolate the fluorescence from the Ce dopants from other more abundant elements in the samples. At the absorption edges, the incident energy was increased in 0.1 eV steps with an integration time of 10 s at each energy, with larger 0.5 eV steps in the featureless regions of the spectrum. Spectra were normalized by the incident photon flux, a step-function background was subtracted to account for electron excitation into the continuum, and the absorption signal at the M_5-edge was set to unity. The energy was calibrated by setting the M_5-edge of Ce_2O_3 to 883.8 eV. The calibration was constant for each beam time over the two days of data acquisition, but shifted by $\sim$1 eV during the 2 mo. between the two beam times when these data were taken.

TABLE I
LIGHT YIELD OF $3 \times 4 \times 1$ mm^3 LSO:Ce SINGLE CRYSTAL SAMPLES

Designation	Ce conc. (%)*	Color	Light yield (ph/MeV)
LSO - 1	0.2	None	25,000
LSO - 2	0.2	None	11,900
LSO - 3	0.2	None	28,500
LSO - 4	0.2	Yellow	24,200
LSO - 5	0.2	None	25,800

*Ce concentration in the melt from which the crystal was grown; the actual Ce concentration is lower by a factor of 0.22, i.e. the solid-liquid distribution coefficient.

III. RESULTS

A. Scintillation Properties

Following several years of development for application in positron emission tomography, LSO:Ce scintillator crystals have reached a rather mature stage where large quantities of crystals are produced with uniformly high light yield and consistent decay time [5]. Occasionally, however, unintentional deviations in the growth process or contamination of raw materials may result in crystals with low light yield or yellow discoloration. Such cases provide an opportunity to study the various factors that affect the scintillation performance. For this investigation we chose samples that represented a range of light yield in order to test the hypothesis that differences in light yield result, at least in part, from variations in the Ce^{3+}/Ce^{4+} ratio in the crystals. Samples LSO-1, LSO-3, and LSO-5 were colorless crystals with high light yield ranging from 25 800 ph/MeV to 28 500 ph/MeV. Sample LSO-2 was also colorless, but had an anomalously low light yield (11 900 ph/MeV) that was less than half of the other crystals. Sample LSO-4 had a yellow discoloration but with only slightly lower light yield (24 200 ph/MeV) than the best crystals. The samples are summarized in Table I along with the light yield measured under 662 keV gamma-ray excitation from a ^{137}Cs source.

B. X-Ray Absorption

Powdered samples of Ce_2O_3 and CeO_2 were used as model samples of Ce^{3+} and Ce^{4+}, respectively. The X-ray absorption spectra of these samples are shown in Fig. 2 where one sees two sets of sharp lines for each sample due to transitions between the 3d core levels and the 4f valence level. For Ce^{4+} the lines are shifted to significantly higher energies compared to Ce^{3+} due to reduced electron screening and consequently tighter binding of the core levels. The fine structure in the absorption features reflects differences in the site symmetry and ligand field strength of the cubic CeO_2 and the hexagonal Ce_2O_3. Thanks to the intrinsically narrow lines of these inner shell transitions and the energy resolution of the measurement system, the patterns for the two samples are easily distinguished from each other.

Fig. 3 shows the absorption spectrum for sample LSO-1 superimposed on the model compounds. The centroids of the absorption edges in the LSO-1 spectrum match the Ce^{3+} model extremely well, with virtually no evidence of Ce^{4+}, thus confirming that essentially all of the cerium in this sample is in the trivalent state. This might be expected for this particular sample since its scintillation properties are quite good. The small differences in the fine structure of the Ce absorption edges between

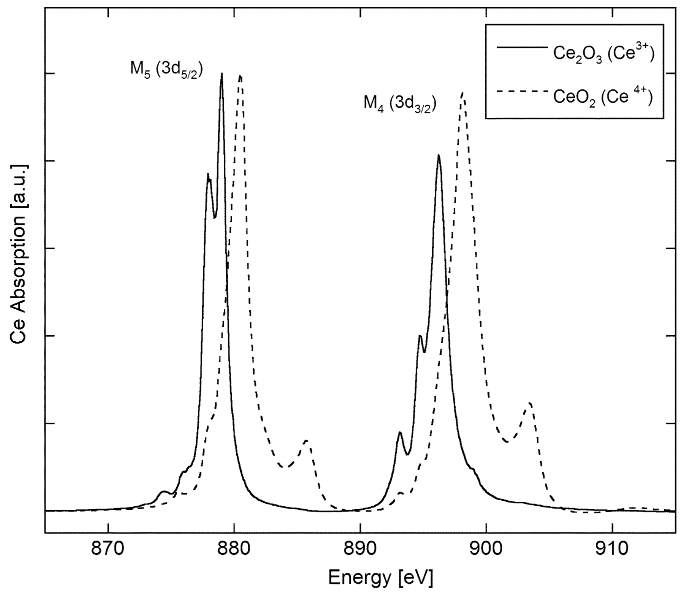

Fig. 2. X-ray absorbance of Ce^{3+} and Ce^{4+} model samples showing the shift in the M_4 and M_5 edges due to the difference in screening by the outer electron shells.

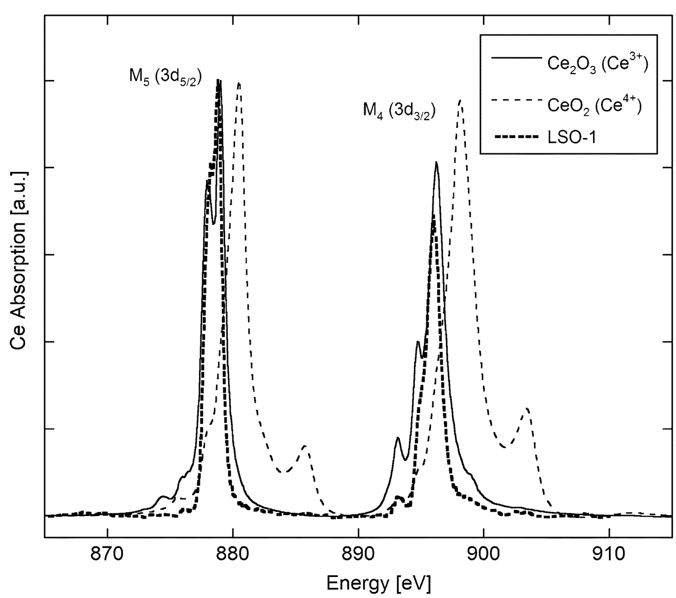

Fig. 3. X-ray absorbance spectra comparing the Ce M_4 and M_5 edges in LSO:Ce to the Ce^{3+} and Ce^{4+} model compounds.

LSO-1 and Ce_2O_3 result from the different symmetry and ligand fields. In LSO-1, i.e., in cerium doped LSO, the cerium resides at two sites with sixfold and sevenfold oxygen coordination, compared to the hexagonal structure of Ce_2O_3.

The X-ray absorption spectra for all four of the cerium doped LSO crystals are shown in Fig. 4. Clearly, all four spectra are virtually identical to the LSO-1 spectrum shown in Fig. 3, displaying little evidence of Ce^{4+}. This is surprising in the case of LSO-2 (low light yield) and LSO-4 (yellow color) since low light output and yellow color are often assumed to suggest the presence of Ce^{4+}. Apparently, this is not the explanation for the scintillation properties of these two crystals.

Although the samples in this study were selected because they display a range of light yield and color and therefore were

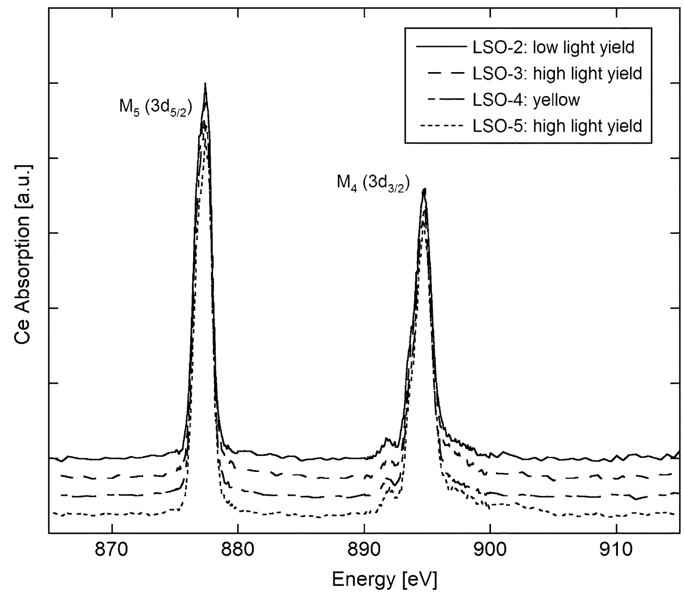

Fig. 4. X-ray absorption spectra of LSO:Ce crystals with both low and high light yield and one crystal exhibiting a yellow discoloration. The spectra are displaced vertically for clarity.

thought to have varying amounts of Ce^{4+}, all of the samples displayed X-ray absorption spectra that were nearly identical to the best LSO:Ce crystal, i.e., LSO-1. The lack of any observable Ce^{4+} in these crystals is a significant result because it means that different proportions of Ce^{3+} and Ce^{4+} cannot explain the differences in light yield as well as the yellow coloration of some samples. Thus, it appears likely that variations in the energy migration process, possibly due to different populations of charge carrier traps, may be responsible for the differences in light yields of rare earth oxyorthosilicate scintillators.

IV. Summary and Conclusion

To our knowledge, this is the first direct and simultaneous measurement of both Ce^{3+} and Ce^{4+} in single crystal scintillators. The high resolution of the beamline and of the superconducting tunnel junction detector array allow distinct signatures for Ce^{3+} and Ce^{4+} to be observed. The differences in the M_4 and M_5 absorption edges result from shifts in the binding energies due to the oxidation state of Ce.

When comparing experimentally determined scintillation properties to the predicted scintillation efficiency of theoretical models, the quantum efficiency of the luminescence centers must be determined. Since cerium may exist as either 3+ or 4+, but only the 3+ state results in scintillation emission, it is crucial to know the relative proportions of the two states. In addition, knowledge of the relative populations of the two oxidation states will aid in the optimization of crystal growth processes to maximize the scintillation efficiency.

Surprisingly, all of the samples investigated in this study, whether high or low light yield, colorless or yellow, contained Ce^{3+} only. No evidence of Ce^{4+} was observed, despite that fact that the $Ce^{4+}O_2$ model compound demonstrated that Ce^{4+} would be easily observable if it were indeed present. Evidently, the low light yield of one crystal and the yellow coloration of another crystal must be explained by other phenomena.

Although we did not attempt to quantitatively determine the sensitivity of the XAS technique for detecting either Ce^{3+} or C^{4+}, we estimate that 5% of either species should be readily detectable at typical dopant concentrations.

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