Effect of the X-ray dose on the luminescence properties of Ce:LYSO and co-doped Ca,Ce:LYSO single crystals for scintillation applications

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A R T I C L E   I N F O

Article history:
Available online 28 April 2013

Keywords:
Scintillation
Cerium
Orthosilicate
Oxyorthosilicate
Traps

A B S T R A C T

Mono-doped Ce:LYSO (Lu1.80Y0.2:Ce) and co-doped Ca,Ce:LYSO and Mg,Ce:LYSO single crystals were prepared by the Czochralski technique. Effects of the X-ray irradiation on the emission spectra and on the light yield are reported. A decrease of the longest wavelength emission (at about 500 nm) and a light yield increase are observed after 1 h under X-ray irradiation. As electron paramagnetic resonance (EPR) evidenced no change in the two cerium sites occupancy along with the irradiation time a mechanism based on the evolution of the oxygen vacancies as neighbors of Ce3+ ions is proposed.

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1. Introduction

Medical imaging equipment requires scintillator crystals with outstanding scintillating performances. In Positron Emission Tomography (PET) modality BGO has been replaced by cerium doped Lu5SiO7 (Ce:LSO) and Ce:Lu1.80Y0.2SiO5 (Ce:LYSO) single crystals which show high density, very high light yield (>30,000 photons/MeV) and fast response time (40 ns). In order to improve the scintillation performances the effect of oxidizing annealing treatments on Ce:LYSO has been reported [1–3]. In particular these works have pointed out the impact of point defects such as oxygen vacancies on the scintillation properties. It was also observed that co-doping with Ca and Mg for instance allows an afterglow reduction and large improvement of the light yield.

In LSO and LYSO hosts two different crystallographic sites exist for the rare earth cation, namely RE1 (7 neighboring oxygen) and RE2 (6 neighboring oxygen). The corresponding coordination polyhedra [RE1-07] and [RE2-06] are of low symmetry (C1) and form chains along the a axis. Due to this difference in their site dimensions, emission features are different if Ce3+ ions are located in the larger site (Ce1) or in the smaller one (Ce2). For Ce1 the mean Ce–O distance is 2.32 Å while for Ce2 it is 2.23 Å. Several distinct works [4–6] have shown that Ce2 emission is weak and hidden by the presence of the very strong Ce1 emission centered at about 420 nm at room temperature. This is related to the very high ratio of trivalent cerium in Ce1 site (about 95%) [5]. Indeed the size of the RE1 site is more compatible with the large radius of the trivalent cerium cation. Based on this result, Jary et al. [7] have studied the influence of the yttrium content in Ce:LYSO on the emission properties. These authors have published that increasing the Y content enhances Ce2 emission. Yang et al. have also reported that Ca co-doping reduces the Ce2 contribution in the radioluminescence – also called X-ray excited optical luminescence (XREOL) – spectrum of Ca,Ce:LSO single crystals at low temperature [8]. However Spurrier et al. have reported no change at room temperature for the same compositions [9]. In previous works it was demonstrated that point defects can impact the luminescence properties [10–13].

The present paper reports on the influence of the X-ray excitation dose. We discuss the possible role of the oxygen vacancies on the evolution of the scintillation properties of Ce:LYSO, Ca,Ce:LYSO and Mg,Ce:LYSO. An efficient way to differentiate co-doped Ce:LYSO from non-co-doped Ce:LYSO is also presented.

2. Experimental

Ce:LYSO, and co-doped Ca,Ce:LYSO and Mg,Ce:LYSO single crystals were grown by the Czochralski technique by Saint-Gobain Cristaux & Délecteurs as described in Ref. [1]. Samples with a size of 10 × 10 × 1 mm3 with the two large faces polished were prepared. For all samples, the yttrium content is 10 at% and the nominal cerium content is 0.22 at% and the nominal Ca and Mg concentration is 0.1 at%.

X-ray excited optical luminescence (XREOL) was performed at 20 K and 300 K with a Molybdenum source operating at 50 kV and 20 mA. The emission was collected via an optical fiber by a Roper Pix-100 CCD camera cooled at −65 °C coupled with an Acton SpectraPro 1250i monochromator. The emitted light was collected...
from the irradiated side of the sample at 45° to the sample surface. The CCD camera shutter aperture time was set to 1 s. For the measurements at 20 K the crystal was glued with silver paint to a copper sample holder attached to the cold head of a Janis Cryostat and placed under vacuum.

Electron paramagnetic resonance (EPR) measurements were performed with X-band Bruker spectrometers ESP 300E and Elexsys E 500 spectrometers equipped with an Oxford Instrument variable temperature device. 3\textsuperscript{rd} samples were cut oriented and polished and were mounted on a Perspex sample holder allowing various orientations with respect to the magnetic field. Measurements were performed at 300 K on samples previously bleached for 15 min at 650 K in air and on samples then irradiated for 60 min with X-rays.

3. Results

The XREOL emission spectra at 20 K and 300 K of the Ce:LYSO single crystal (initially bleached at 650 K) are presented in Fig. 1 with increasing irradiation times and therefore X-ray dose delivered to the material. At both temperatures a strong evolution occurs with the irradiation time. At 300 K when the X-rays irradiation increases, the emission around 525 nm decreases while the 420 nm emission band increases. Furthermore one can clearly notice an isobestic point at 458 nm which is usually characteristic of an exchange between two emitting species. It can also be noted that the evolution is rather slow as a steady state is reached after about 30 min of irradiation for both temperatures. In Ce-doped orthosilicates the emission at 420 nm is ascribed to Ce\textsuperscript{1} emission while the weaker emission at about 500 nm is characteristic of Ce\textsuperscript{2} emission [4]. According to the mean distances between the cerium and the oxygen surrounding in the two sites, larger crystal field for Ce\textsuperscript{2} leads to the shift toward longer wavelengths.

Fig. 2 shows the first and the last emission spectra obtained at 20 K simulated with four Gaussians for Ce\textsuperscript{1} and Ce\textsuperscript{2} sites corresponding to a double cerium band for each crystallographic site. In the fit corresponding to 10 s (Fig. 2a) and 90 min (Fig. 2b) of X-rays irradiation the position and Gaussian shapes of the emission site were kept identical. The results show a strong variation of the long wavelength contribution to the whole emission varying from 25% for the initial time down to 5% after 90 min. This last value is consistent with the already published sites occupancies with only 5% of the Ce\textsuperscript{3+} ions being located in Ce\textsuperscript{2} site [5]. Therefore a direct correlation is evidenced between the emission intensity and the sites occupancy. This is not surprising as the emission probability should be about the same due to the low symmetry of both sites. To determine the site occupancy before and after X-ray exposure the location of the Ce\textsuperscript{3+} ions was investigated by EPR. This was performed at 12 K as trivalent cerium can be only detected at low temperature. The obtained spectra are presented in Fig. 3. Ce:LYSO crystal was first annealed at 650 K for 15 min in order to remove all possible trapped charges and the EPR data were collected before and after 60 min of X-ray excitation at room temperature. According to [5] the peak located at 325 mT is ascribed to Ce\textsuperscript{3+} ions in site Ce\textsuperscript{1} while the peak around 520 mT is characteristic of Ce\textsuperscript{3+} in Ce\textsuperscript{2}.
The site occupancy by Ce³⁺ in the previous results site while 5% in Ce³⁺. Furthermore, the Ce³⁺ site. X-ray irradiation produces no significant change in the spectral content in Ce³⁺ ions occurs during X-ray irradiation.

The same variation of XREOL spectra was also observed for co-doped Ca,Ce:LYSO (and for Ce,Mg:LYSO not presented here) as shown in Fig. 4. For both temperatures a variation occurs in the emission spectrum shape. At 300 K however the evolution appears much less important than at 20 K and much less significant than for standard Ce:LYSO in similar conditions. The difference between the XREOL spectra a few seconds after the irradiation initiated and after 60 min of irradiation at 20 K is depicted in the inset of Fig. 4b. It shows a Gaussian-like shape peaking around 2.6 eV (475 nm). This behavior was not obvious in the Ce:LYSO sample presented in Fig. 1.

4. Discussion

We have also observed that this effect is totally reversible after the crystal is bleached in air at 650 K for several minutes, and reproducible. In addition when a crystal is excited with X-rays for 10 min, kept in the dark for several days and then excited again, the first emission spectrum is very similar to the one observed after 10 min of exposure. This point led us to consider electronic point defects as the origin of the observed evolution.

The following explanation could therefore be proposed. It was reported that the oxygen vacancies which affect the scintillation properties are mainly located around the Ce³⁺ doping ions and are the main defects reported in the orthosilicate matrix. Ce³⁺ presents a larger ionic radius than Lu³⁺ and Y³⁺ cations and this is the origin of a low cerium insertion in this host (segregation coefficient $K = 0.2$ [14]). When the crystal is first annealed at 650 K all electronic traps are emptied and the oxygen vacancies are positively charged [11]. The scintillation process during XREOL consists in:

(i) trapping of a hole by Ce³⁺ to form Ce⁴⁺, followed by
(ii) trapping of an electron by Ce⁴⁺ to form excited (Ce³⁺)⁺, and finally
(iii) radiative de-excitation with characteristic blue photon emission.

The first step (trapping of a hole) has an efficiency which depends on the absorption cross-section of the Ce³⁺ ions for holes. Thus if positively charged vacancies are located around Ce³⁺ ions the affinity of the latter for holes may decrease. The oxygen vacancies may thus screen Ce³⁺ ions from holes. During X-ray irradiation the oxygen vacancies are progressively filled by thermalized electrons. This could possibly lead to a color center formation. This also means that the positive charge around Ce³⁺ progressively decreases along with irradiation time. Consequently the affinity of Ce³⁺ for holes increases with the X-ray dose. In other words the trapping of holes by Ce³⁺ becomes more and more efficient as exposure goes on.

With that process the scintillation efficiency could possibly be enhanced. Furthermore Ce₁, which is dominant and which presents a radiative decay time shorter than Ce₂ (33 ns and 46 ns at 300 K, and ~35 ns and ~50 ns at 20 K for Ce₁ and Ce₂ sites, respectively [4]) shows an increase of its luminescence intensity. This model could explain the evolution of the emission spectra with the X-ray irradiation dose as depicted in Fig. 1. Scintillation light yield enhancement was also evidenced by pulse height measurements (under $^{137}$Cs–662 keV and $^{22}$Na–511 keV gamma excitations). The photopoint position after 2 h of X-ray irradiation at 300 K is shifted to higher channel and a light yield increase was measured to be up to
7% as compared to that of the bleached crystal. This analysis confirms that first irradiation indeed has a positive effect on the luminescence intensity.

To go further in the investigations, similar emission measurements were performed on Ca and Mg co-doped Ce:LYSO crystals both at 20 K and 300 K (after bleaching the samples at 650 K during 15 min). These crystals present significantly less defects as previously demonstrated by TSL measurements (see for instance [1,15]). As the amount of oxygen vacancies is less important for these latter crystals their impact on the luminescence process is expected to be weaker. Measurements for Ca,Ce:LYSO at 20 K are reported in Fig. 4. They show that both emission bands at 500 nm and 420 nm decrease. In the case of Ca,Ce:LYSO and Mg,Ce:LYSO the decrease of the emission at longer wavelengths could be related to a color center formation during X-ray irradiation (see the inset of Fig. 4 for the shape of the difference). This phenomenon was reported in others scintillators [16]. However no additional bands were clearly observed on the absorption spectra of Ce:LYSO, Ca,Ce:LYSO and Mg,Ce:LYSO. The intensity is either too small to be detected or the color centers may not be stable at room temperature. This has to be confirmed in a future work by using a low-temperature set-up allowing X-ray excitation and absorption measurement.

5. Conclusions

In this paper unexpected effects of X-ray irradiation dose on the luminescence properties of Ce:LYSO, Ca,Ce:LYSO and Mg,Ce:LYSO crystals were observed. A decrease of the long wavelength emission is demonstrated without variation of the Ce\(^{3+}\) distribution in the two sites of the orthosilicate matrix. This effect is particularly important for Ce:LYSO and may be linked to oxygen vacancies which are progressively filled due to electron trapping. An increase of the scintillation light yield was also observed at room temperature. Possibly an absorption band only observed at low temperature may also be present in some crystals after X-ray irradiation. But as orthosilicate matrix is known to be radiation resistant [17,18] further investigations may be required, possibly including other excitation sources. It could be interesting to measure in a future work the decay time at low temperature under X-ray excitation since it would probably favor the Ce\(^{3+}\) emission with shorter decay time.

Furthermore this behavior during X-ray excitation can be used as an efficient tool to differentiate co-doped Ce:LYSO from non-co-doped Ce:LYSO.

References