Evidence and Consequences of Ce⁴⁺ in LYSO:Ce, Ca and LYSO:Ce, Mg Single Crystals for Medical Imaging Applications

S. Blahuta, A. Bessière, B. Viana, P. Dorenbos, and V. Ouspenski

Abstract—Lu₂(1-x)Y₂xSiO₅:Ce (10 at% Y) single crystals co-doped with Ca²⁺ and Mg²⁺ were prepared by the Czochralski technique. It is shown that co-doping leads to significant improvements of the scintillation performances. Afterglow following X-ray excitation is reduced down to 200 ppm after 20 ms and light yield is increased from 28,000 ph/MeV up to 34,000 ph/MeV under ²³⁵Cs-662 keV excitation. X-ray Absorption Near Edge Spectroscopy (XANES) was used to demonstrate that a significant part of the Ce ions are stabilized in the Ce⁴⁺ oxidation state in co-doped crystals. A new scintillation mechanism involving Ce⁴⁺ is proposed.

Index Terms—Afterglow, Ce⁴⁺, co-doping, LYSO, oxygen vacancies, scintillation mechanism, scintillator, thermoluminescence.

I. INTRODUCTION

LAST generation medical imaging equipment requires scintillators which possess outstanding scintillating performances. Among these a high light yield allows reducing the irradiation dose received by the patients during medical application and a more accurate diagnostic. For Positron Emission Tomography (PET), BGO was replaced since the early 2000s by LSO:Ce and LYSO:Ce single crystals. These materials show high density (7.4), high light yield (≈30,000 photons/MeV) and fast decay time (38 ns) and are of main interest for time-of-flight applications (TOF-PET). This is due to their good Coincidence Resolving Time (CRT) which improves the events statistics i.e., the rapidity of the TOF-PET systems [1]. The timing resolution of a scintillator is characteristic of its ability to determine the moment when the incoming photon was absorbed.

In order to improve the scintillation performances, we have recently reported [2] the positive effect of oxidizing annealing on LYSO:Ce, also shared by Ding et al. [3] and Chai [4], [5]. This work has pointed out the impact of point defects (oxygen vacancies in LSO and LYSO) on the scintillation properties.

In this paper, we report another efficient way to improve LYSO:Ce scintillation properties: co-doping with Ca²⁺ or Mg²⁺. The possibilities of co-doping Ce-doped rare-earth orthosilicates in general laser materials were reported by Zagumennyi et al. [6] and Zavartsev et al. [7]. Co-doping LYSO:Ce single crystals particularly with divalent cations such as Ca²⁺ and Mg²⁺ was actively studied in our laboratory [8] and patented with Saint-Gobain Crystals [9], [10]. Similar studies were carried out by Spurrier et al. on LSO:Ce compositions [11]. The choice of divalent cations is made for charge compensation considerations. Positively charged oxygen vacancies are efficient electron traps and their number or trapping efficiency may be reduced when introducing a lack of positive charges, e.g., by substituting a trivalent cation from the host by a divalent co-dopant. Charge compensation mechanisms will be discussed in depth in this paper.

The presence of Ce⁴⁺ in Ce-doped single crystals has always been a big issue. Many examples in the literature ascribe a yellowish coloration of orthosilicate crystals to Ce⁴⁺ [4], [5], [12]–[15]. Furthermore the presence of Ce⁴⁺ is also thought to be responsible for light yield losses. Consequently, it is common to try to minimize the amount of Ce⁴⁺ and it was shown by Melcher et al. [12] that no Ce⁵⁺ can be detected in typical LSO:Ce single crystals.

In this paper we first show that co-doping LYSO:Ce single crystals with Ca²⁺ or Mg²⁺ significantly improves both the light yield and the afterglow of this scintillator. We show for the very first time the presence of a significant quantity of Ce⁴⁺ in co-doped LYSO:Ce crystals. We then suggest a new mechanism involving Ce⁴⁺ participation in the scintillation process. We will also emphasize the fact that Ce⁴⁺ does not lead to any coloration in Ca²⁺ and Mg²⁺ co-doped LYSO:Ce.

II. EXPERIMENTAL

LYSO:Ce, and co-doped LYSO:Ce, Ca and LYSO:Ce, Mg single crystals were grown by the Czochralski technique by Saint-Gobain Crystals as described in [2]. Samples with a size of 10 x 10 x 10 mm with all faces polished were used for Pulse Height measurements whereas samples with a size of 10 x 10 x 1 mm with the two large faces polished were used for afterglow, optical absorption and thermoluminescence (TL) measurements. For all samples, the yttrium content is about 10%, the nominal cerium content is 0.22 at% and the
nominal co-dopant concentration is 0.1 at%. Due to segregation during the growth the final contents (given in wt. ppm) obtained by Glow Discharge Mass Spectrometry in the crystals (Head/Foot) were Ce (340/600) for LYSO:Ce, Ce (170/590) and Ca (32/43) for LYSO:Ce,Ca and Ce (170/580) and Mg (5/26) for LYSO:Ce,Mg.

The light yield and energy resolution of each crystal were determined by Pulse Height using a $^{137}$Cs (662 keV) source. The crystal was optically coupled to the window of a Hamamatsu R877-100 photomultiplier tube and covered with two Teflon reflector layers. The absolute value of the light yield was determined by comparing the channel of the photopeak with that of a LYSO:Ce single crystal reference exhibiting 28,000 photons/MeV. Variation of measurements on several samples from the same boule was ±1000–1500 ph/MeV.

Afterglow was measured after an X-ray excitation of several seconds provided by a tungsten tube operating at 120 kV and 13.3 mA. The afterglow measurements were carried out with a 1 ms integration time. Uncertainty is ±10–15 ppm.

Optical absorption was performed from 800 nm to 190 nm using a UV-Vis Cary 6000i double beam spectrophotometer.

For thermoluminescence (TL) measurements the samples were glued with silver paint to a copper sample holder attached to the cold head of a Janis cryostat and placed under vacuum. The sample was first excited in situ at 10 K for 10 minutes by a Molybdenum X-ray source operating at 50 kV and 20 mA. The beam goes through a Beryllium window in the cryostat and hits the sample surface at a 45° angle. The sample was heated at 20 K/min between 10 K and 650 K using a LakeShore 340 temperature controller. Luminescence was collected via an optical fiber by a Roper Scientific CCD camera cooled to −65°C coupled with an Acton SpectraPro 1250i monochromator equipped with a grating to allow spectral resolution. The emitted light was collected from the irradiated side of the sample at 45° to the sample surface. The same equipment was used for measuring X-ray excited luminescence (XRL) from 650 K to 10 K. The CCD camera shutter aperture was set to 1 s for XRL and 2 s for TL, allowing good signal to noise ratio.

X-ray Absorption Near Edge Spectroscopy (XANES) measurements were performed at the ANKA synchrotron facility of the Karlsruhe Institute of Technology, Germany. Analyses were done at the L$_3$ edge of Cerium from 5580 eV to 6116 eV in fluorescence mode. Powder references were used: CeF$_3$ and Ce(NO$_3$)$_3$$_2$ for Ce$^{3+}$ and CeO$_2$ for Ce$^{4+}$. Acquisition time was set at 12 s per point every 0.5 eV for the measurements on single crystals and 2 s per point every 0.5 eV for the references.

III. RESULTS

A. Scintillation Properties of Co-Doped LYSO:Ce

The light yield and energy resolution of LYSO:Ce, LYSO:Ce,Mg and LYSO:Ce,Ca single crystals were measured by pulse height technique and the obtained values are given in Table I. The relative XRL intensities were also determined by integrating the area under the emission spectra in the 300–800 nm range. Co-doping significantly increases the light yield, up to 12% with Mg$^{2+}$ and 21% with Ca$^{2+}$. Similar improvements can be noticed in the XRL intensity. Ca$^{2+}$ co-doping of LSO:Ce was also studied by Spurrier et al. and Yang et al. [16], [17]. A light yield increase was also reported with co-doping. Nevertheless, the energy resolution is only slightly improved for our crystals whereas Syntfeld-Kazuch et al. have reported an improvement up to 7.35% for some of their LSO:Ce,Ca crystals [18].

TL measurements were performed on LYSO:Ce and co-doped LYSO:Ce single crystals. The TL curves are given in Fig. 1. It can be seen that co-doping significantly reduces TL intensity, by a factor of 8 with Mg$^{2+}$ and a factor of 20 with Ca$^{2+}$. Furthermore, all peaks remain located at the same temperatures, i.e., 43, 113, 160 and 197 K for low-temperature peaks, and 354, 408, 462 and 525 K for peaks above 250 K, proving that traps are of same nature, as also shown in [2] for LYSO:Ce and LYSO:Tb. A last peak at about 557 K of lower intensity is only observed for LYSO:Ce.

In a recent work [2] we have evidenced that oxygen vacancies are the main defects in LYSO single crystals and are efficient electron traps. The TL curves evolution in Fig. 1 shows that Ca$^{2+}$ and Mg$^{2+}$ co-doping does not add additional traps and significantly reduces oxygen vacancies trapping efficiency. When comparing with our previously published results on air annealing effects [2] one can see that co-doping is more efficient in reducing TL intensity than air annealing. As the TL intensity decrease is not associated with a light yield reduction, the co-dopants do not act as quenching centers like for example Ce$^{3+}$ in Gd$_2$O$_3$:Pr$^{3+}$, Ce$^{3+}$ ceramics [19].

### Table I

<table>
<thead>
<tr>
<th>Crystal Composition</th>
<th>Light Yield (photons/MeV)</th>
<th>Energy Resolution</th>
<th>XRL Rel. Intensity</th>
</tr>
</thead>
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<tr>
<td>LYSO:Ce</td>
<td>28,000</td>
<td>8.9%</td>
<td>1</td>
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<tr>
<td>LYSO:Ce,Mg</td>
<td>33,000</td>
<td>8.4%</td>
<td>1.12</td>
</tr>
<tr>
<td>LYSO:Ce,Ca</td>
<td>34,000</td>
<td>8.5%</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Fig. 1. Color online—TL glow curves of LYSO:Ce (···), LYSO:Ce,Mg (→) and LYSO:Ce,Ca (—) single crystals after 10 min X-ray excitation at 10 K; $\beta = 20$ K/min.
In Ce-doped oxyorthosilicates as in other Ce-doped scintillators, the luminescence mechanism occurs in 3 steps:

1) $\text{Ce}^{3+} + \text{h}^+ \rightarrow \text{Ce}^{4+}$ (hole trapping)
2) $\text{Ce}^{4+} + e^- \rightarrow (\text{Ce}^{3+})^*$ (electron trapping leading to Ce$^{3+}$ in an excited state)
3) $(\text{Ce}^{3+})^* \rightarrow \text{Ce}^{3+} + \nu$ (radiative de-excitation followed by photon emission).

Oxygen vacancies as electron traps directly compete with Ce$^{3+}$ ions in electron trapping and it is known that deep traps (with depth $E \gg k_B T$) reduce the light yield [20], [21]. As shown in Fig. 1 co-doping significantly reduces TL intensity above 300 K which is therefore consistent with the light yield improvement reported in Table I. Furthermore traps with corresponding TL peaks around 350 K are known to be responsible for afterglow [22]–[24]. Thus LYSO:Ce afterglow, which is known to be important, is expected to be reduced by co-doping as a direct consequence of the TL intensity reduction observed around 350 K.

Afterglow measurements were performed on these crystals and the corresponding curves are given in Fig. 2. As expected co-doping significantly reduces delayed luminescence, up to one order of magnitude with Ca$^{2+}$. Similar improvements were also reported by Yang et al. for LSO:Ce,Ca though to a lower extent [17]. It is interesting to note that the achievable afterglow intensity at 20 ms is 200 ppm, a value which is comparable with that of Gd$_2$O$_2$:Pr,Ce ceramics that are used for Computed Tomography applications. Hence this result unveils that co-doped LYSO:Ce could be envisaged for CT applications.

As mentioned previously oxygen vacancies are the main electron traps in LYSO:Ce. Particularly, vacancies of the so-called oxygen 5 (the non-silicon bonded oxygen) are more likely to be created [25], [26]. This is due to loose $\text{O}_5$-RE bonding (RE stands for Lu or Y) for this anion in comparison to the other oxygen anions bonding in the oxyorthosilicate host [27], [28]. Divalent co-doping introduces a local lack of positive charges as Ca$^{2+}$ and Mg$^{2+}$ both substitute Lu$^{3+}$/Y$^{3+}$ cation of the host. This assumption is made regarding the sixfold-coordinated ionic radii of the co-doping ions (1.00 and 0.72 Å for Ca$^{2+}$ and Mg$^{2+}$, respectively) with that of the host cations (0.86 and 0.90 Å for Lu$^{3+}$ and Y$^{3+}$, respectively). Consequently a charge compensation mechanism most probably occurs between positively charged oxygen vacancies and negatively charged Ca$_{RE}$/Mg$_{RE}$ substitutions. This would lead to a reduction of electrons trapping efficiency by oxygen vacancies and therefore result in lower TL intensity, improved light yield and weaker afterglow.

### B. Evidence and Quantification of Ce$^{4+}$

The optical properties of the co-doped single crystals were investigated. Fig. 3 shows the absorption spectra of the LYSO:Ce and Ca$^{2+}$/Mg$^{2+}$ co-doped samples. The Ce$^{3+} \rightarrow 5d$ transitions are observed at 357, 294, 262 and 219 nm [29]. For the co-doped crystals an additional broad band is also noticed which peaks around 260 nm (4.8 eV). This absorption starts below 400 nm which is consistent with the fact that co-doped crystals are fully colorless. In order to get more information on the nature of this band several crystals were annealed in oxidizing atmosphere (48 h at 1500°C in air) and some in reducing atmosphere (12 h at 1200°C in Ar + 5% H$_2$). Their optical absorption was then characterized and the corresponding spectra are given in Fig. 4(a) for LYSO:Ce and in Fig. 4(b) for LYO:Ce,Mg (Ca co-doping gives similar results).

These measurements show that the broad absorption band intensity also depends on the crystal thermal treatment. It is less intense after reducing annealing and more intense after an oxidizing treatment. Furthermore, its intensity evolution is inversely correlated with that of Ce$^{3+} \rightarrow 5d$ band at 357 nm since a reducing treatment increases the Ce$^{3+}$ concentration while an oxidizing annealing reduces it. These observations are clearly in favor of the broad absorption band at 4.8 eV related to Ce$^{4+}$. More precisely it can correspond to a charge transfer (CT) band from the oxygen 2p orbitals of the valence band (VB) to the Ce$^{4+} 4f$ orbitals.

In order to confirm this hypothesis X-ray Absorption Near Edge Spectroscopy (XANES) at $L_\gamma$ edge of cerium was performed. LYSO:Ce,Mg and LYSO:Ce,Ca single crystals spectra...
are shown and compared with references spectra in Fig. 5. These measurements indeed confirm our hypothesis: Ca$^{2+}$ and Mg$^{2+}$ co-doped LYSO:Ce contain Ce$^{4+}$. Furthermore the ratio between Ce$^{3+}$ peak at 5727 eV and Ce$^{4+}$ peak at 5740 eV indicates that LYSO:Ce,Ca contains more Ce$^{4+}$ than LYSO:Ce,Mg. This is also in agreement with its more intense wide absorption band observed in Fig. 3.

XANES measurements also allowed an estimation of the relative amounts of Ce$^{4+}$ and Ce$^{3+}$ in both crystals by linear combination of the reference spectra for Ce$^{3+}$ and Ce$^{4+}$, respectively. LYSO:Ce,Mg and LYSO:Ce,Ca were found to contain about 20% and 35% of Ce$^{4+}$, respectively, which is far from being negligible (Table II). XANES spectra presented by Melcher et al. for LSO:Ce in [12] evidenced that non co-doped LSO crystals do not contain any Ce$^{4+}$. The estimated error made with this method of linear combination is ±10%.

To summarize LYSO:Ce,Mg and LYSO:Ce,Ca single crystals contain Ce$^{4+}$ ions in a non-negligible amount. The following parts of this paper are dedicated to possible scintillation mechanisms involving Ce$^{3+}$.

### C. Charge Transfer to Ce$^{4+}$ Ions in Co-Doped LYSO:Ce

To explain and predict CT energies a model for the trivalent lanthanides Ln$^{3+}$ was presented in [30]. It was shown that for VB to Ln$^{3+}$ CT transitions the energy $E^{\text{CT}}$ is roughly equal to the energy difference between the top of the VB and Ln$^{2+}$ ground state energy level ($\Delta E_{\text{VB} - \text{4f}}$). This model accurately allowed to determine the energy level positions of all Ln$^{2+}$ ions in several hosts [30] and was confirmed by thermoluminescence measurements for instance in YPO$_4$ [31], [32]. The question is now to determine whether it can be applied for CT to tetravalent lanthanides such as Ce$^{4+}$. If so the CT energy from VB to Ce$^{4+}$ in LYSO would be given by $E^{\text{CT}} \sim \Delta E_{\text{VB} - \text{4f}}$ where $\Delta E_{\text{VB} - \text{4f}}$ is the energy difference between the top of the VB and Ce$^{2+}$ 4$f$ ground state energy. Fig. 6 represents the main energy levels of Ce$^{3+}$ in LYSO. The bandgap is about 7.4 eV and the position of Ce$^{3+}$ 4$f$ levels was taken from [33]. The Ce$^{5+}$ 5$d$ levels were located thanks to LYSO:Ce absorption spectrum. According to this diagram one would expect VB to Ce$^{4+}$ CT energy at about 3.5 eV. Such transition would give rise to an absorption band with a component in the visible range (peaking around 376 nm).
This is the reason why it is common to think that Ce$^{4+}$ leads to a yellowish coloration of crystals [4], [5], [12]–[15]. The co-doped crystals that were prepared for this study are totally colorless while containing a significant amount of Ce$^{4+}$. However during our experience of many years of preparing LYSO:Ce single crystals some happened to be yellowish without any obvious explanation. Fig. 7 compares pictures and absorption spectra of one colorless LYSO:Ce,Mg single crystal with one non co-doped yellowish LYSO:Ce crystal. The absorption spectrum of the latter does not show any broad absorption band around 260 nm. Its coloration comes from the existing absorption starting around 525 nm. For better understanding the difference between the absorption spectrum of a yellowish crystal with that of a colorless LYSO:Ce,Mg was investigated in the 550 to 375 nm range. As shown in the inset of Fig. 7(c) this difference is partly hidden due to the beginning of the Ce absorption bands. Nevertheless it can be somehow simulated with a Gaussian band peaking around 3.2 eV. This value shows that the absorption which causes the coloration could be similar to the VB to Ce$^{4+}$ CT as expected according to the model of [30].

Nevertheless for co-doped LYSO:Ce single crystals the CT absorption band is observed around 4.8 eV rather than at 3.5 eV. The model described in [30] is based on 3 parameters: $E^{CT}$, $E_{rel}$, the relaxation energy of the system and $E_{n-h}$, the Coulomb interaction between the electron which was transferred and the hole which is kept on the anions. For CT to Ln$^{3+}$, both $E_{n-h}$ and $E_{rel}$ are about 0.5 to 1 eV and thus compensate each other, which explains why $E^{CT} \sim \Delta E_{VB-\gamma f}$. In the case of Ce$^{4+}$, a difference of 1.3 eV exists between $E^{CT}$ and $\Delta E_{VB-\gamma f}$. This suggests that the Coulomb interaction does not compensate for the relaxation energy of the system. Following the CT transition the final state is a Ce$^{3+}$ ion with a hole delocalized over the neighboring ligands. This charge-transfer state then transfers to its lowest energy by lattice relaxation. One possible explanation to our observations is that the co-dopant plays a role when it is located close to a Ce$^{4+}$ ion.

Another explanation can be found in the work of Fasoli et al. [34]. They have shown that the absorption spectrum of SiO$_2$:Ce which contains 100% Ce$^{4+}$ (and no co-doping) is only composed of a wide absorption band peaking at 4.8 eV. This could mean that the absorption signature of Ce$^{4+}$ is the same for similar hosts e.g., silicates in this case. This feature was also mentioned in [35] based on Jørgensen’s empirical formula to estimate the position of CT absorption band in Sr$_2$CeO$_4$. Thus for LYSO:Ce co-doping ions may only promote the stabilization of Ce$^{4+}$. To conclude the model in [30] which is suitable for CT to Ln$^{3+}$ has to be adapted to explain CT to Ln$^{4+}$. Finally this shows that the unexpected yellowish coloration of some LYSO:Ce crystals (Fig. 7) is not caused by Ce$^{4+}$ but rather by other defects or impurities.

D. Roles of Ce$^{4+}$ in Co-Doped LYSO:Ce

Co-doping LYSO:Ce single crystals with Ca$^{2+}$ and Mg$^{2+}$ significantly improves the light yield while decreasing the number of Ce$^{4+}$ luminescent centers, up to 35% less with 0.1% Ca in the bath. It seems that a positive compromise between two opposite effects occurs: the reduction of electron trapping by oxygen vacancies (positive effect) and the decrease of available Ce$^{3+}$ centers (negative effect). It is however puzzling to see that when the crystal contains 35% less Ce$^{3+}$ centers the light yield can be increased by 20%. Even more surprising results were reported by Yang et al. for LSO:Ce,Ca [17]. For 0.4% of Ca, a 13% light yield increase is measured. Interestingly the corresponding absorption spectrum shows a very intense CT absorption band at 260 nm and the Ce$^{3+}$+$\gamma f$ to $5d_{\gamma}$ band can barely be seen (see details in [17]). The following question arises: how can the light yield increase be explained when the number of Ce$^{3+}$ centers is decreased in such a way? This point is unfortunately not discussed in [17]. Finally in a recent work by Moretti et al. [35] it is shown that the XRL intensity of SiO$_2$:Ce which contains 100% Ce$^{4+}$ is similar to that of SiO$_2$:Ce with only Ce$^{3+}$. All these observations suggest that Ce$^{4+}$ cations indeed play a role.

Sr$_2$CeO$_4$ is one of the rare examples where Ce$^{4+}$ luminescence has been reported [35], [37]. In this material the emission was assigned to a ligand-to-metal CT transition of Ce$^{4+}$. However the spin-forbidden nature of this CT luminescence leads
to a decay time in the $\mu$s range which is not observed in our work on co-doped LYSO:Ce. Furthermore excitation spectra of co-doped LSO:Ce,Ca did not reveal any characteristic signal of Ce$^{3+}$ meaning that no energy transfer from Ce$^{4+}$ ions to Ce$^{3+}$ centers occurs [17]. Finally, no difference can be observed in the XRL emission spectra of LYSO:Ce, LYSO:Ce,Mg and LYSO:Ce,Ca or in LSO:Ce,Ca with different Ca concentrations [17]. These facts clearly mean that only Ce$^{3+}$ emission is observed. But how can Ce$^{3+}$ emission arise from Ce$^{4+}$ ions? Such a mechanism was proven in cathodoluminescence by Rotman et al. for YAG:Ce,Ca crystals [38]. A Ce$^{4+}$ ion traps an excited electron from the CB in one of its empty $5d$ energy levels which results in an excited Ce$^{3+}$ ion. The latter then de-excites radiatively giving the typical Ce$^{3+}$ emission. We suggest a similar luminescence mechanism considering Ce$^{3+}$ (Fig. 8).

An excited electron coming from the CB may be trapped by a Ce$^{4+}$ ion, leading to an excited Ce$^{3+}$ ion which then de-excites radiatively. This mechanism is only efficient if no direct electron-hole recombination occurs. In co-doped LYSO this is possible since holes can be trapped at Ca$^{2+}$/Mg$^{2+}$ co-doping ions or at Ce$^{3+}$ ions. In the latter case, while a Ce$^{4+}$ ion traps an excited electron, a Ce$^{3+}$ ion will trap a hole. After the emission step the trapped hole may be released and recombine non-radiatively with the electron so that the system is back to its initial state.

This mechanism explains our observations as well as those of Yang et al. [17] and Moretti et al. [36]. It is consistent with the latter where the existence of temporary Ce$^{3+}$ centers following irradiation was suggested.

To confirm this model luminescence quenching with temperature was also investigated. In order to have the same energy difference between $4f$ and $5d$ levels for Ce$^{3+}$ and Ce$^{4+}$ the Ce$^{4+}$ lowest $5d$ level is assumed to be located closer to the bottom of the CB than for Ce$^{3+}$ (Fig. 8). Since for Ce$^{3+}$ thermal ionization to the conduction band occurs around room temperature [29], a difference is expected with Ce$^{4+}$. Fig. 9 shows the XRL intensity of the single crystals of LYSO:Ce and LYSO:Ce,Ca measured from 650 K to 10 K and LYSO:Ce,Mg from 650 K to 100 K. The measurements were performed from high to low temperatures to avoid any possible contribution from thermally released charge carriers to the luminescence [22], [39]. These measurements show that quenching indeed starts at lower temperature for co-doped samples. More precisely, the more important the Ce$^{4+}$ concentration in the crystal the lower the temperature at which quenching starts. This shows that there could be a link between quenching temperature and Ce$^{4+}$ concentration, which reinforces our model. This comparison appears like a direct proof that luminescence of Ce$^{4+}$ via Ce$^{3+}$ ions occurs. Of course this mechanism occurs in addition to the well-known 3-steps process with Ce$^{3+}$ already presented earlier. To further confirm that efficient Ce$^{3+}$ emission occurs from Ce$^{4+}$ LYSO:Ce$^{4+}$ (with 100% Ce$^{4+}$) single crystals could be grown, but this has never been reported so far and seems pretty challenging.

IV. Conclusion

In this work it was first shown that co-doping LYSO:Ce single crystals with Ca$^{2+}$ or Mg$^{2+}$ significantly improves the key scintillation performances for medical imaging applications. The light yield can be increased up to 21% and the afterglow decreased by one order of magnitude.

For the very first time we provide a direct evidence of the presence of Ce$^{4+}$ in co-doped LYSO:Ce using XANES. An es-
timation of its quantity is also made: Ce$^{4+}$ concentration is not negligible as it reaches 35% in our LYSO:Ce,Ca samples. This work also evidenced for the first time the existing link between enhanced scintillation properties and important Ce$^{4+}$ content in co-doped crystals.

Finally, the necessity to consider the role of Ce$^{4+}$ in the light yield improvement led us to suggest a new luminescence mechanism. This model has been confirmed by a lower emission quenching temperature for Ca$^{2+}$ and Mg$^{2+}$ co-doped crystals. Many consequences could result from this mechanism. One of them is the suppression of one step out of three in the scintillation mechanism since the trapping of a hole by a cerium ion occurs after the emission step. Thus energy losses may be reduced which enhances excitation transfer efficiency.

This work opens a new path for scintillation properties improvements as it may be extendable to many other scintillators.

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REFERENCES


