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High Efficiency of Lutetium Silicate Scintillators, Ce-Doped LPS and LYSO Crystals for Medical Applications

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Abstract. The paper presents two cerium doped lutetium silicate crystals: pyrosilicate Ce:Lu₂Si₂O₇ (LPS) and Ce: Lu_{2(1-x)}Y_{2x}SiO₅ (LYSO). These two crystals exhibit the expected requirements for gamma detection: high density and high atomic number, high scintillation light yield, good energy resolution and fast response. LPS and LYSO crystals doped with cerium were grown by the Czochralski process. The crystal growth parameters were studied and optimized. Development of scintillators requires good understanding of the scintillation process. The location within the forbidden band gap of the localized lanthanide energy levels is analyzed by time resolved spectroscopy and thermoluminescence studies.

Introduction

A number of cerium doped silicate based scintillators have been developed, GSO (Ce: Gd₂SiO₅) [1], LSO (Ce: Lu₂SiO₅) [2] and LYSO (Ce: Lu_{2(1-x)}Y_{2x}SiO₅) [3, 4]. These materials exhibit desirable qualities for gamma-rays detection: high density, scintillation decay times shorter than 100 ns and light output exceeding that of BGO (Bi₄Ge₃O₁₂), which is still used for gamma-rays detection.

Cerium doped lutetium pyrosilicate (LPS), Ce³⁺: Lu₂Si₂O₇, is an inorganic scintillator, which displays particularly promising performance for applications such as positron emission tomography (PET) or oil well logging [5-7]. PET is a powerful medical method to follow the metabolism, blood flow and neurotransmission and the market is rapidly increasing. The main properties of Ce:LPS and Ce:LYSO are shown in Table 1, together with the properties of cerium-doped silicate (Gd₂SiO₅) and aluminate (LuAlO₃) scintillators.

Table 1 Properties of cerium-doped lutetium silicate and aluminate based scintillators

	GSO	LuAP	LYSO	LPS
Melting point (°C)	1950	1960	2050	1900
Density (g.cm ⁻³)	6.7	8.34	7.1	6.23
Z _{eff}	59	65	65	64
λ emission	430nm	365nm	420nm	385nm
LY (ph/MeV)	8,500	11,300	33,000	26,000
Decay times	56ns, 600ns	18ns	41ns, >2000s	38ns
Energy Resolution	/	/	7.5-9.5%	9.5-12.5%

Material

For the presented work, LPS and LYSO crystals were grown from the melt by a vertical pulling method (Czochralski process) using an iridium crucible. For LYSO, the yttrium content is 10% atomic.

The distribution coefficient (equal to $k=C_s/C_l$ where C_s and C_l are the cerium concentrations in the solid and the liquid phase, respectively) is 0.1 and 0.25 for Ce:LPS and Ce:LYSO, respectively. The low value for Ce:LPS is due to a larger radius of Ce^{3+} compare to Lu^{3+} ions which are substituted. In LPS structure (C2/m), there is a single crystallographic site for lutetium ions, with six oxygen neighbors. On the contrary, in the LYSO matrix, with a C2/c structure, the lutetium ions occupy two crystallographic sites, with seven and six oxygen neighbors respectively. Larger lutetium-oxygen distances are observed for lutetium with seven oxygen neighbors. The Ce^{3+} ion can more easily substitute lutetium in this large site, involving higher distribution coefficient in the LYSO structure.

Samples about 1 cm³ were cut and polished for scintillation measurements (see Fig. 1). The following part of the paper is mainly focused on the sample optical and scintillating properties.

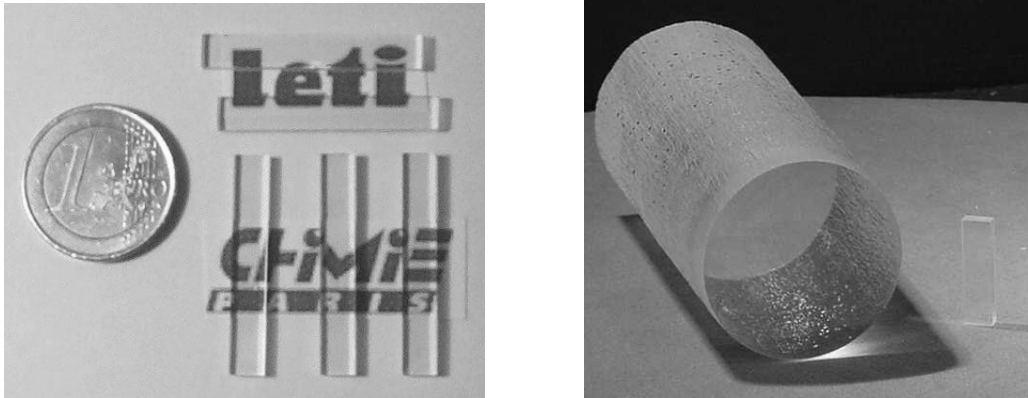


Fig. 1 On the left, LPS cut samples; on the right, LYSO crystals.

Optical Properties

In Fig. 2, the absorption (solid lines) and emission (dashed lines) spectra of LPS: Ce and LYSO: Ce, at room temperature, are presented. The main optical properties deduced from these experiments are gathered in Table 2.

Table 2 Optical properties of Ce-doped LPS and LYSO crystals art.

	LPS	LYSO
Absorption	349 / 303 nm	357 / 295 / 262 nm
Emission	378 / 405 nm	397 / 427 nm
Stokes shift	2,200 cm ⁻¹	2,800 cm ⁻¹

Figure 3 presents the temperature dependence of the decay time under UV-excitation for both materials. The rollover points of the decay time are close to 450 and 350 K for LPS and LYSO, respectively. For both materials, two distinct trends are observed. First, below the rollover point, the decay time slightly increases with temperature. Second, beyond the rollover point, when the temperature increases, the experimental lifetime strongly decreases.

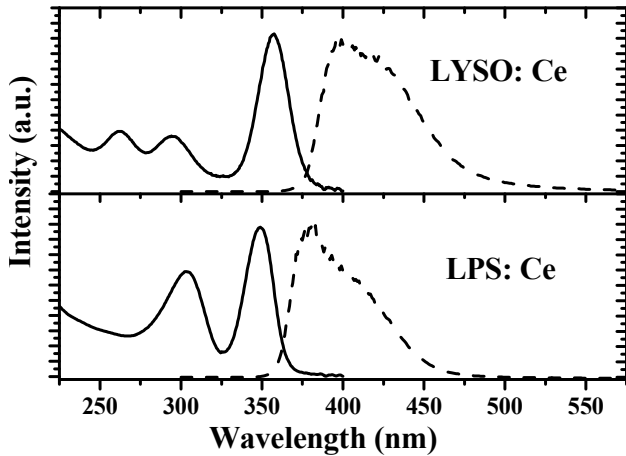


Fig. 2 Optical characteristics of $\text{Lu}_2\text{Si}_2\text{O}_7:\text{Ce}$ and $\text{Lu}_{1.8}\text{Y}_{0.2}\text{SiO}_5:\text{Ce}$ crystals at room temperature: absorption spectra (solid lines) and emission spectra (dashed lines) under X-ray excitation.

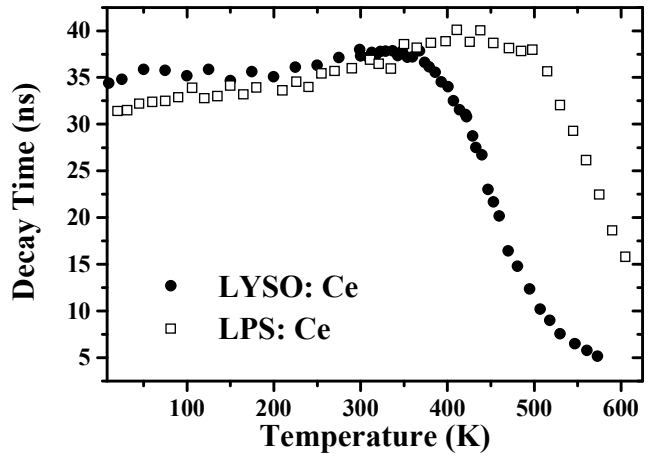


Fig. 3 Decay times ($\lambda_{\text{exc}}=355$ nm) of Ce^{3+} in LPS ($\lambda_{\text{em}}=385$ nm) and in LYSO ($\lambda_{\text{em}}=393$ nm) as a function of temperature.

Below rollover points, radiative transitions dominate and slow linear increase of τ_R with increasing temperature is observed for both compounds. For Ce-doped LPS, this increase is about twice that of LYSO: Ce. Such a thermal dependence of decay time is attributed to self-absorption phenomenon [8,9]. Ce^{3+} -emission can be delayed by self-absorption when an overlap between cerium absorption and emission bands exists (see the overlap in Fig. 2). As this delay depends on the overlap, it is linked to the band width and consequently to the temperature. In LPS, the Ce^{3+} -Stokes shift is smaller than in LYSO (Table II), so the self-absorption phenomenon is stronger in LPS, leading as observed to a more significant increase of the decay time with temperature.

Above rollover points, the rapid decrease of the decay time values means that non-radiative deexcitation dominates.

If we assume, as in [10], that quenching of Ce^{3+} luminescence is caused by autoionization of the $5d$ electron into the conduction band, then the lowest $5d$ level in LYSO is closer to the top of the conduction band than in LPS. The energy levels location within the forbidden band gap of the lanthanide localized energy levels is analyzed using several approaches: time resolved and XPS spectroscopies. The results are gathered in [11].

Scintillation Properties

Light output and energy resolution

Samples extracted from several boules present an average light yield of $26,300 \pm 3,000$ ph/MeV for LPS and $33,800 \pm 2,200$ ph/MeV for LYSO. The energy resolution ranges between 7.5 and 9.5% for LYSO, and between 9.5 and 12.5% for LPS (see Table 1).

The intrinsic background activity from the crystal itself was also measured. This background, obtained without excitation, arises from the beta decay of ^{176}Lu isotope, which represents 2.6% of natural Lu abundance. The intrinsic background activities of LPS: Ce and LYSO: Ce (10% Y) are equal to 219 and 263 $\text{counts}\cdot\text{s}^{-1}\cdot\text{cm}^3$ respectively, which is less than for LSO: Ce or LuAP: Ce (318 and 323 $\text{counts}\cdot\text{s}^{-1}\cdot\text{cm}^3$, respectively [12]).

High-temperature luminescence efficiency

Under gamma-ray excitation (^{137}Cs), the emission intensity as a function of temperature was measured for Ce-doped LPS and LYSO (Fig. 4). For LYSO: Ce, the light efficiency decreases significantly above room temperature, as it was observed for LSO crystals [13]. On the contrary, for

LPS: Ce, the luminescence efficiency remains very high when the temperature increases up to 450 K.

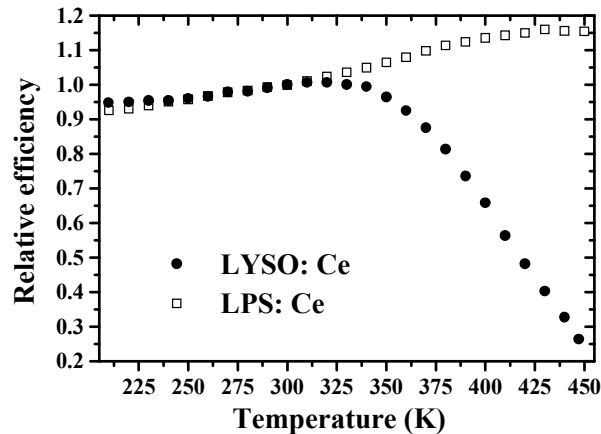


Fig. 4 Luminescence efficiency under gamma-ray excitation of LPS: Ce³⁺ and LYSO: Ce³⁺ as a function of temperature. For room temperature, the light yield (shaping time: 12 μ s) was normalized.

The different behaviors in term of high-temperature efficiency can be explained by the energy levels position of the 5d levels with regards to the conduction band position. The activation energy between the lowest 5d level and the conduction band is 0.28 eV in Ce:LYSO and 0.66 eV in Ce:LPS, therefore a lower quenching temperature is expected in LYSO, which is indeed observed in Fig. 4 [6]. This major difference in thermal behaviors could allow Ce: LPS scintillation detectors to be used under relatively high temperature conditions. For oil well logging, for instance, the temperature is about 90°C (385 K) at –2,000 meters depth and reaches 170°C (445 K) at about –5,000 m [14]. This material could be developed for this very important application.

Afterglow Consideration

For the afterglow analysis, we have first investigated the Ce:LSO material, which is well known to present a strong afterglow [15]. Then, Ce:LPS is compared to Ce:LSO and finally we have tried to limit the afterglow in Ce:LYSO. This latter aspect is indeed very important and is only slightly suggested here.

In thermoluminescence (TL) experiments, the afterglow phenomenon is linked to the peaks observed just above room temperature. Figure 5b shows the thermoluminescence glow curves for LPS: 0.25% Ce and LSO: 0.2% Ce crystals after exposure to β -irradiation. For LPS: Ce, the very low intensity of the 346 K-peak is in good agreement with the absence of afterglow experimentally observed. On the contrary, for LSO crystal, the 337 K-peak is very intense, consistent with the observed strong afterglow. For Ce:LYSO, a TL glow curve at about 340 K is also observed [16].

In Ce-doped rare-earth oxyorthosilicates, traps observed by thermoluminescence are linked to oxygen vacancies. In the case of YSO (Y₂SiO₅), which has the same structure as LSO and LYSO compounds, the TL glow peak around room temperature was attributed to vacancies located on one “not silicon-bound oxygen”, while TL glow peaks at higher temperature are due to oxygen vacancies in SiO₄ groups [17,18]. This can be easily understood by considering interatomic distances (Fig. 5a). As Lu-O distances are larger than the Si-O ones (about 2.2 Å and 1.6 Å, respectively), it is energetically more favorable to create vacancies on “loose” oxygen.

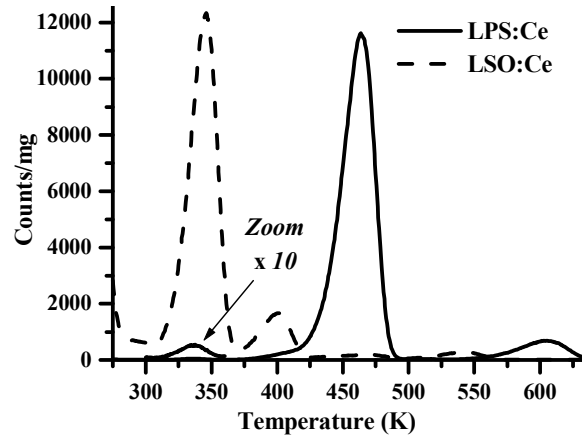
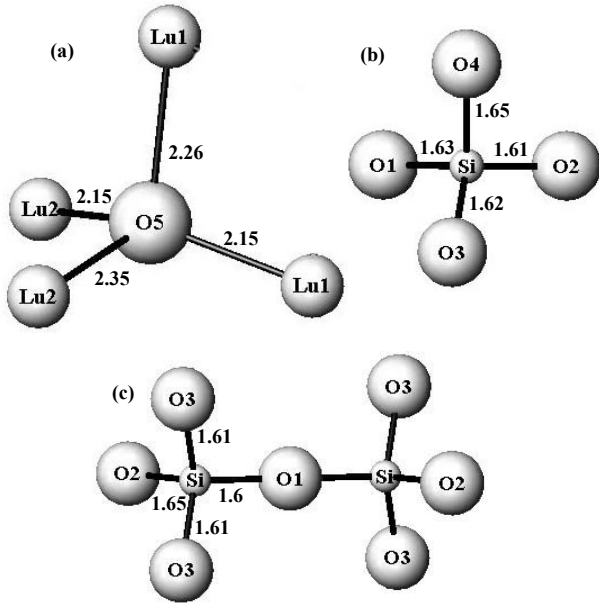


Fig. 5a Oxygen surroundings in LSO and LYSO structure: not silicon-bonded oxygen (a) and SiO_4 group (b). Si_2O_7 group in $\text{Lu}_2\text{Si}_2\text{O}_7$ (LPS) structure (c). Interatomic distances given in Angstroms.

Fig. 5b Thermoluminescence glow curves of LPS: 0.25% Ce and LSO: 0.2% Ce crystals (0.5 mm thick), recorded at a heating rate of 0.5 K.s^{-1} , after exposure for 20 s to β -irradiation ($^{90}\text{Sr} / ^{90}\text{Y}$ source, 1 mGray.s^{-1}).

On the contrary, all oxygens of the LPS structure ($C2/m$ crystal symmetry) are involved in Si-O bounds, via Si_2O_7 groups (Fig. 5c). In $\text{Lu}_2\text{Si}_2\text{O}_7$, all oxygens are bound to silicon and consequently, there are no potential oxygen vacancies linked to afterglow. So, the different behaviours in terms of trap creation and therefore of afterglow phenomenon could be explained by major differences between the crystallographic structures of LPS and LYSO, and more precisely, by differences in term of oxygen surroundings.

Considering Ce:LYSO, the TL glow curve around 340 K could be strongly modify by either thermal annealing or by modifying the sample composition to reduce the oxygen vacancies. Experiments are still in progress to fully understand this behaviour [19].

Conclusions

The scintillation properties of laboratory made LPS and LYSO samples were studied, they are gathered in the following Table. Even if $\text{Lu}_{1.8}\text{Y}_{0.2}\text{SiO}_5$ (LYSO) stopping power remains higher than that of $\text{Lu}_2\text{Si}_2\text{O}_7$ (LPS), Z_{eff} values are comparable and both of these scintillators display quite comparable behaviors in terms of light output and energy resolution. LYSO: Ce keeps advantages thanks to a high crystalline quality. However, LPS: Ce has minimal afterglow and promising high-temperature luminescence efficiency, contrary to lutetium oxyorthosilicates.

Table 3 Summary of scintillation properties and qualities of Ce:LPS and Ce:LYSO.

	Light Yield	Energy resolution	Decay time	Advantages
LPS	26,300 ph/MeV	9.5–12.5 %	38 ns	No afterglow High-temperature luminescence efficiency
LYSO	33,800 ph/MeV	7.5–9.5 %	41 ns afterglow	High light yield Good optical quality High stopping power

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