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Christelle Mansuy, Christophe Dujardin, Rachid Mahiou, Jean-Marie Nedelec. Characterization and Scintillation properties of Sol-Gel derived $\text{Lu}_2\text{SiO}_5:\text{Ln}^{3+}$ ($\text{Ln} = \text{Ce}, \text{Eu}, \text{Tb}$) powders. *Optical Materials*, 2009, 31, pp.1334-1336. 10.1016/j.optmat.2008.10.008 . hal-00395398

HAL Id: hal-00395398

<https://hal.science/hal-00395398>

Submitted on 15 Jun 2009

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Characterization and Scintillation properties of Sol-Gel derived $\text{Lu}_2\text{SiO}_5:\text{Ln}^{3+}$ (Ln = Ce, Eu, Tb) powders.

C. Mansuy^{1,2}, C. Dujardin³, R. Mahiou¹ and J.M. Nedelec^{1*}

¹Laboratoire des Matériaux Inorganiques, CNRS UMR 6002, Université Blaise Pascal,
Clermont-Ferrand 2 et Ecole Nationale Supérieure de Chimie de Clermont-Ferrand,
24 Avenue des Landais, 63177 Aubière Cedex, France

²Synthèse, Structure et Fonctions de Molécules Bioactives, CNRS, UMR 7613,
Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris, Cedex 05, France

³Laboratoire de Physico-Chimie des Matériaux Luminescents, CNRS UMR 5620
Université de Lyon, Université Claude Bernard Lyon 1, 6 rue A.M. Ampère, 69622
Villeurbanne Cedex, France.

* Corresponding author : Dr J.M. Nedelec
Laboratoire des Matériaux Inorganiques CNRS UMR 6002
Université Blaise Pascal, 24 Avenue des Landais, 63 177 Aubière Cedex, FRANCE
Tel 00 33 4 73 40 71 95
Fax 00 33 4 73 40 53 28
E-mail : j-marie.nedelec@univ-bpclermont.fr

Abstract

In this paper, we report the synthesis, the characterization and the scintillation properties of sol-gel derived Lu_2SiO_5 (LSO) powders. Ce^{3+} , Eu^{3+} and Tb^{3+} doped LSO powders have been synthesized by an original sol-gel process. The purity of the materials has been checked by X-Ray diffraction, confirming the elaboration of monophasic powders even for doped samples. Finally, the scintillation properties of the rare earth doped materials have been studied, the substitution of Ln^{3+} (Ln: Ce, Eu or Tb) for Lu^{3+} is confirmed, the scintillation yields have been calculated and the afterglow have also been measured, confirming the potentiality of the sol-gel derived LSO.

Keywords : Scintillation, LSO, sol-gel, medical imaging, X-ray conversion

1. Introduction

Since its discovery by Melcher and Schweitzer in 1992 [1,2], lutetium oxyorthosilicate Lu_2SiO_5 (LSO) has presented a great interest as scintillating material. Indeed, this material doped with Ce^{3+} ion yields a scintillator that shows a high scintillation yield (27300 photons/MeV), a short decay time (40 ns) and a high density (7.4 g/cm^3). These properties are particularly interesting for medical imaging applications and LSO seems to be a promising scintillator. It is now replacing BGO, a conventional scintillator, in positron emission tomography (PET). Generally, LSO is prepared as single crystal, but it is difficult to produce high quality single crystal and the maximum reachable concentration of doping ion is quite low. So we decided to synthesize this material by an original soft chemistry route, the sol-gel process, which allows to produce LSO at low cost with a control of the nanostructure of the materials and to reach high concentration of doping ion without any change of the material composition.

2. Experimental section

2.1 Powders preparation

$\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$, Eu^{3+} or Tb^{3+} powders have been elaborated by a sol-gel process described in a previous paper [3]. Samples in the 0.2% to 1%, 0.5% to 5% and 1% to 5% range have been prepared respectively for $\text{LSO}:\text{Ce}^{3+}$, $\text{LSO}:\text{Eu}^{3+}$ and $\text{LSO}:\text{Tb}^{3+}$.

2.2 Characterization

X-Ray diffraction patterns have been recorded on a Siemens D501 diffractometer working in the Bragg-Brentano configuration with Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$).

The excitation spectra of all the powders, doped with Eu^{3+} or Tb^{3+} , were recorded at room temperature using a Xenon lamp as continuous excitation source and a Triax 320 monochromator coupled with a CCD detector.

The scintillation spectra were recorded with a Jobin-Yvon Triax 320 monochromator coupled with a CCD camera after excitation of the samples with a tungsten X-ray tube working at 35 kV and 15 mA. Quantitative measurements were performed following conditions described elsewhere [4,5].

3. Results and discussion

3.1 Characterization

The X-Ray diffraction pattern recorded for LSO powders heated at 1200°C for 6h show the purity of the powders (Figure 1), whatever the doping ion and its concentration. The diffractogram corresponds exclusively to the LSO phase with no evidence for Lu_2O_3 or $\text{Lu}_2\text{Si}_2\text{O}_7$ phases. However, previous work [6] has shown the presence of Lu_2O_3 impurity in $\text{LSO}:\text{Eu}^{3+}$ samples by luminescence measurements. In effect, the sensitivity of XRD is quite low and so the contribution of impurity presents less than a few percent is undetectable.

3.2 Optical properties

Excitation spectra

The excitation spectra (not shown here) of LSO powders doped with Ce^{3+} , Eu^{3+} and Tb^{3+} ions have been recorded at room temperature by fixing the emission wavelength at respectively 420nm, 610 nm and 541nm. Excitation spectra for all doping concentration are similar. For $\text{LSO}:\text{Ce}^{3+}$, two bands characteristic of the transitions between $^2\text{F}_{5/2}$ ground state and the excited 5d levels $^2\text{T}_2$ and ^2E of Ce^{3+} are observed confirming the efficiency of the doping procedure. In the case of Eu^{3+} doped LSO, several bands are observed which correspond to

4f-4f transitions. A band observed at about 470 nm is attributed to ${}^7F_0 \rightarrow {}^5D_2$ transition and the ones situated in the 300 to 430 nm range correspond to ${}^7F_0 \rightarrow {}^5F_2, {}^5H_1, {}^5D_4, {}^5G_1, {}^5L_8, {}^5L_6, {}^5D_3$ transitions. An excitation band located below 250 nm should be assigned to the charge transfer absorption [7].

The excitation spectra recorded for LSO:Tb³⁺ powders, in the 300 to 400nm range, are characteristic of 4f-4f transitions. They correspond to ${}^7F_6 \rightarrow {}^5H_6, {}^5H_7, {}^5L_8, {}^5L_9, {}^5D_2, {}^5G_5, {}^5L_{10}, {}^5G_6$ and 5D_3 transitions [8].

Scintillation spectra

The room temperature emission spectra recorded under X-ray excitation for LSO powders doped with different concentrations of Ce³⁺, Eu³⁺ and Tb³⁺ ions are presented in Figure 2. BGO (Bi₄Ge₃O₁₂) and Gadox (Gd₂O₂S:Tb) emission spectra have also been recorded in order to estimate the scintillation yields. BGO and Gadox will respectively allow the scintillation yields measurements of Ce doped materials and Eu and Tb doped materials.

Figure 2(a) presents the emission spectra of LSO:Ce³⁺ powders. According to the crystallographic structure of LSO, Ce³⁺ ion can occupy the two crystallographic sites of Lu³⁺, both of C₁ symmetry. At room temperature, a broad band is observed in the 350 to 600 nm range, which is composed of two emission bands, characteristic of the $5d \rightarrow {}^2F_{7/2}$ and $5d \rightarrow {}^2F_{5/2}$ transitions of Ce³⁺, as previously observed by Melcher and al. [9]. The most intense emission is observed for LSO:Ce³⁺ (0.5%). The cerium doped materials present an emission in the UV-blue range.

The emission spectra recorded for LSO:Eu³⁺ powders consist of several bands in the 575 to 725 nm, which are characteristic of the ${}^5D_0 \rightarrow {}^7F_J (J = 0-4)$ transitions of Eu³⁺ ions (**Erreur ! Source du renvoi introuvable.**2(b)). The spectral distribution of the Eu³⁺ doped materials

results in a global orange-red emission. The presence of Lu_2O_3 impurity, highlighted in LSO:Eu^{3+} sample [6], is observed and contributes to the global emission.

For LSO:Tb^{3+} powders, the emission spectra exhibit in the 450 to 650 nm range, several bands characteristic of ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ ($J = 3-6$) transitions of Tb^{3+} ions (Figure 2(c)). ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition is the most intense and confers to the materials a green emission.

Scintillation yields

Scintillation yields have been calculated for all the powders by comparing the integrating areas of the emission spectra of the sample and the reference (BGO or Gadox). Scintillation yields under γ -rays excitation are respectively 8060 photons/MeV [10] and 78000 photons/Mev [11] for BGO and Gadox. The yields of our materials were calculated from reference values which are obtained under γ -ray excitation. Our measurements have been performed under X-ray excitation, so the results given for the scintillation yields under γ -ray excitation might be under-estimated [12]. The scintillation yields for all the samples and their evolution as a function of the doping ion concentration is presented in Figure 3.

The optimum are found for LSO:Ce^{3+} (0.5%), LSO:Eu^{3+} (2%) and LSO:Tb^{3+} (1.5%) with respectively scintillation yields of about 19000, 3000 and 13000 photons/MeV. The scintillation yield value obtained for LSO:Ce^{3+} is in good agreement with the literature [9] and very high besides the demonstrated presence of Ce^{4+} ions in sol-gel derived Ce doped scintillators [13].

Afterglow

Knowledge of the afterglow value of our materials is important for practical applications. The afterglow was only recorded on the materials corresponding to the optimal concentrations. The afterglow of Gadox ($\text{Gd}_2\text{O}_2\text{S:Tb}$) was also measured as a reference. The

materials present an afterglow 1 s after X-ray turn-off of 0.06%, 1%, 2% and 0.007% for LSO:Ce³⁺ (0.5%), LSO:Eu³⁺ (2%), LSO:Tb³⁺ (1.5%) and Gadox respectively. The afterglow effect for LSO:Ce³⁺ is weak and clearly not a limitation for practical applications whereas the one for LSO:Eu³⁺ is higher. In the case of LSO:Tb³⁺, the relatively high afterglow could be restrictive for practical applications.

4. Conclusion

The sol-gel process has been developed for the preparation of scintillating rare earth-doped LSO in form of polycrystalline powder. The advantages of the sol-gel process compared to traditional syntheses are a homogeneous distribution and a morphology control of the particles, the lower temperature of treatment and the good crystallinity.

The scintillation properties of Ce³⁺, Eu³⁺ and Tb³⁺ doped LSO were studied for different concentrations of doping ion. LSO:Ce³⁺ (0.5%) presents a high scintillation yield of about 19000 photons/MeV with a low afterglow which clearly demonstrates the interest of the sol-gel derived LSO scintillator for medical imaging.

Figures captions

Figure 1: XRD patterns recorded for LSO powders heated at 1200°C for 6h with the corresponding ASTM reference patterns (dotted lines)

Figure 2: Emission spectra recorded, at room temperature, under X-ray excitation on (a) LSO:Ce³⁺ (b) LSO:Eu³⁺ and (c) LSO:Tb³⁺, with different concentrations of Ce³⁺ (0.2% to 1%), Eu³⁺ (0.5% to 5%) and Tb³⁺ (1% to 5%).

Figure 3: Relative scintillation yields of (a) LSO:Ce³⁺, (b) LSO:Eu³⁺ and (c) LSO:Tb³⁺ samples.

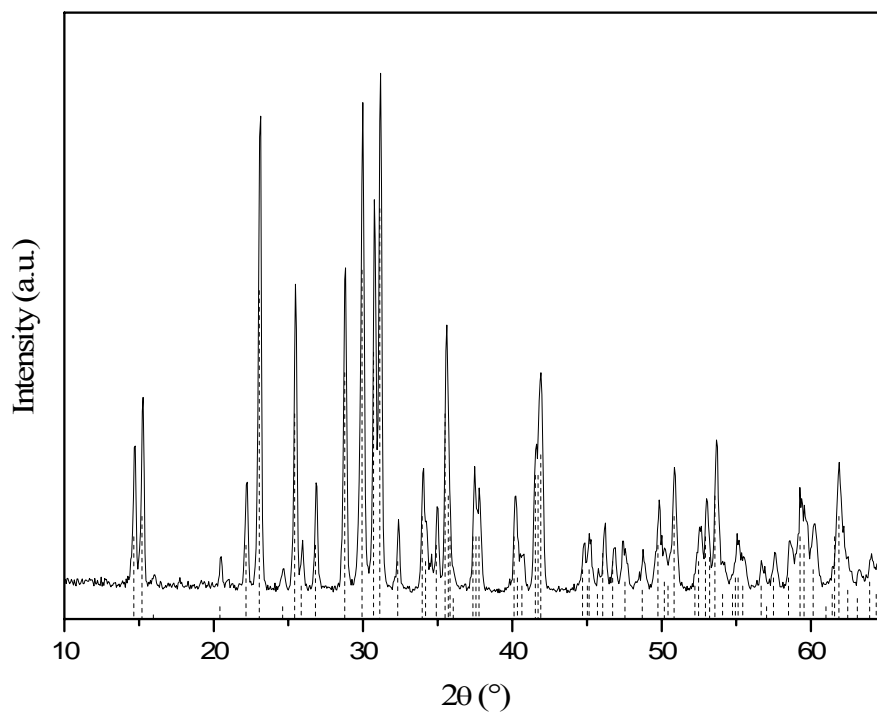


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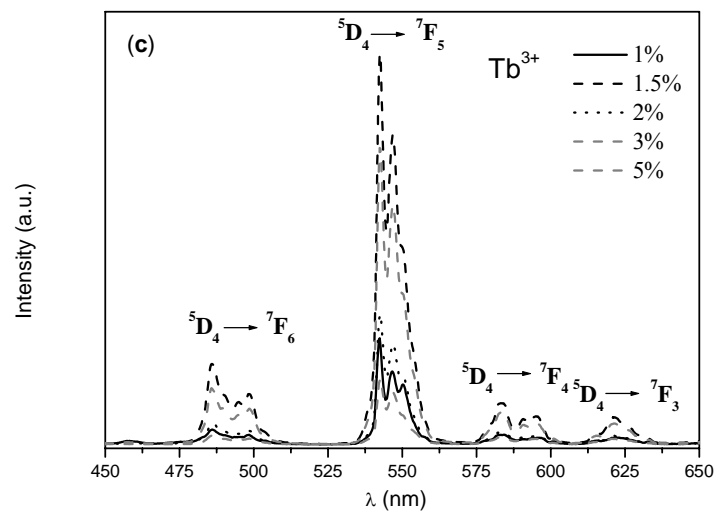
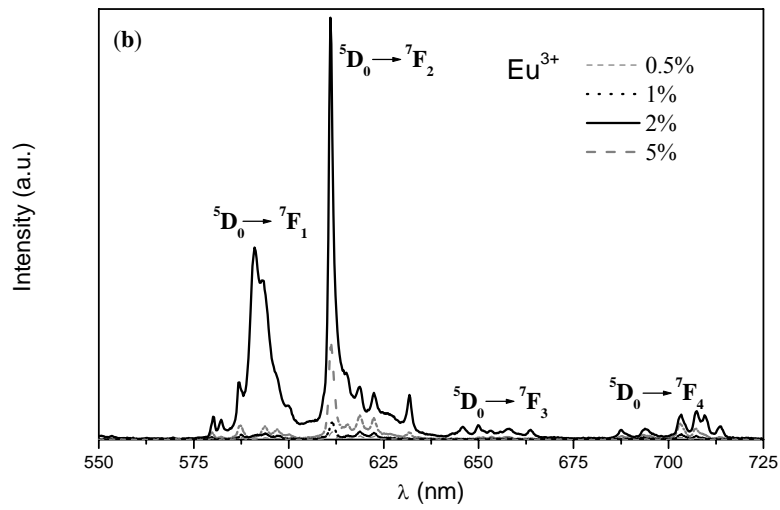
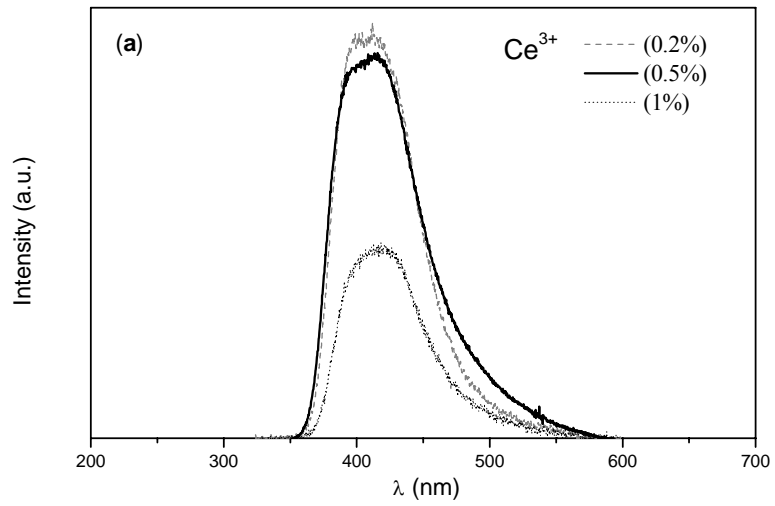


Figure 2: Emission spectra recorded, at room temperature, under X-ray excitation for (a) LSO:Ce³⁺ (b) LSO:Eu³⁺ and (c) LSO:Tb³⁺, with different concentrations of Ce³⁺ (0.2% to 1%), Eu³⁺ (0.5% to 5%) and Tb³⁺ (1% to 5%).

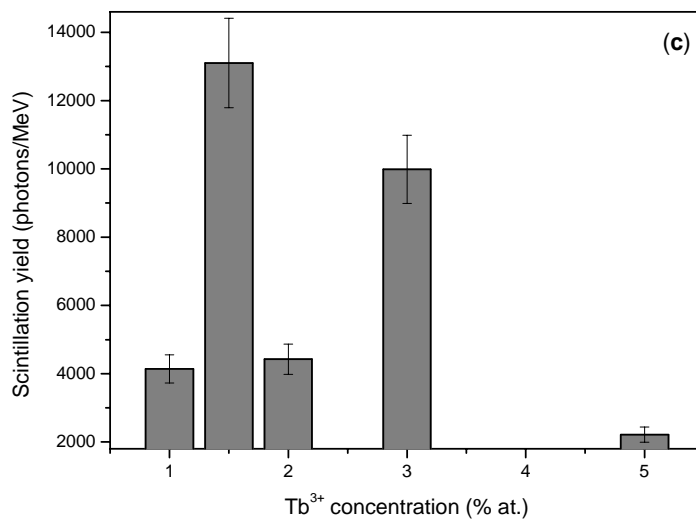
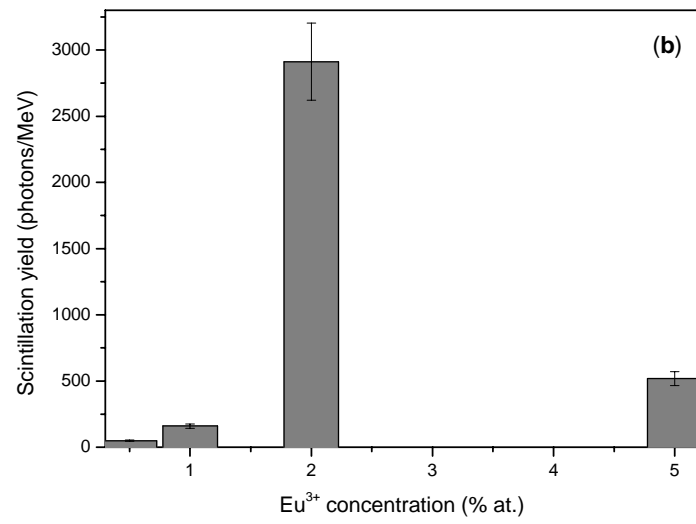
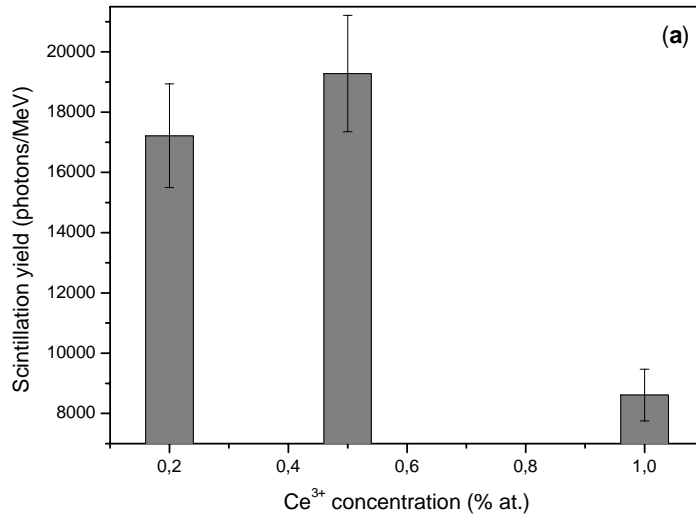


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