A New Sol−Gel Route to Lu_2SiO_5 (LSO) Scintillator: Powders and Thin Films

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Inorganic scintillators play a major role in high-energy physics, in medical diagnostic imaging modalities that use X-rays or γ-rays, and in industrial nondestructive measuring systems. Since its discovery by Melcher and Schweitzer in 1992,[1,2] Lutetium oxyorthosilicate Lu_2SiO_5 (LSO) has attracted a great deal of attention and has been recognized as one of the best scintillating materials. In effect, this material is the best compromise among fast scintillators (e.g., BaF_2), high light output scintillators (e.g., Gd_2O_2S:Tb), and dense scintillators (e.g., $Bi_4Ge_3O_{12}$). LSO itself does not scintillate and requires further doping with a luminescent center. Rare earth ions are particularly valuable and in particular Ce^{3+} ion with its allowed interconfigurational (5d to 4f) transitions and the 30000 cm^{-1} energy gap below its lowest 5d state. Activation of LSO with Ce^{3+} ion yields a scintillator that shows the highest light output (27300 photons/MeV) for oxide materials. Nevertheless, the production of high-quality LSO single crystal is difficult, the cost is very high, and the maximum reachable concentration of Ce^{3+} is quite low.

The aim of this communication is to report an original approach to produce LSO-based scintillating materials at low cost and with a control of the nanostructure of the materials. A sol−gel process has been developed to produce LSO doped with various rare earth ions (this communication will focus on Ce^{3+}). The sol−gel process allows the elaboration of LSO both as a powder and as a thin film. Bescher et al.[3] have proposed a sol−gel route to lutetium-containing scintillator but the scintillating phase was embedded in an amorphous matrix and was not clearly identified. So it is for the first time, to the best of our knowledge, that a specific sol−gel route has been proposed for LSO. The use of molecular precursors allows the control of the morphology and the texture of the powders and also the production of thin films.[4,5] Thin films are particularly interesting with the idea of producing X-ray intensifying screens where the scintillator is required as a homogeneous coating.

LSO materials were prepared by reacting Lutetium and silicon alkoxides in 2-propanol. Because of its cost and reactivity, the Lutetium alkoxide was produced in situ by a nucleophilic substitution on $LuCl_3$ by $^iPrO^-$, the alcoholate being prepared by reacting metallic potassium with anhydrous 2-propanol. The general scheme is

$$LuCl_3 + 3\,^iPrOH + 3K \rightarrow Lu(O^iPr)_3 + 3KCl\downarrow$$

The nucleophilic attack was performed by refluxing the metallic potassium with 2-propanol for 2 h under argon. Doping with rare earth ions was performed by adding the required amount of $LnCl_3$ to $LuCl_3$.

The silicon was introduced as tetraethoxysilane 99.99%. The solution was then stirred for 4 h at room temperature. KCl precipitate was filtered off by centrifugation.

For the preparation of powders, the resulting sol was then hydrolyzed to yield an amorphous powder, which was then densified at 1200 °C for 6 h to obtain the LSO powder.

For the preparation of thin films, the sol was used in a dip-coating process. Films were deposited onto silica substrates with a withdrawal rate of 8 cm/min. Four consecutive layers were stacked to obtain the final film with a heat treatment at 100 °C for 15 min followed by a treatment at 1000 °C for 15 min after each layer.

X-ray diffraction (XRD) performed on the powders obtained clearly demonstrates that a pure LSO phase is obtained (Figure 1b). XRD of thin films (Figure 1a) shows diffraction lines that correspond to the most intense lines of LSO surimposed onto a broad contribution of the amorphous substrate (silica). These first results confirm that the sol−gel process allows the preparation of pure LSO. It has also been observed that doping LSO with Ce^{3+}, Eu^{3+}, or Tb^{3+} up to 5 at. % does not affect the structure of the material and that the LSO phase is maintained with efficient substitution of Ln^{3+} for Lu^{3+}.

The morphology of the powders and thin films has been studied by scanning electron microscopy (SEM); typical images can be found in Figure 2. Figure 2a demonstrates the very low corrugations obtained for thin films. The film is highly homogeneous and its composition as checked by EDX corresponds to Lu_2SiO_5. Efficient doping with Ce^{3+} at. % was also confirmed by EDX. Figure 2b−d correspond to a LSO polycrystalline powder. The densification scheme can be reconstructed thanks to these pictures. The first step is the germination and growth of small spherical particles of about 450 nm. These particles can be observed in Figure 2b. The size distribution of these particles is very uniform, which can be seen as a direct consequence of the use of the sol−gel process. The second step is a coarsening of these primary particles. Figure 2c suggests a dissolution and reprecipitation process[6] driven by the difference of solubility between regions of positive and negative curvature. This leads to the creation of necks between

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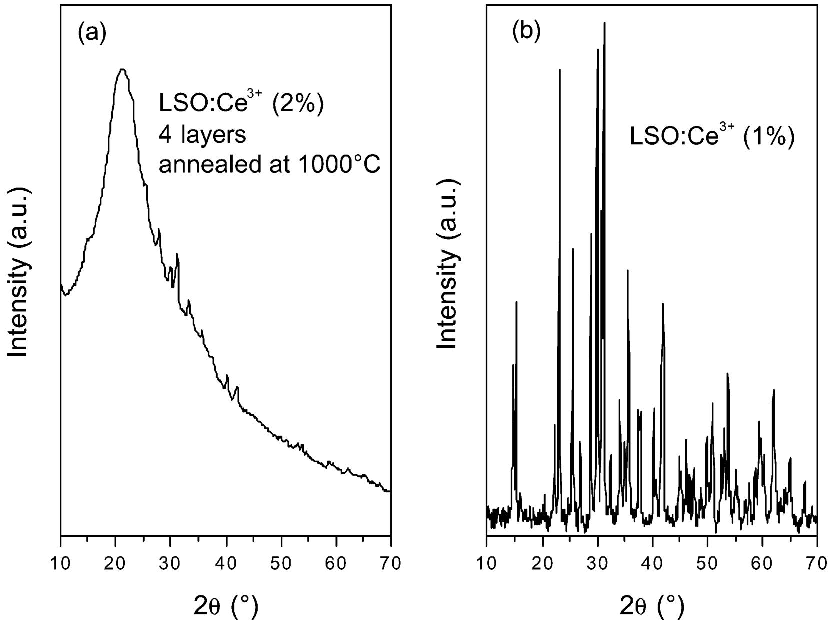

Figure 1. X-ray diffraction patterns for (a) LSO:Ce^{3+} 2% film consisting of four layers heat-treated at 1100 °C and (b) LSO:Ce^{3+} 1% powder.

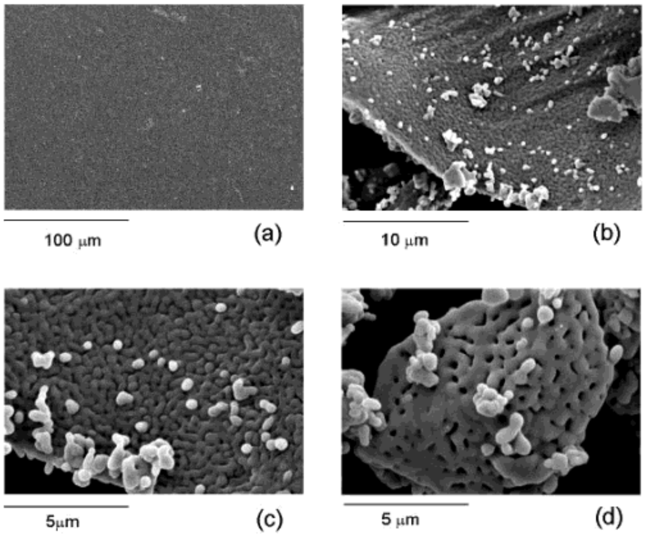

Figure 2. Scanning electron microscope images for (a) LSO thin film and (b), (c), and (d) LSO powder with different magnifications.

particles and a reinforcement of the network. It is also interesting to note that, as shown in Figure 2d, residual porosity still exists in the final grains. The coarsening and the porosity can be controlled by adjusting the heat treatment procedure; this is a very unique feature offered by the sol−gel approach.

Samples doped with Ce^{3+}, Eu^{3+}, and Tb^{3+} ions have been prepared and our method can be generalized to all rare earth ions. Results concerning Ce^{3+}-doped LSO will be given.

Figure 3 displays the scintillation spectrum of LSO:Ce^{3+} 0.5% obtained under X-ray excitation. A very broad spectrum ranging from 360 to 500 nm with two distinguishable components corresponding to the doublet $^2F_{5/2}$ $^2F_{7/2}$ is observed, as is usually the case for LSO.[7] A comparison of this spectrum with the one obtained in the same conditions for polycrystalline BGO ($Bi_4Ge_3O_{12}$) allows the determination of the relative efficiency of X-ray conversion for LSO:Ce^{3+}. Integration of the spectra over the whole wavelength range gives a scintillation yield of about 20000 photons/MeV (BGO: 8500 photons/MeV). This value is in good agreement with results published for LSO. The very high yield obtained clearly demonstrates the interest of the sol−gel-derived LSO scintillator. Further modifications of the conditions of preparation (alkoxides ratio, alcohol/alkoxide ratio, pH, etc.) would allow an optimization of the scintillation yield. In particular, the concentration of Ce^{3+} ions has not yet been optimized and the sol−gel route offers this unique possibility to vary it. Finally, afterglow measurements have been performed and show a similar behavior with the one already observed for LSO,[8] confirming the potentiality of this new route to LSO.

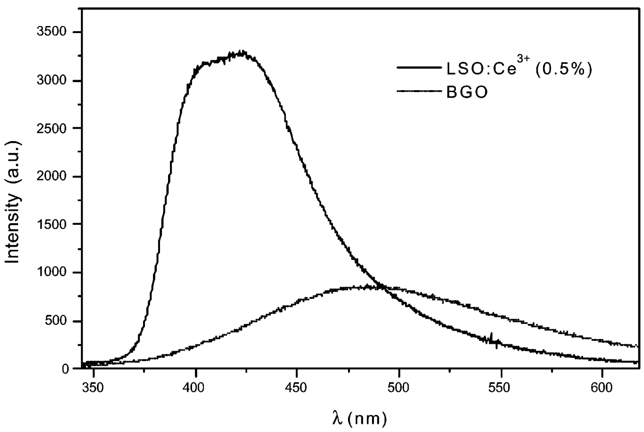

Figure 3. Scintillation spectra recorded under X-ray excitation for LSO:Ce^{3+} 0.5% and BGO powders.

In conclusion, a sol−gel process has been developed for the preparation of rare earth-doped LSO as poly-

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crystalline powder and thin films. In all cases, the unique phase observed is the monoclinic LSO.[9] The scintillation of these materials is very high and approaches that of LSO single crystal.[10,11] The sol−gel process offers a unique and low-cost way to control LSO scintillator morphology on a nanoscopic scale and to prepare homogeneous thin films while conserving the exceptional scintillation properties of the solid-state-derived material.

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