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Surface characterization of sol-gel derived scintillating rare-earth doped Lu₂SiO₅ thin films

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Abstract. Rare earth doped Lu₂SiO₅ thin films have been prepared by combining sol-gel process and spin coating. Annealing treatment results in the crystallization of the film and efficient incorporation of rare earth doping ions. XPS and RBS spectroscopies showed that the composition of the films is close to the nominal one. Adventitious carbon has been observed and attributed to incomplete pyrolysis of metal-organic precursors. XPS concentrations profiles show a good homogeneity for the films. RBS demonstrated some inter-diffusion between amorphous carbon substrate and silicate films resulting in a gradient of carbon at the interface between the substrate and the film itself.

1. Introduction

The development of efficient scintillating materials is a very active area. It has been demonstrated in the past few years that sol-gel chemistry constitutes an interesting alternative to solid state preparation of scintillators [1,2]. Among the various advantages of using the sol-gel process, the possibility to prepare easily thin films from the solution is very attractive. The high homogeneity of the sol-gel derived films coupled with the low processing cost associated with techniques like dip or spin coating or spray pyrolysis makes this technique suitable for industrial purposes. In the case of scintillators, the possibility to prepare high optical quality scintillating thin films is very valuable from the application point of view. In effect, such films would theoretically show very little scattering and thus higher resolution for imaging applications. Furthermore, the transparency of these thin films allows detecting the converted light in the transmission configuration which is very interesting for designing efficient and compact detecting systems. These thin scintillating films will also be of great interest for some fundamental studies such as absorption measurements in high energy range.

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 non-destructive measuring systems. Since its discovery by Melcher and Schweitzer in 1992 [3, 4], Lutetium oxyorthosilicate Lu₂SiO₅ (LSO), has attracted very much attention and has been recognized as one of the best scintillating materials. In effect, this material is the best compromise between fast scintillators (e.g. BaF₂), high light output

scintillators (e.g. $\text{Gd}_2\text{O}_2\text{S:Tb}$) and dense scintillators (e.g. $\text{Bi}_4\text{Ge}_3\text{O}_{12}$). 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 inter-configurational (5d to 4f) transitions and the 30 000 cm^{-1} energy gap below its lowest 5d state. Activation of LSO with Ce^{3+} ion yields a scintillator which shows the highest light output (27 300 photons/MeV) for oxide materials. In this paper, we report on the characterization of sol-gel derived LSO thin films doped with rare earth ions. X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectroscopy (RBS) have been used to check the composition of the films and to confirm the effective doping with rare earth ions. Profiles recording during XPS measurements give us some information on the homogeneity of the films, whereas modeling of the RBS curve brings evidence for diffusion during the annealing process.

2. Experimental section

2.1. Films preparation

LSO sol, used for the elaboration of the films, has been prepared by a sol-gel process described elsewhere [5, 6]. Doping ions concentrations have been chosen according to previous results obtained on sol-gel derived powders. The films have been deposited by spin coating on silica, CaF_2 and amorphous carbon substrates carefully cleaned following procedures detailed elsewhere [7]. The program used for the spin coating is the following: the first step, characterized by a slow rotation speed (200 rpm), allows depositing the sol at the middle of the substrate. Then, several 10 seconds steps are successively performed with a rotation speed of 1000, 2000, 3000, 4000, 5000 and 6000 rpm. Several coatings operations are necessary in order to have films with suitable thickness.

2.2. Characterization

All samples have been checked by X-Ray diffraction on a Philips Xpert Pro operating with the $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

X-ray photoelectron spectra were recorded using a VG Scientific 220XL Escalab. The monochromatized $\text{Al K}\alpha$ source operated at 150 W (spot diameter~1 mm). The energy analyser operated in a constant pass energy mode of 30 eV using the magnetic mode facility. Due to the insulating character of the samples, an electron flood gun source of 6 V was applied to the samples during analysis to compensate the charging effect. The pressure in the analysis chamber was lower than 10^{-9} mbar. The binding energy scale was refereed to the position of the C 1s line at 285 eV of the adventitious carbon.

Depth profiles were recorded using Ar^+ -ion beam with the following experimental parameters: argon gas pressure $1.1 \cdot 10^{-7}$ mbar, ion energy 3 keV, ion current 1 μA , rastered area $7.5 \times 7.5 \text{ mm}^2$. The present spectra of Ce $3d_{3/2,5/2}$, Si 2p, Lu 4d, Lu4f, O 1s, Ca 2p, F 1s and C 1s levels were recorded with a higher pass energy of 50 eV, using a smaller spot diameter (500 μm) to avoid edge effect of the crater.

Rutherford backscattering spectra were recorded at CERI-CNRS Orleans, France. The equipment consists of a Van-de-Graaff linear accelerator with an energy range from 0.5 to 2.5 MeV. The measurements were carried out with 2 MeV 4He^+ ions. The integrated charge was 20 μC and the ion current 15 nA. The thin films deposited on amorphous carbon were about 150-250 nm thick, the RBS measurements probed consequently both the thin films and the underlying substrate since the penetration depth of the ions was several microns. The spectra were analyzed with SIMNRA software version 5.0 [8].

3. Results and discussion

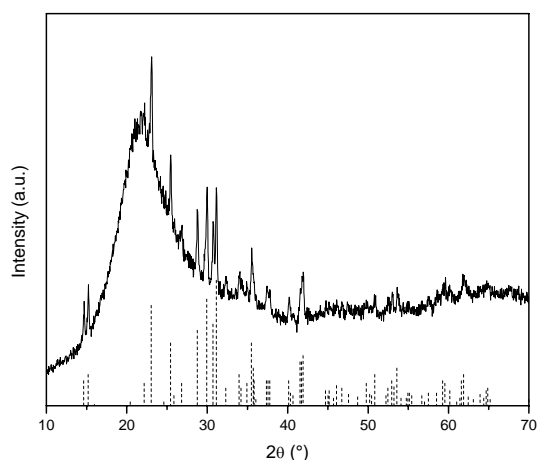


Figure 1 : X-Ray Diffraction pattern for a LSO:Tb 5% film.

All the recorded diffractograms are identical (Figure 1) and show the LSO crystalline phase. A broad band at 20° is observed and is assigned to amorphous silica substrate. The substitution with rare earth ions (Tb, Ce, Eu) does not modify the structure of the material. XPS spectrum recorded on LSO : Ce 1% film deposited by a single step spin coating is presented in Figure 2. Cerium concentration has been increased up to 1% at. (actual optimum concentration for scintillation 0.5 % at.) to decrease the required acquisition times while keeping a value close to the optimum. Photopeaks corresponding to the expected elements are observed together with carbon C 1s. The adventitious carbon probably comes from the incomplete decomposition of the alkoxides precursors.

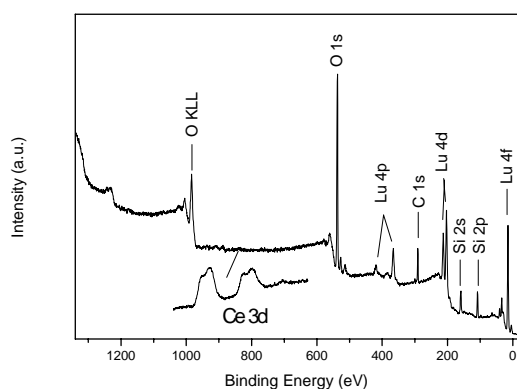


Figure 2: XPS spectrum of a LSO:Ce 1% film with enlarged view (870-930eV) of the cerium region

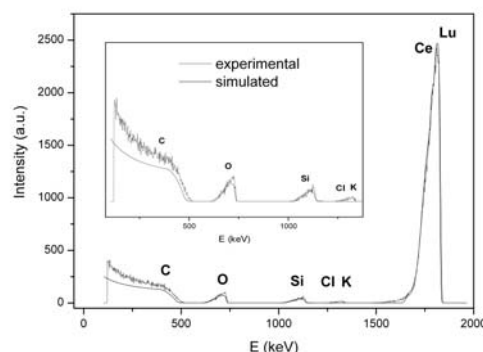


Figure 3: RBS spectrum of a LSO:Ce 1% film and corresponding fit (dotted line)

Atomic Ratio	Si/Lu	O/Lu	Ce/Lu
XPS	0.4	2.68	0.0056
RBS	0.505	2.526	0.0099
Theoretical	0.495	2.475	0.01

Table 1: Atomic ratios determined from XPS and RBS measurements for a LSO: Ce1% film

Depth profiles have been obtained within the film by Ar⁺ etching. From the obtained values in the constant part of the profiles, the composition of the film has been determined (Table 1). The doping with Ce³⁺ ions appears to be effective but the concentration is somewhat lower than the expected value. Quantification of cerium is difficult and performed only with the 3d_{3/2} peak because of the overlapping of F auger and Ce 3d_{5/2} peaks. The measured composition is close to the nominal one.

The surface contamination by C species resulting from the calcination of organic products initially present in the coating solution decreases rapidly upon etching (from 12 % to about 2% after 100 min etching) indicating that the contamination is mainly limited to the top surface of the film. The interface between the silicate film and the CaF₂ substrate is quite well-defined and the film appears to be homogeneous in a wide range of depth. Nevertheless, the profile of the cerium is quite different, for

the distribution of Ce^{3+} ions varies throughout the film with a maximum plateau observed around the middle of the film. However, some diffusion of Ce into the CaF_2 substrate seems to occur as suggested by the nonzero concentration below the film–substrate interface [9].

An RBS spectrum measured on a LSO: Ce 1% film deposited by 8 consecutive coating steps on a vitreous carbon substrate shows contributions of all the elements of the film (Figure 3). The thickness of the layer and its stoichiometry were extracted from the spectrum. Due to the overlapping of the Lu and Ce contributions, and the low concentration of cerium, its quantification is difficult and not very accurate but the value has been confirmed by XPS. In addition to the expected elements, a contribution corresponding to K and Cl is also observed. This potassium chloride (about 4 at. % KCl.) is a side product of the metathesis reaction for the preparation of the rare earth alkoxides. This impurity not observed in XPS measurements could be easily eliminated by careful centrifugation and washing during the synthesis. The atomic ratios of the film derived from the analysis of the RBS spectrum are given in Table 1. The composition is very close to the nominal one. Assuming the density of the film to be the one of the dense silicate (7.4), one can also derive the thickness of the film which is 97 ± 10 nm.

If one looks into details, the complex shape of the spectrum suggests some possible diffusion between the elements of the film and the substrate. A careful fitting has been performed taking into account 15 layers. The first layer is assumed to have the $\text{Lu}_2\text{SiO}_5:\text{Ce}$ composition (see Table 1) whereas layer 15 is the carbon substrate. Intermediate layers (2-14) containing various amount of carbon have been introduced to fit the experimental profile and the final fit is presented in Figure 3. The experimental spectrum is very well reproduced and this confirms the diffusion of carbon in the film. This diffusion might be a consequence of the porous nature of both the carbon substrate and the as deposited sol-gel film. Annealing treatment performed after each coating step would favor the interdiffusion of the two layers and progressive stacking of the layers results in a gradient of carbon in the silicate film. It is also worthy to note that, as already mentioned before, some carbon surely comes from the decomposition of the non reacted alkoxides group of the precursors.

4. Conclusion

Crystalline rare earth doped Lu_2SiO_5 films have been successfully prepared by the sol-gel process. The composition of the films is very close to the nominal one and doping with rare earth ions is efficient. Carbonaceous residues coming from the precursors are observed in the first atomic layers possibly limiting the scintillation yield of the film. Diffusion of Cerium ions towards the silica substrate is observed by XPS and inter-diffusion between the amorphous carbon substrate and the whole layer is evidenced by RBS. The difference in behavior is attributed to the nature of the substrate.

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