CONDENSED MATTER

EFFECT OF ALUMINUM SUBSTITUTION ON THE PHASE STABILITY AND LUMINESCENCE PROPERTIES OF Eu-DOPED LANGANITE NANO-POWDERS SYNTHESIZED BY A CITRATE SOL-GEL METHOD

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Abstract. Eu-doped langanite ($La_3Ga_{5.5}Nb_{0.5}O_{14}$) nanopowders with 10% at. gallium substituted by aluminum were prepared by a citrate sol–gel method and annealed in air at various temperatures between 700ºC and 1100ºC. For annealing temperatures up to 900ºC, only the langanite phase is observed. For higher annealing temperatures, very small quantities of langanite transform in β-Ga_2O_3, as evidenced in XRD spectra. The reddish color of the powders due to color centers associated to oxygen defects intensifies with increasing annealing temperature. A clear correlation between the area of the Eu^{3+} absorption bands (extracted from the diffuse reflectance spectra) and the integral luminescence was observed.

Key words: langanite, nanopowder, sol–gel, Eu^{3+}, luminescence.

1. INTRODUCTION

The search of new and efficient phosphors for solid-state lighting is a problem of great interest in present. The rare earth doped phosphors are efficient, but the matching between the emission of the LED and the narrow absorption lines of the phosphor remains an open problem. A solution could be the use of partially disordered crystals as hosts for rare-earth ions showing wider absorption lines [1, 2]. Such hosts could be the crystals from the langasite family (generic – LGX), namely langasite (LGS – $La_3Ga_5SiO_{14}$), langanite (LGN – $La_3Ga_{5.5}Nb_{0.5}O_{14}$) and langatate (LGT – $La_3Ga_{5.5}Ta_{0.5}O_{14}$). In Ref. [1], the Eu-doped LGX powders were

obtained by milling single crystals grown previously by Czochralski method, but this is a rather expensive approach. Other methods resulting directly in powders would be of interest. Such a method, involving lower temperature synthesis, is the sol–gel approach [2, 3–6].

Recently, we synthesized Eu-doped langanite powders using the sol-gel method [2, 3]. The powders were annealed in air at temperatures between 700ºC and 1 000ºC. Pure langanite phase was obtained for the samples annealed at 700ºC and 800ºC. For higher annealing temperatures, part of the langanite phase transforms in perovskite ($LaGaO_3$). In order to evaluate the effects of the thermal treatments on the performances of the Eu-doped LGN powders as red phosphors, the stability of the LGN phase for higher calcination temperatures is of a real interest. In this paper we present the preliminary results concerning the effects of the partial substitution of Ga^{3+} by Al^{3+} on the stability of the langanite phase and on the luminescence properties of Eu-doped langanite synthesized by a citrate sol-gel method. The effect of thermal treatments is examined using XRD and optical spectroscopy.

2. EXPERIMENTAL

The Eu (3 at.%)-doped $La_3(Ga_{0.90}Al_{0.10})_{5.5}Nb_{0.5}O_{14}$ (LGAN) powder was obtained using the citrate sol–gel method [5-7]. For preparing the nanoparticles, $La(NO_3)_3 \cdot 6H_2O$, $Ga(NO_3)_3 \cdot 5H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Nb(OH)_5$ and citric acid were used as precursors, in the corresponding ratios. First of all, $Nb(OH)_5$ was synthesized by fully dissolving Nb_2O_5 in HF, followed by the addition of ammonia. The white powder of $Nb(OH)_5$ was then dissolved in an aqueous solution of citric acid. The resulting sol was stirred until a clear solution has been achieved. Then, an aqueous mixture containing La^{3+}, Ga^{3+}, Al^{3+}, and Eu^{3+} nitrates has been added to the Nb-citrate system, with constant stirring. The final solution was stirred for another 1 h, heated in an oven at 80ºC, until a very viscous gel has been formed. The brown-yellow colloid was dried at 110ºC, and then calcined in air at temperatures between 700ºC and 1 100ºC.

XRD measurements were performed on a PANalytical X'Pert PRO MPD diffractometer (CuKα). The fluorescence of the Eu:LGAN was excited using a ScienceTech Xe-Hg 350-W lamp with suitable filters. The fluorescence spectra were recorded using a Horiba Jobin-Yvon 1000M monochromator, an S-20 photomultiplier and an SR830 lockin amplifier from Stanford Research Systems. The experimental setup for diffuse reflectance measurements was described elsewhere [1, 8, 9]. All measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

In Fig. 1 are shown the XRD patterns for Eu-doper LGAN powders annealed at temperatures between 700°C and 1100°C. For the samples annealed at 700°C, 800°C and 900°C, all the observed diffraction lines belong to the LGN phase. For higher annealing temperatures (100°C and 1100°C), besides the diffraction lines corresponding to the LGN phase, other diffraction lines, but with very low intensities, are identified as belonging to β-Ga_2O_3 (denoted with stars in Fig. 1).
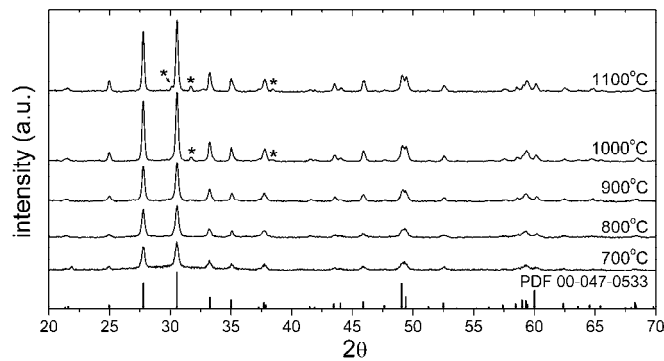

Fig. 1 – XRD patterns for LGAN nanopowders annealed for five hours in air at temperatures between 700ºC and 1100ºC. The dominant phase is LGN (card PDF 00-047-0533). The diffraction extra-lines, denoted by *, observed for the samples annealed at 1000ºC and 1100ºC, belong to β-Ga_2O_3 phase (card PDF 00-043-1012).
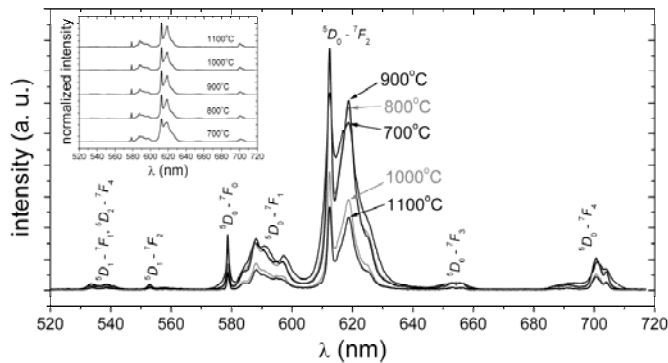

Fig. 2 – Luminescence spectra of Eu^{3+} in LGAN nanopowders annealed at various temperatures. The spectra are not corrected for the spectral sensitivity of the experimental apparatus. Inset: normalized luminescence spectra, for a better visualization.

The luminescence spectra of Eu^{3+} in LGAN powders were excited in the 360-400 nm domain (absorption transitions $^7F_0 \rightarrow ^5D_4$, ^5G_J, $^5L_7$, $^5L_6$). In Fig. 2 is given the luminescence spectrum of Eu^{3+} in LGAN. Besides the luminescence lines

originating in $^5D_0$, lines from $^5D_1$ and $^5D_2$ levels are also observed. In inset, the spectra are normalized for a better visualization. Though the intensity of the luminescence spectra diminishes with the annealing temperature, the shape of the luminescence spectra remains practically unchanged.
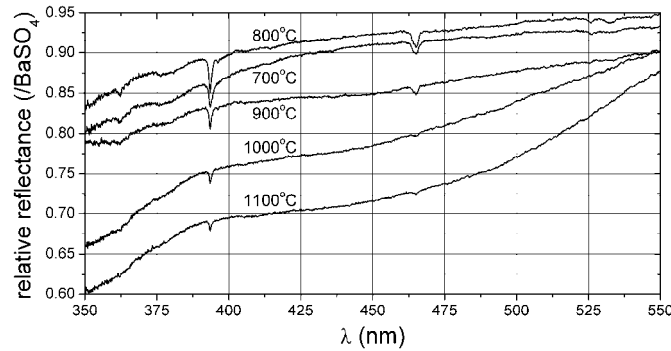

Fig. 3 – Reflectance spectra of Eu:LGAN nanopowders annealed at various temperatures. The reduction of the area of the $^7F_0 \rightarrow {}^5L_6$ transition (at ~ 395 nm) is evident.

The diffuse reflectance spectra of the Eu:LGAN powders are given in Fig. 3. The spectra are given in rapport with the 'white' $BaSO_4$. The absorption lines corresponding to the transitions from $^7F_0$ and $^7F_1$ levels (populated at room temperature) are visible. The baselines of the diffuse reflectance spectra are tilted towards shorter wavelengths, more tilted for higher annealing temperatures (i.e. the reddish coloration of the samples is intensified with the annealing temperature). The red coloration of the crystals from the langasite family is related to point defects involving oxygen [10–12]. Besides the intensification of the reddish coloration, the reduction of the Eu^{3+} absorption bands is observed. This reduction is very clear for the $^7F_0 \rightarrow {}^5L_6$ absorption band (at ~395 nm), the main absorption band in our pumping conditions.
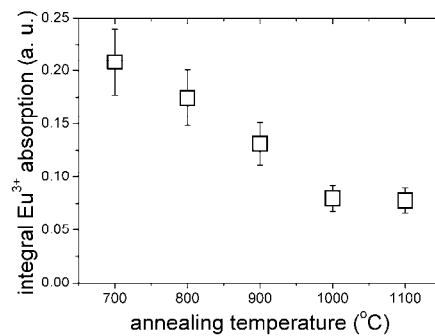

Fig. 4 – Integral area of the Eu^{3+} absorption bands (in the 360-400 nm domain) in LGAN nanopowders, function of the annealing temperature.

In Fig. 4 is given the area of the Eu^{3+} absorption bands calculated in the 360-400 nm domain (the pumping domain, in our experimental conditions) as a function of the annealing temperature. The area of the absorption bands decreases rapidly for the annealing temperatures between 700ºC and 1000ºC and more slowly for higher temperatures.
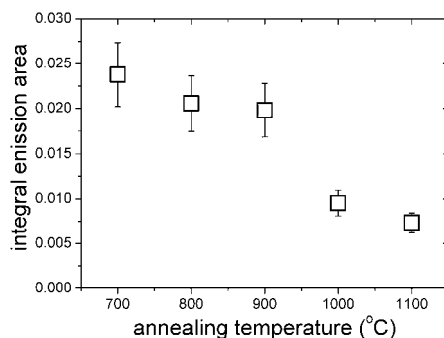

Fig. 5 – Luminescence intensity of Eu^{3+} (area of the luminescence spectra)
in LGAN nanopowders, function of the annealing temperature.

The dependence of the area of the luminescence lines of the Eu:LGAN nanopowders on the thermal treatment temperature is shown in Fig. 5. Comparing Figs. 4 and 5, a correlation is visible between the Eu^{3+} absorption (calculated from the diffuse reflectance spectra) and Eu^{3+} emission. It results that the reduction of the emission efficiency for increasing annealing temperatures is done mainly by the reduction of the effective absorption of Eu^{3+} due to the screening effect of the color centers, in spite of the improved crystallinity and removal of the adsorbed impurities. The same behavior was observed previously for Eu-doped LGN nanopowders [2], but in the case discussed in the present paper, for pumping in f lines, there is practically no superimposed influence of the phase transformation and the correlation between absorption (Fig. 4) and emission (Fig. 5) is meaningful.

4. CONCLUSIONS

Eu-doped langanite powders with Ga^{3+} partially substituted by Al^{3+} (10 at. %) were obtained from a citrate sol–gel synthesis and thermally treated at temperatures between 700ºC and 1100ºC. For annealing temperatures up to 900ºC, only the langanite phase is observed in XRD. For higher annealing temperatures, very small intensity diffraction lines belonging to the β-Ga_2O_3 phase are observed.

We found a correlation between the area of the Eu^{3+} absorption lines (extracted from the diffuse reflectance spectra) and the area of the luminescence spectra. This correlation indicates that the reduction of the emission efficiency for

increasing annealing temperatures is done mainly by the reduction of the effective absorption of Eu^{3+} due to the screening effect of the color centers, in spite of the improved crystallinity and removal of the adsorbed impurities.

In order to estimate the real possibilities of Eu-doped langanite powders as red emitting phosphors, the formation of color centers should be avoided. Thermal treatments in controlled atmosphere could preclude the formation of such color centers. Such experiments are now in progress.

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