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Synthesis dependent luminescence efficiency in Eu^{3+} doped polycrystalline YBO_3†

Damien Boyer, Geneviève Bertrand-Chadeyron,*‡ Rachid Mahiou, Christophe Caperaa and Jean-Claude Cousseins

Laboratoire des matériaux Inorganiques ESA 6002, Université Blaise Pascal et ENSCCF, F. 63177 Aubière Cedex, France. E-mail: chadeyr@chimtp.univ-bpclermont.fr

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The influence of the synthesis method on the luminescence efficiency of the orthoborate $YBO_3:Eu^{3+}$ was studied by comparing the optical performances of samples prepared by three routes: solid state reaction (SR), wet process (WP) and sol–gel processing (SG). On the basis of X-ray powder diffraction, SEM micrographs and photoluminescence measurements, SG appears to be the most efficient method to prepare high quality compounds for practical applications. Such a conclusion is reinforced by the existence of an important gain in the luminescence efficiency using this procedure.

Introduction

The renewal of interest in studying rare-earth (RE) doped orthoborate materials is due to their high UV transparency, their non-linear properties and their exceptional optical damage threshold which allows them to withstand the harsh conditions present in vacuum discharge lamps or screens. Among the orthoborates $LnBO_3$ (Ln = RE, Y), YBO_3 shows interesting luminescence properties when activated by RE ions[1] such as Eu^{3+}.

Among the parameters which govern the luminescence efficiency, the method of preparation of these materials[2] has appeared to be the most significant. It is well established that the use of alternative synthesis routes such as a wet method and, notably, sol–gel processing offer the possibility to obtain materials of high quality and allow, in addition, one to obtain them in various shapes and/or in layers, as well as to control their microstructure. In particular, the quality of powders obtained by these soft chemistry routes, the small and narrow particle size distribution and non-agglomeration, allow sintering at low temperatures without sintering aids.

In this paper we present data related to the effect of the synthesis method on the luminescence efficiency of $YBO_3:Eu^{3+}$. Three comparative routes were used to prepare the $YBO_3:Eu^{3+}$ phases: the usual solid state reaction (SR), a wet process (WP)[3] and a sol–gel process (SG).[4]

The concentration of Eu^{3+} ions in the samples was kept constant at 2 mol% and this value was checked by chemical analysis. The properties of the powders resulting from the three routes were characterised and estimated by using X-ray diffraction (XRD), infrared absorption (IR) and photoluminescence (PL) in relation to thermal treatments. Correlation with the microstructure was tentatively made by analysing the surface morphology using SEM images.

Synthesis

SR polycrystalline $YBO_3:Eu^{3+}$ samples were obtained by direct reaction between yttrium oxide, europium oxide and boric acid. The reactants were weighed, finely ground and mixed. The mixture was transferred into a platinum crucible and heated in a furnace.

The second method used was a wet process (WP). It involved reaction between the rare earth nitrate and a boric acid solution. Starting materials were $Y(NO_3)_3\cdot 6H_2O$ (0.2 M), $Eu(NO_3)_3\cdot 6H_2O$ (0.2 M) and H_3BO_3 (0.2 M) solutions and a 20% ammonia solution. Appropriate volumes were mixed while stirring for half an hour. The ammonia solution was added very slowly up to pH = 7. After half an hour, the mixture was centrifuged. The gel obtained was dried at 120 °C for 24 hours to yield a xerogel, and finally this xerogel was heated in a furnace.

The third method used was based on the sol–gel technique (SG). The first step of the synthesis was the preparation of boron yttrium and boron europium heterometallic alkoxides from lanthanide salts, after which the conventional steps of the sol–gel process were used (hydrolysis and condensation). The gel obtained was submitted to several thermal treatments.

Experimental section

The diffractometer employed was a Siemens DATA MP D501 with Cu-Kα radiation. IR spectra were obtained on a Nicolet 5 SXC spectrophotometer using the KBr pellet technique.

Micrographs were recorded using a Cambridge Scan-360 microscope operating at 20 kV. Specimens were prepared by dispersing small amounts of the powder in acetone. After sonicating the solution and evaporating the solvent, the powders were deposited on adhesive carbon film and a 20 nm Au coating was sputtered onto the surface. Luminescence measurements were performed using the experimental set-up described in ref. 5. Relative luminescence efficiencies were estimated by using the 254 nm radiation supplied by an Hg lamp as an excitation source. Appropriate filters were positioned before and after the sample to avoid any signal induced by the scattered radiation. A surface area of 2×1 cm^2 was illuminated. The luminescence emitted in the overall solid angle was collected by means of a convergent lens and focused at the entrance slit of a 1 m Jobin-Yvon HR1000 monochromator. The detector was a Hamamatsu R1104 photomultiplier tube. Data were analysed with the digital signal processor IPC-DAS 1600.

X-Ray powder diffraction

XRD patterns showed that the crystallization of YBO_3 takes place at 700 °C and 800 °C for the SG and WP phases respectively. In comparison, the SR vaterite sample heated over a period of 4 hours at 800 °C contains some unreacted

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Y_2O_3 as observed by XRD and shown in Fig. 1(a). A heat treatment lasting 4 hours at 1000 °C is necessary to obtain a single YBO_3 phase.

As we have mentioned, the sol–gel process allows a decrease in the sintering temperature. This is strongly dependent on the powder's physical characteristics. An ideal powder must present, in addition to high purity, a small particle size and narrow size distribution. The XRD patterns presented in Fig. 1 clearly indicate an increase in the homogeneity of the size distribution from SR to SG samples. The insert in Fig. 1 shows that the half-widths of the XRD peaks decrease notably for the SG sample relative to the other samples.

Infrared spectroscopy

The conversion of a wet gel to a monolithic dry gel and its sintering raise several problems owing to the elimination of the solvent and organic residues. The infrared spectrum of the vaterite form of the YBO_3 structure has already been described.[6] It consists of fourfold co-ordinated boron with B–O group vibrations ranging from 850 to 1100 cm^{-1}.

Fig. 2(a) shows the FTIR spectrum of a YBO_3 sample prepared by the sol–gel process after heat treatment at 800 °C for 4 hours. This spectrum shows, in addition to the B–O

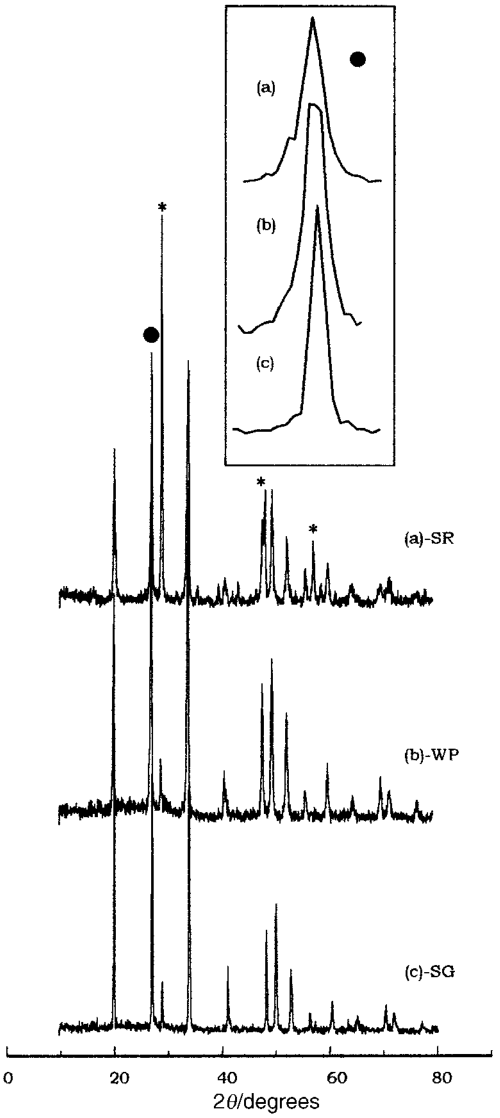

Fig. 1 XRD patterns for $YBO_3:Eu^{3+}$ gels, heated for 4 hours at 800 °C, prepared by (a) solid state reaction, (b) the wet process and (c) the sol–gel method (* indicate peaks due to Y_2O_3 and the insert shows magnification of the peaks indicated by a black circle).

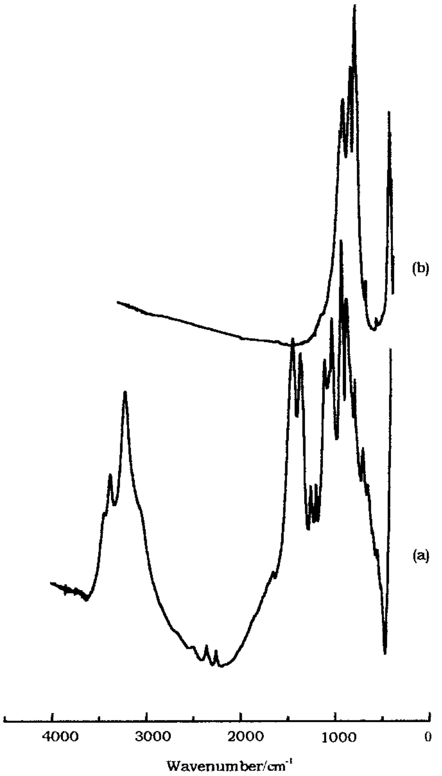

Fig. 2 FTIR spectra of $YBO_3:Eu^{3+}$ prepared by the sol–gel process, heated for (a) 4 hours at 800 °C and (b) 12 hours at 1300 °C.

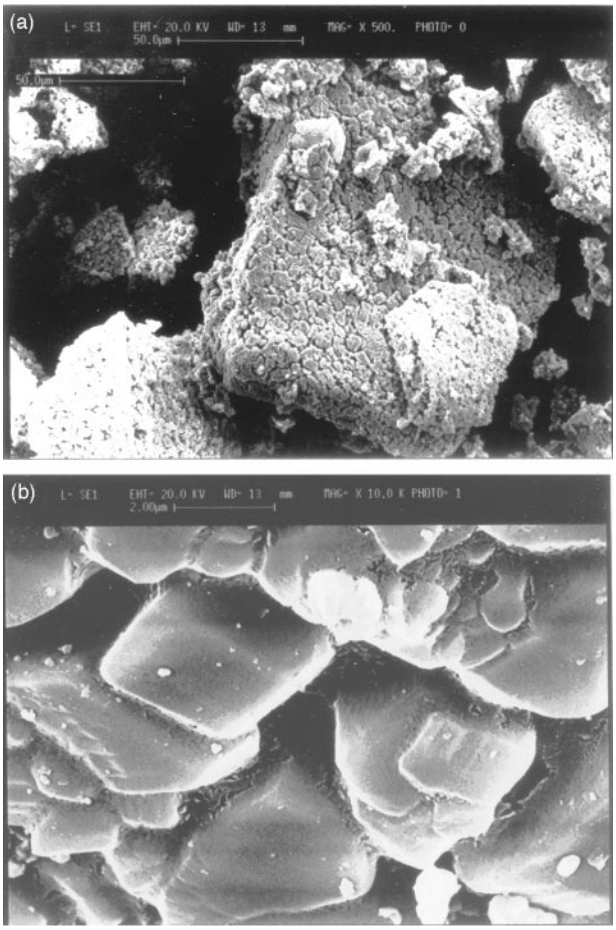

Fig. 3 SEM images of $YBO_3:Eu^{3+}$ prepared by the sol–gel (SG) process heated at 800 °C for 4 h, (a) 500 × magnification and (b) 10000 × magnification.

group vibrations, frequencies in the ranges 3000–3500 cm^{-1} and 1100–1650 cm^{-1} which are assigned to C–H and C–O stretching arising from residual alkoxy groups. Additionally, bridging and terminal ν(C–OM) (M = Y, B) are present in this region.[4] After treatment for 4 hours at 1300 °C the number and the intensity of these absorptions decrease and finally disappear after treatment of the sample for 12 h at 1300 °C [Fig. 2(b)].

This result clearly indicates that these absorptions are only due to unreacted organic residues. The presence of carbon, as revealed by the observation of C–O and C–H stretches in the IR spectra, is confirmed by the elemental analysis. However, the concentration of carbon is less than 0.2 mol% after sintering for 4 hours at 800 °C. On the other hand, such vibrations are not expected to induce notable modifications in the luminescence spectra or in the intensity of this luminescence.

SEM micrographs

The SEM photographs of the samples recorded at 500 × magnification [Fig. 3(a)] show that the SG sample heated at 800 °C exhibits aggregate boundaries composed of a large number of small grains. As seen at higher magnification [10000 ×, Fig. 3(b)], grains with paving-stone morphology are homogeneous and well defined. Such an observation is correlated to complete crystallisation. Sintering at temperatures higher than 800 °C does not produce any important change in the microstructure.

In the case of the WP and SR powders heated at 1000 °C, a temperature which corresponds to good crystallinity, the sintering seems to be better for the WP [Fig. 4(a)] than the SR sample [Fig. 5(a)]. In both cases [Fig. 4(b), 5(b)] the quasi-well defined grains are partially agglomerated and irregular. As in the case of the SG samples, sintering at temperatures higher than 1000 °C produces no significant change in the microstructure. Nevertheless, an increase in the densification is observed and can explain the increase of the luminescence intensities observed for both WP and SR samples after the thermal treatments, as mentioned in the next section.

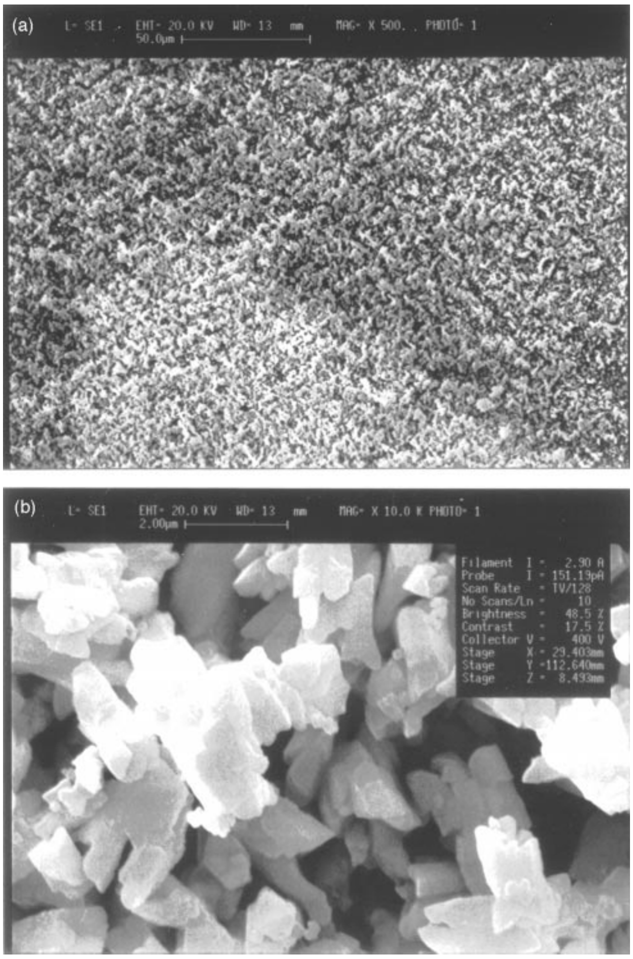

Fig. 4 SEM images of YBO$_3$:Eu^{3+} prepared by the wet process (WP) heated at 1000 °C for 4 h, (a) 500 × magnification and (b) 10000 × magnification.

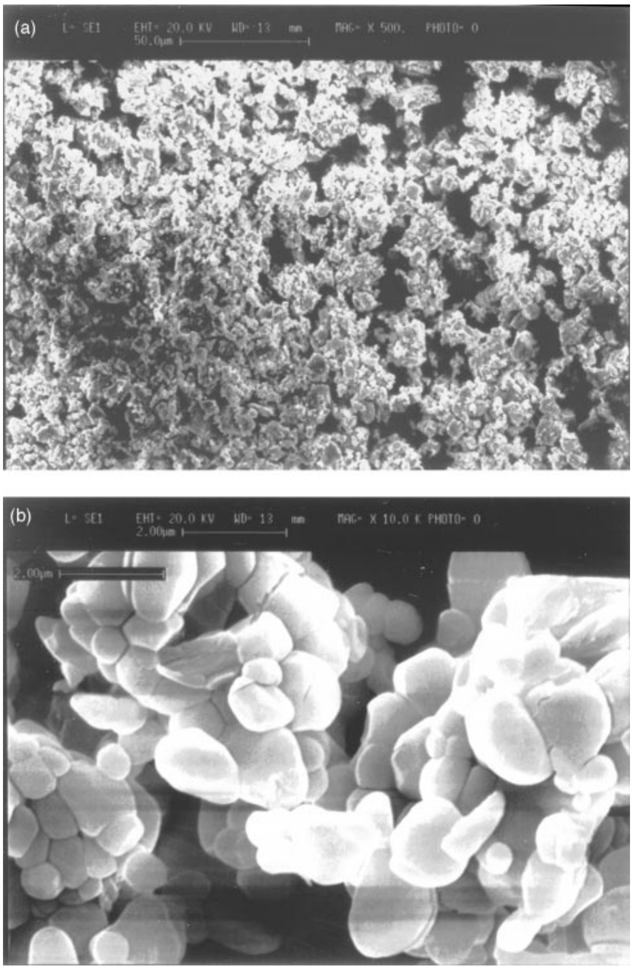

Fig. 5 SEM images of YBO$_3$:Eu^{3+} prepared by solid state reaction (SR) heated at 1000 °C for 4 h, (a) 500 × magnification and (b) 10000 × magnification.

Optical measurements

Fig. 6 shows PL $^7F_0 \rightarrow {}^5D_0$ excitation spectra of the three samples, recorded by monitoring the $^5D_0 \rightarrow {}^7F_2$ luminescences at 14 K. Deconvolution of the shapes as gaussian functions clearly indicates three contributions, in agreement with the existence of three cationic sites over which the Eu^{3+} ions are distributed.[6,7]

Important variations are observed in the intensities and the half-widths of the three gaussians. Such observations agree with a site distribution which is strongly dependent on the method of preparation. Nevertheless, the observed variations can result from the statistical distribution of some of the oxygen atoms as mentioned in the structural description.[6] The SG sample presents the narrowest spectral distribution. Since the lifetimes of the Eu^{3+} $^5D_0$ levels in the three samples are of the same order (typically *ca.* 2.5 ms between 300 and 14 K), the above-mentioned feature confirms the better quality and homogeneity of the SG sample, as shown in the SEM micro-

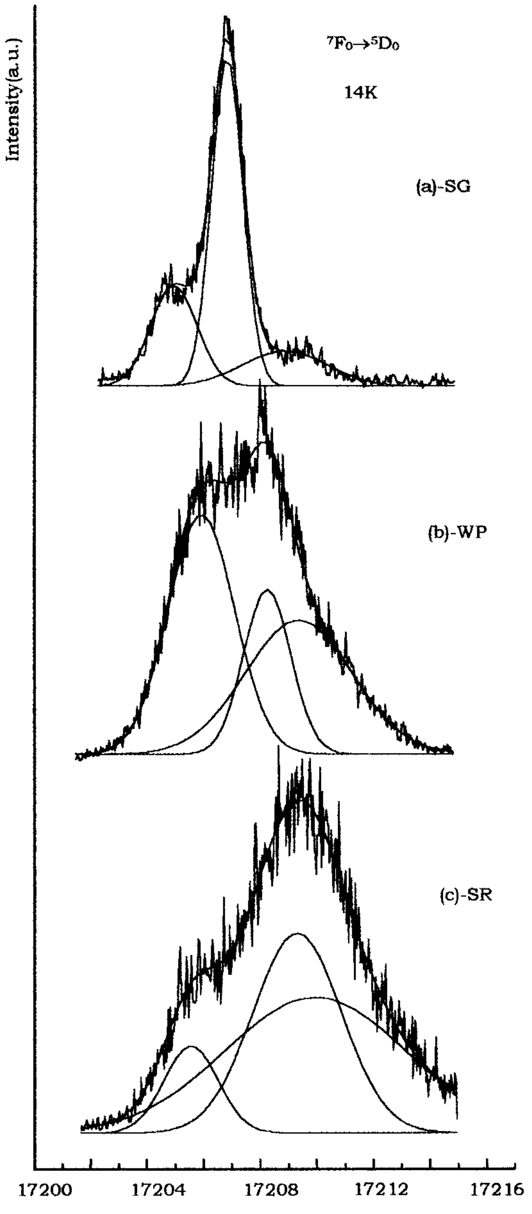

Fig. 6 $^7F_0 \rightarrow {}^5D_0$ excitation spectra of $YBO_3:Eu^{3+}$ at 14 K and their deconvolution as the sum of three gaussian bands for samples prepared by (a) the sol–gel method (SG), (b) the wet process (WP) and (c) solid state reaction (SR).

graphs. This conclusion is reinforced when analysing the relative luminescence efficiencies.

Fig. 7(a) and (b) show the evolution of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ luminescence intensities, respectively, recorded at 300 K for $YBO_3:Eu^{3+}$ against sintering temperature for the three synthesis routes. For the two transitions, maximum intensity is observed for the SG samples. After sintering at 800 °C, the efficiency for the two emissions is more than twice as high for the SG sample as for the two others. However, an increase of the sintering temperature leads to an increase of the emission intensity for the SR and WP samples, while the result obtained for the SG sample remained unchanged for treatment at 800 °C, 1000 °C and 1300 °C. However, the gain remained important even at 1300 °C.

These results indicate that the densification of the small particles is already important at 800 °C for YBO_3 prepared by the SG method, whereas sintering to the same extent is achieved only above 1300 °C for the other synthesis processes.

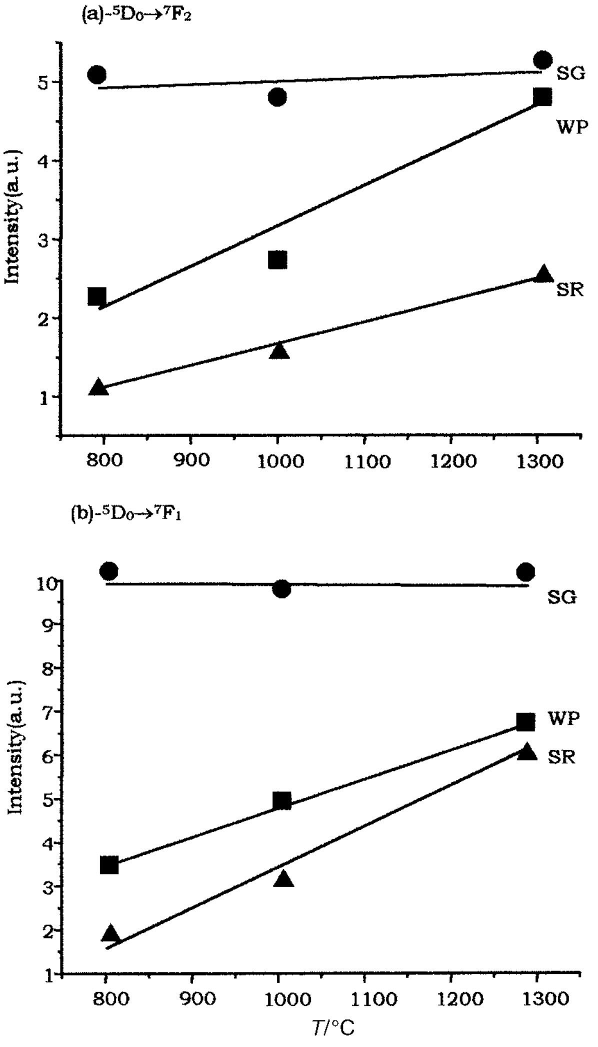

Fig. 7 Evolution at 300 K of the intensities of (a) $^5D_0 \rightarrow {}^7F_2$ and (b) $^5D_0 \rightarrow {}^7F_1$ luminescence of Eu^{3+} in YBO_3 *versus* the sintering temperature for each of the syntheses: ● SG, ■ WP, ▲ SR.

Conclusion

It is clear that the sol–gel method provides a convenient alternative to the traditional preparation of the orthoborate $YBO_3:Eu^{3+}$. The advantages of the sol–gel process over the solid state reaction or soft routes, such as a wet process, include lower temperature processing, higher sample homogeneity and purity, and the opportunity to prepare thin and thick films or fibers. The luminescence efficiency gain in the SG samples obtained by this way is also important.

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