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Solvothermal method to obtain europium-doped yttrium oxide

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Abstract

Pure yttrium oxide or mixed with europium oxide (3 at%) were treated in supercritical isopropanolic suspension at 500°C for 20 h and filling degree of 50%. Products were supercritically dried and characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), infrared spectroscopy (IR) and luminescence spectroscopy (LS). Particle shape is irregular with an equivalent diameter of ca. 5 μm. Cubic crystalline phase is mainly obtained and hydroxide ion in low concentration is detected by IR vibrational spectrum. Europium in this concentration does not extensively change such observed characteristics from the pure yttrium oxide. Luminescence spectra show that the doped product is a mixture of the two oxides added by oxyhydroxide impurities. Nevertheless, this precursor sample, after being heated at 900°C during 1 h, has all characteristics, especially luminescent ones, of the P22 commercial phosphor.

Keywords: Y_2O_3:Eu; Solvothermal; Isopropanol; Luminescence

1. Introduction

Y_2O_3:Eu is an important doped compound for many phosphor applications such as in plasma display panels or in fluorescent lamps [1]. Many methods have been mentioned in literature to prepare yttrium oxide or its precursors in powder samples with specific characteristics: solid-state decomposition reactions [2], homogeneous precipitation [3] and hydrothermal treatment [4–7]. In a previous work [8], mixtures of Y_2O_3 and Eu_2O_3 in different proportions, 1%, 2%, and 3%, were treated under supercritical ethanolic solution trying to prepare doped materials. A mixture of precursors including oxyhydroxide was obtained and doping only occurred with low europium content. Other solvents, less hygroscopic, can be used to avoid oxyhydroxide precursors. To prepare some materials and its precursors, solvothermal method, which can be defined as the treatment of a solution or precursor suspensions in a specific solvent at elevated temperature in a pressurized vessel, presents some advantages for several reasons [9]. This method has been used to obtain or to treat different types of materials, from oxides, αFe_2O_3 [10], Cu-based superconductors [11], sulfides like SnS_2 nanocrystals [10], molybdenum coordination compounds [12], to doped materials like alumina-doped zirconia [13]. Due to the difference in polarity of the solvent, the reaction mechanism for the synthesis of powder might be different. Physical and chemical properties of solvents show significant changes at high temperature and pressure and induce solvent interaction with solid reactants that at supercritical state activate the solubilization process. Complex formation can preferentially promote one crystal structure or a homogeneous distribution of dopants in a material. Then, among the different methods to dope oxides, solvothermal treatment is an alternative route in which the solvent in supercritical condition takes an important role on chemical reactivity.

The aim of this work is to study pure or mixed yttrium oxide with europium oxide treated in supercritical isopropanolic suspensions by using SEM, XRD, IR and luminescence spectroscopies as characterization techniques, as well as to compare the results with those from standard commercial P22 phosphor.

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2. Experimental

Yttrium oxide 99.99% (Aldrich) as well as the yttrium oxide and europium oxide 99.999% (Aldrich) mixture were treated under supercritical isopropanol in hermetically closed autoclaves with controlled pressure, at temperature of 500°C during 20 h and filling degree of 50%. All samples were washed with ethanol. The europium concentration in yttrium oxide mixture was 3 at% and this sample was, after solvothermal treatment, heat treated at 900°C during 1 h, without flux, in conventional furnace. The samples were dispersed in kerosene and examined in a scanning electron microscope Jeol JSM-T330A. Infrared spectra (FT-IR) were obtained from a Nicolet Impact 400 spectrometer by dispersing sample in potassium bromide and pressing disks. The samples were concentrated to emphasize the high wave number range. X-ray diffractograms from powder samples were obtained with a Carl Zeiss HGZ 4B diffractometer by using an Fe filtered Co$K\alpha$ radiation. Luminescence spectra were carried out with a Fluorlog spectrofluorimeter Spex F212L equipped with a 450 W xenon lamp radiation source and a Hamamatsu photomultiplier R928. All spectra were obtained in the same experimental conditions. XRD and luminescence spectra were also performed for monoclinic Eu_2O_3 prepared by heat treatment of europium oxide 99.999% (Aldrich) at 1400°C for 12 h.

3. Results and discussion

3.1. X-ray diffractometry

X-ray diffractograms recorded for doped and undoped yttrium oxide prepared samples, as well as commercial P22 and Eu_2O_3, are shown in Fig. 1. All diffraction patterns are characteristic for yttrium oxide with C-form structure except that for europium oxide B-form structure (JCPDS 34-72). Yttrium oxide, as well as the entire rare earth sesquioxide series, presents polymorphic forms, denoted as A, B and C classified as being hexagonal, monoclinic and cubic, respectively. The C-form structure is of the cubic bixbyite type related to a doubled-edge fluorite structure with one-fourth of the oxygen sites vacated in a regular way, and for Y_2O_3, it is known as the low-temperature form at ordinary pressures [14]. According to X-ray diffraction data, Fig. 1, there are no differences observed between oxide samples before and after solvothermal treatment, independent of the presence of doping ion, considering the technique detection limit. Therefore, solvothermal treatment in isopropanolic media does not cause structure modification in yttrium oxide, while structural change occurs in ethanolic media. In that case, yttrium oxide, solvothermally treated in ethanol at 500°C for 20 h, changed from cubic structure to a mixture of cubic yttrium oxide and monoclinic yttrium oxyhydroxide [8].

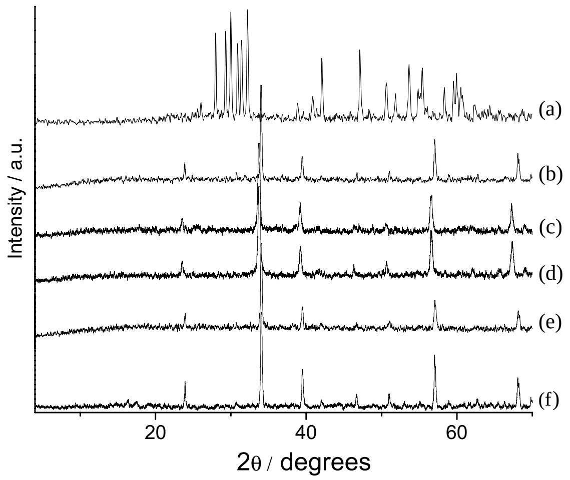


Fig. 1. X-ray diffractograms recorded at atmospheric pressure and room temperature of (a) Eu_2O_3—monoclinic strutucture; (b) Y_2O_3—Aldrich, 99.99% before treatment; (c) after treatment in supercritical isopropanolic suspension at 500°C for 20 h; (d) mixed with Eu_2O_3 (3 at%) and also treated in the same conditions as (c); (e) Y_2O_3:Eu^{3+} described in (d) and heat treated at 900°C during 1 h; and (f) P22 standard.

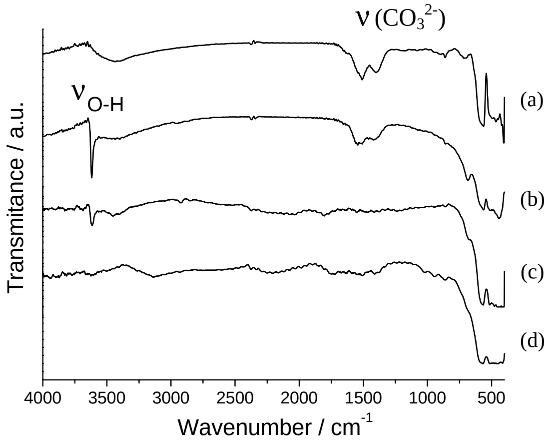


Fig. 2. Infrared vibrational absorption spectra recorded of (a) Y_2O_3—Aldrich, 99.99% before treatment; (b) after treatment in supercritical isopropanolic suspension at 500°C for 20 h; (c) mixed with Eu_2O_3 (3 at%) and also treated in the same conditions as (b); (d) Y_2O_3:Eu^{3+} described in (c) and heat treatment at 900°C during 1 h.

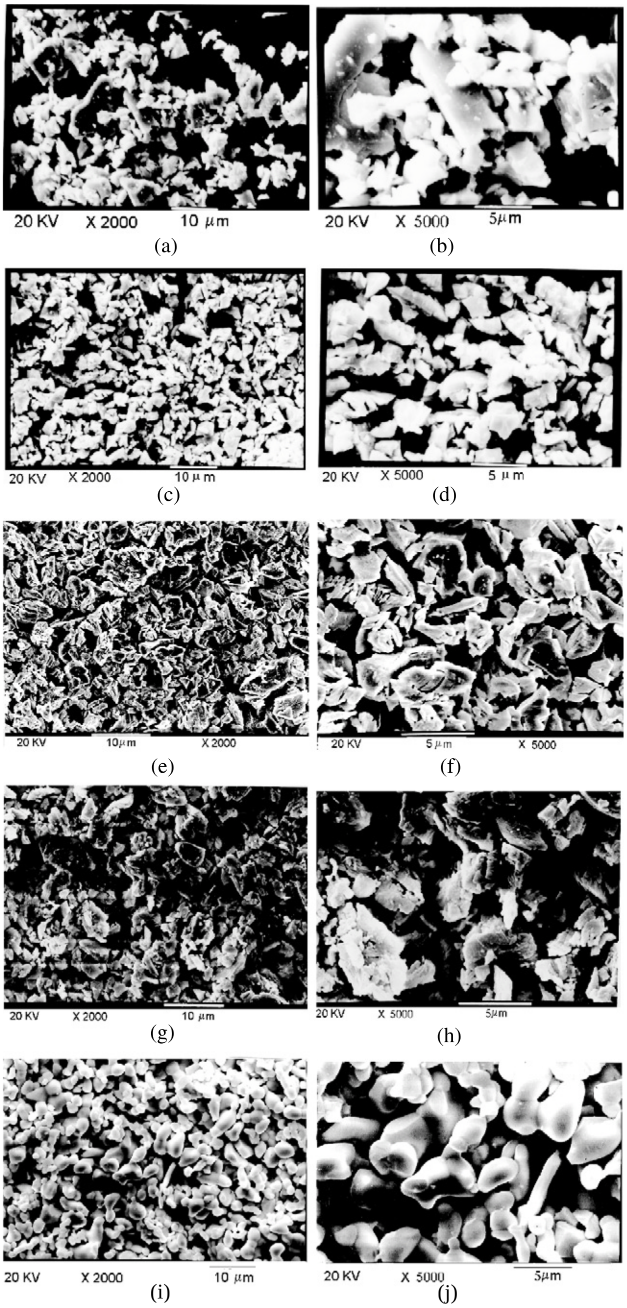
3.2. Infrared spectroscopy

Infrared spectra recorded for pure or Eu-doped yttrium oxide samples prepared after treatment in supercritical isopropanolic suspension at 500°C for 20 h are shown in Fig. 2, which also compares commercial yttrium oxide spectrum before solvolthermal treatment with the other oxides. Throughout IR spectra analysis it is possible to observe that commercial yttrium oxide powder spectrum, Fig. 2(a) shows bands below

650 cm^{-1} assigned to Y–O vibrational modes as well as a split band around 1450 cm^{-1}, which also indicates the presence of carbonate group. This carbonate group probably arises from air CO_2 absorption. On the other hand, in Fig. 2(b) and (c), a sharp band at 3600 cm^{-1} assigned to O–H stretching is an evidence of a localized OH group probably in yttrium hydroxide and/or oxyhydroxide that can be formed after solvothermal treatment of both doped or non-doped yttrium oxide sample. Gadolinium oxide also treated with supercritical isopropanolic suspension resulted in hexagonal gadolinium oxide, as reported before, and IR data also showed evidences of the presence of hydroxyl group [4]. When doped sample prepared from solvothermal treatment is heat treated at 900°C during 1 h, Fig. 2(d), this hydroxyl group as well as the carbonate one is eliminated. Therefore, by using IR spectroscopy it is possible to detect the presence of impurities that are not detected from XRD data. Then, thermal treatment is necessary after solvothermal one in order to eliminate carbonate and hydroxyl groups.

3.3. Scanning electron microscopy

Fig. 3 shows scanning electron microscopy results of all prepared yttrium oxide samples, including the commercial one and P22 standard. It is possible to observe that after treatment in supercritical isopropanolic suspension yttrium oxide particles, Fig. 3(a) and (b), become smaller with equivalent diameter of ca. 5 μm and more homogeneously distributed. The grain shape remains irregular independent of the doping ion presence, Fig. 3(c–f). When Y_2O_3:Eu^{3+} sample viewed in Fig. 3(e) and (f) is heated at 900°C during 1 h, Fig. 3(g) and (h), the thermal treatment results in a slight increase of particle size. Standard P22, Fig. 3(i) and (j), also shows particles with size dimension similar to those prepared by solvothermal treatment, although presenting rounded irregular shape. Ideally spherical fine shaped particles of europium-doped yttrium oxide were obtained from basic carbonate precursor prepared by homogeneous precipitation method [3].



(a) (b) (c) (d) (e) (f) (g) (h) (i) (j)

Fig. 3. Scanning electron microscopy of Y_2O_3—Aldrich, 99.99% (a, b) before treatment; (c, d) after treatment in supercritical isopropanolic suspension at 500°C for 20 h; (e, f) mixed with Eu_2O_3 (3 at%) and also treated in the same conditions as (c, d); (g, h) Y_2O_3:Eu^{3+} obtained in (e, f) and after heat treatment at 900°C during 1 h; and (i, j) P22 standard.

3.4. Luminescence spectroscopy

The excitation and emission spectra at room temperature of Eu^{3+}(3 at%) doped yttrium oxide samples prepared by solvothermal treatment, the same sample heat treated at 900°C, 1 h as well as Eu_2O_3 monoclinic phase, and the P22 standard are in Figs. 4 and 5, respectively. In both cases, it is possible to observe optical transitions that are related to Eu^{3+} activator. The excitation spectra measured fixing the highest intensity of $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} relaxation transition for each case (620 or 610 nm) in Fig. 4 show the group of Eu^{3+} excitation transitions from $^7F_0$, $^7F_1$ to the ^5D_J ($J = 1-3$) and higher excited levels of the $4f^6$ configuration. Excitation spectra are not so different in line positions. However, fluctuations in the relative intensities of the several lines are detected, especially in the excitation range below 400 nm. Comparing spectra from Fig. 4(c) and (d), such intensity fluctuations can be related to non-radiactive decay probably due to the presence of impurity phases. The corresponding

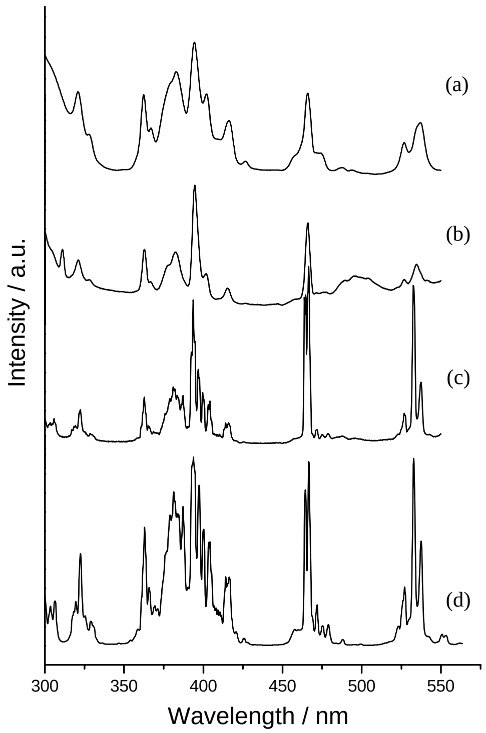


Fig. 4. Excitation spectra at room temperature of (a) Eu_2O_3 monoclinic, $\lambda_{em} = 622$ nm; (b) Y_2O_3 mixed with Eu_2O_3 (3 at%) and treated in supercritical isopropanolic suspension at 500°C for 20 h, $\lambda_{em} = 620$ nm; (c) the same sample described in (b) after heat treatment at 900°C during 1 h, $\lambda_{em} = 610$ nm; and (d) P22 standard, $\lambda_{em} = 610$ nm.

emission spectra using the 393.6 nm excitation $^7F \rightarrow {}^5L_6$ transition, shown in Fig. 5, consist of a set of relaxation transitions $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ in the red region attributed to the Eu^{3+} in low symmetry sites. Fig. 5(b) shows that after solvothermal treatment the resulting phase mixture decreases spectrum resolution. Analyzing both Figs. 4 and 5, it is possible to verify that the spectral feature of yttrium oxide, prepared after heating, Figs. 4(c) and 5(c) are very similar to the P22 standard, Figs. 4(d) and 5(d). The presence of a low intensity emission band at ~622 nm in the heat treated sample, Fig. 5(c), could be assigned to monoclinic phases of europium oxide and/or oxyhidroxide. Nevertheless, in Fig. 5 the amplified inset showing $^5D_0 \rightarrow {}^7F_0$ (0–0) region reveals that for the Eu_2O_3 monoclinic phase (Fig. 5a), as well as for the solvothermal treated sample before heating at 900°C, Fig. 5(b), the Eu^{3+} has more than one 0–0 line at different positions, that is different from the others, Fig. 5(c) and (d). These 0–0 lines indicate that the Eu^{3+} ion is occupying more than one site, i.e., in agreement with the impurities presence, showed by IR data. Although Y_2O_3 with C-form and cubic structure has two crystallographically different rare-earth sites with symmetries C_2 and S_6 [15], according to selection rules in S_6 symmetry 0–0 transition is not favored. Then, if another 0–0 line is detected must be related to Eu^{3+} in different phase. Even the standard P22 as well as the yttrium oxide heated at 900°C, Fig. 5(d) and (c), present more than one 0–0 transition. The most intense line at 5786 must be assigned to Eu^{3+} occupying yttrium oxide C_2 symmetry site. The other 0–0 transitions must be related to the impurities present; in the case of P22 standard the presence of carbonate formed after CO_2 absorption also detected by IR and in the case of doped yttrium oxide after solvothermal treatment the probable formation of yttrium hydroxide and/or oxyhidroxide.

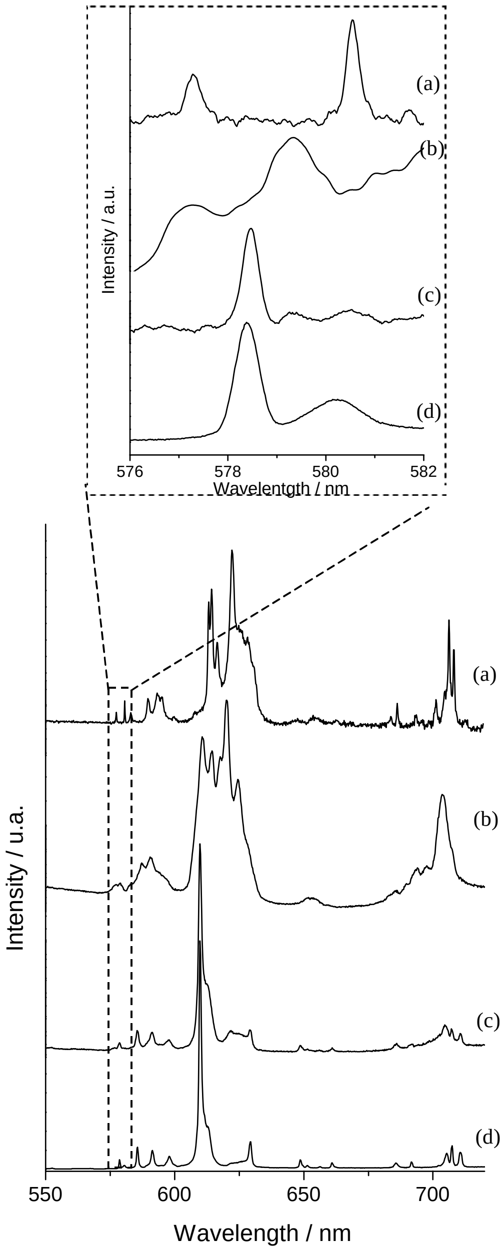


Fig. 5. Emission spectra at room temperature under 393.6 nm excitation of (a) Eu_2O_3 monoclinic, (b) Y_2O_3 mixed with Eu_2O_3 (3 at%) and treated in supercritical isopropanolic suspension at 500°C for 20 h; (c) the same sample described in (b) after heat treatment at 900°C during 1 h; and (d) P22 standard. The amplified region in the inset states for $^5D_0 \rightarrow {}^7F_0$ Eu^{3+} transition.

Once again, it is an evidence of the fact that thermal treatment at 900°C is necessary to eliminate yttrium hydroxide and/or oxyhydroxide phases. The existence of other impurity phases is being investigated by measurements of low temperature luminescence spectra and refinements of XRD Rietveld method, which already showed improved results in similar oxide systems.

4. Conclusion

Europium(III)-doped yttrium oxide powder with high luminescence can be obtained by a heat treatment at 900°C for 1 h of a precursor obtained from the two oxides mixture solvothermally treated in isopropanol at 500°C for 20 h and filling degree of 50%. The europium luminescence spectra feature is comparable with the P22 commercial phosphor. Further studies must be carried out to assure the reaction mechanism.

Acknowledgments

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