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Synthesis and characterization of $Y_2O_3:Pr^{3+}$ phosphor powders by simple solvent evaporation

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Abstract

The synthesis of trivalent praseodymium doped yttrium oxide powders ($Y_2O_3:Pr^{3+}$) by the solvent evaporation method as well as their structural and luminescent (cathodoluminescence and photoluminescence) properties are reported as a function of the concentration of the reagents and annealing temperatures in the 400 to 1100 °C range. These powders become polycrystalline in a cubic Y_2O_3 structure at temperatures above 600 °C. An increase in the diffraction peaks intensity was observed as the temperature is increased. Transmission electron microscopy analysis showed irregular needle like crystallites and the characteristic electron diffraction rings for polycrystalline powders on samples annealing above 600 °C. Scanning electron microscopy showed that these crystallites clump into larger particles of irregular shape. Luminescence spectra show the characteristic peaks at 620 and 630 nm due to $^1D_2$ to $^3H_4$ transitions in Pr^{3+} ions in the Y_2O_3 host.

Keywords: Polycrystalline powders; Yttrium oxide; Trivalent praseodymium; Photoluminescence spectroscopy

1. Introduction

Yttrium oxide has been considered an interesting material for various scientific and technological applications because its physical and chemical properties such as a high dielectric constant (13–18), [1–3] a high refractive index (~2), good thermal expansion coefficient and high thermal conductivity. It also possess large energy bangap (~6 eV) [4] and high mechanical strength [5]. The wide band-gap is quite appropriated for its use as host material for lanthanide elements on light-emitting devices applications [6–8]. Its cubic crystalline form has 8 (C_{3i}) and 24 (C_2) Y sites, which have a high probability of being occupied by lanthanide ions [3]. It also presents a relatively low phonon energy (430–550 cm^{-1}), which can increase the probability of radiative electronic transitions [9,10]. Pr^{3+} doped materials are of great interest, because (Pr^{3+}) trivalent ion has an energy level scheme containing several multiplets resulting in different emissions lines in the visible, although the most intense emission is red light from a $^1D_2$ to $^3H_4$ transition. An additional advantage of Pr^{3+} doped materials is that its luminescence emission can be excited with blue light easily obtainable from GaN diodes (LED, LD) which are commercially available at low cost. Therefore, these materials could be used as luminescent materials for white light emitting diodes, scintillators and 3D visual displays [11–13]. The synthesis of this phosphor by low cost wet based methods includes sol–gel [14,15], urea precipitation [16] and co-precipitation [17,18]. These methods involve multiple steps including: reagents

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dissolution sometimes with heating, and longer reaction time with heating (several hours). In general, the powder obtained is amorphous and requires centrifugation washing, drying and high temperature annealing for crystallization. The crystallite size depends on the annealing temperature (up to 1300 °C) and it is usually larger for higher temperatures [18,19].

In this work, the structural and luminescent characteristics of praseodymium doped yttrium oxide powders by the solvent evaporation method are reported. This method is characterized by its simplicity, low cost, and short sample preparation times. The characterization of these powders was performed as a function of the activator ion concentration and annealing temperatures. High luminescent (photo- and cathodoluminescence) emission intensity was obtained due to intra electronic energy levels transitions $^1D_2$ to $^3H_4$ and $^1D_2$ to $^3H_5$ of the Pr^{3+} ions in the Y_2O_3 host lattice.

2. Experimental procedure

The synthesis of Y_2O_3:Pr^{3+} powders by the solvent evaporation method involved the preparation of mixtures obtained by dissolving $Y(NO_3)_3$ and $PrCl_3$ in methanol, varying the atomic percent (at%) of Pr [0.04, 0.07, 0.15 and 0.30] in relation to the Y content in the starting mixture. These mixtures were heated at 60 °C for 90 min in an oxidizing atmosphere (air) until the solvent was completely evaporated. The obtained powders were annealed in alumina crucibles at different temperatures, 400 to 1100 °C for 3 h. A Siemens D-5000 XRD system with CuK_α (λ=1.5406 Å) was used to determine the crystal structure. The crystal size was estimated by the Scherrer's formula (Eq. (1)) [20].

$$T = \frac{0.9\lambda}{B \cos \theta_B} \quad (1)$$

where: T represents crystallite size, λ the wavelength of CuK_α radiation, B the half width of the diffraction peak and θ_B the Bragg's angle in radians.

Transmission electron microscope (TEM) images were performed using a JEOL 2010 microscope. The surface morphology of the powders was observed by using a scanning electron microscope (SEM) with an accelerating voltage of 10 kV. The luminescence measurements were obtained from the powders pressed into pellets (1.3 cm in diameter and ~1.5 mm thick). A SPEX Fluoro-Max-P spectrofluorometer was used for photoluminescence measurements and a Luminoscope, model ELM-2 MCA, by RELION Co. was used for cathodoluminescence measurements. In this case the diameter of the electron beam on the pellet was approximately 3 mm and the emitted light was collected by an optical fiber and fed into the spectrofluorometer mentioned above. The applied current of electron beam was 0.1 mA with an accelerating voltage in the range from 2 to 7 kV. All luminescence measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows XRD measurements for 0.15 at% Pr^{3+} doped Y_2O_3 powders annealed at different temperatures. The films

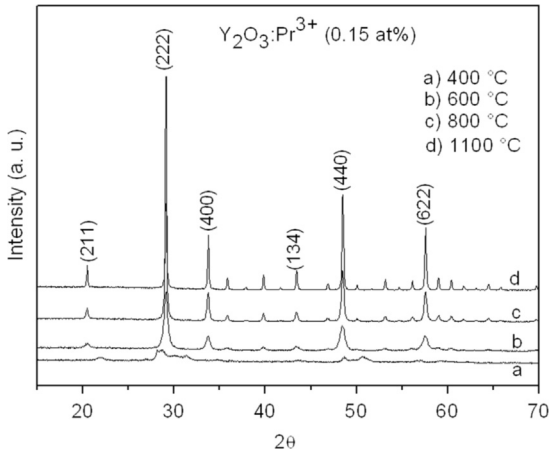

Fig. 1. X-ray diffractograms of the Y_2O_3:Pr^{3+} powders at different annealing temperatures. The $PrCl_3$ concentration in the start mixture was 0.15 at%.

were polycrystalline with a cubic Y_2O_3 crystalline structure. The diffraction peaks increased with increasing annealing temperature indicating that the crystalline structure of the powder was improving. The peaks, located at 2θ=29.1°, 32.9°, 48.5° and 57.6°, are associated with the (2 2 2), (4 0 0), (4 4 0) and (6 2 2) directions, respectively. These lines correspond to the Y_2O_3 cubic phase according to the JCPDS 43-1036 diffraction card; with a lattice parameter of 10.604 Å. Average particle size was estimated with the Scherrer formula to be about 15 nm, for the samples annealed at 600 °C and 35 nm for the sample annealed at 1100 °C. Therefore, it is evident that the Pr^{3+} doped Y_2O_3 powders contain only cubic crystalline phase with an *Ia*3 space group, where Y^{3+} and Pr^{3+} ions are placed at 32 sites in the unit cell, 24 sites with point group symmetry C_2 and 8 sites with C_{3i} symmetry [21]. It is observed that there are not significant differences between the un-doped and the Pr^{3+} doped Y_2O_3 samples XRD patterns, probably because the amount of praseodymium added was low. The chemical similarities between yttrium and praseodymium ions permit the substitution of Y^{3+} ions with Pr^{3+} ions into the Y_2O_3 crystalline structure. Y^{3+} and Pr^{3+} have ionic radius of 104 and 113 pm respectively, therefore it is not surprising that no major crystalline differences are observed between doped and un-doped powders.

To corroborate the polycrystalline nature of the powders, these were studied by SEM and TEM. Fig. 2 shows the micrographs representative of Y_2O_3:Pr^{3+} (0.15 at% Pr^{+3}) annealed powders at 600 and 1100 °C for 3 h. The image for the sample annealed at 800 °C is not included because it is similar to those obtained at 600 °C. Fig. 2a and d correspond to images SEM of annealed powders at 600 and 1100 °C respectively. These images revealed aggregated microstructures of irregular shape with a tendency to get needle-like crystals. In the TEM images (Fig. 2b and e), it can be observed that the powder obtained at 600 °C show needle-like crystals of nanometer size and in the sample annealed at 1100 °C it was revealed rod-like crystal of a larger size. This behavior can be confirmed from selected-area electron diffraction (SAED) pattern recorded perpendicularly to the needle-like crystals which showed concentric rings indicating the presence of the small crystal