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Yttrium-europium oxide doped zinc phosphate glasses, a luminescence study

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ABSTRACT

The luminescent and structural properties of $Zn_3(PO_2)_4$:Y_2O_3/Eu^{3+} glasses synthesized by melting method at a temperature of 1000 °C are described; the doping was performed with Y_2O_3:Eu^{3+} powders which were synthesized by the simple evaporation method at 1100 °C with a concentration of 4.3% Eu^{3+} as determined by EDS. These glasses have a transparency above 90% within the range 400–700 nm, they present an intense luminescence that is associated with characteristic intra-electronic energy levels of Eu^{3+} ion transitions. The dominant emission peak is at 613 nm, corresponding to the $^5D_0$ to $^7F_2$ transition and the dominant excitation peak is at λ_{exc} = 395 nm. The XRD results indicate that they remain amorphous even when they are doped with different masses of the powders Y_2O_3:Eu^{3+}; the CIE diagram shows that the luminescence of these glasses $Zn_3(PO_2)_4$:Y_2O_3/Eu^{3+} and Y_2O_3:Eu^{3+} powders lies in the red region.

1. Introduction

Glasses composed by phosphates, borates, vanadates, germanates, silicates and mixed lattices of aluminum silicates, boron silicate, nitrides, oxynitrides and others, [1,2,3,4] have the capacity to include in their structure a wide range of chemical compounds as dopants, and at the same time, those dopants could incorporate high concentrations of rare earths into their own structure, transferring its (optical) properties to the glasses. Phosphates have been extensively studied because of their interesting properties, such as low melting point, high coefficient of thermal expansion, low refractive index and their optical properties. Making them important for many applications such as sealing materials, medical use, as well as potential applications in many fields of industry suitable for the manufacture of optical fibers, sensors and laser technology [1–5].

The latest reported research on the properties of glass in terms of its structure, chemical and physical durability and elastic properties point out that these can be improved by the addition of metallic oxides such as ZnO, PbO, Al_2O_3, TiO_2, and Bi_2O_3 [1]. Besides it is well known that the optical spectrum of rare earth ions often exhibit vibronic characteristics. According to the general theory the following transitions $\Delta J = 0, 2$ correspond to the selection rules that are accompanied by these vibronic characteristics and in particular Eu^{3+} ion has been widely considered due to the simple structures of its electronic energy levels characterized by the transition ($^7F_0$/$^5D_0$, $^5D_2$ or $^5D_0$/$^7F_0$, $^7F_2$) of absorption, excitation and emission spectra, accompanied by the presence of those vibronic characteristics [6].

The Eu^{3+} ion, of which the lowest excited level ($^5D_0$) of the $4f^6$ configuration is situated below the $4f^55d$ configuration. It shows very sharp emission lines extending from the visible to the near-infrared region [7].

Compared to crystals, glasses have proven favorable as hosts for high-density memory devices due to their broad inhomogeneous width. Oxide glasses, in particular, have proven favorable as host materials for rare earth elements because of their high transparency, compositional variety, and because they are easy to mass produce [8].

In this work the results of $Zn_3(PO_2)_4$:Y_2O_3/Eu^{3+} glasses synthesized by melting method at temperature of 1000 °C doped with different masses of doped yttrium oxide powders are reported; the luminescent powders were obtained by means of the solvent evaporation method at a temperature of 1100 °C, and were analyzed by the techniques of XRD, photoluminescence, cathodoluminescence, SEM and EDS; the $Zn_3(PO_2)_4$:Y_2O_3/Eu^{3+} glasses were analyzed by UV–vis spectroscopy and XRD, in addition photoluminescence, cathodoluminescence, were

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also measured.

2. Experimental

Layered Y_2O_3: Eu^{3+} nano-phosphors were prepared by simple solvent evaporation method, this is an inexpensive, atmospheric pressure technique that has been widely used to obtain powders of different materials, mainly metal oxides [9]. It consists of heating a chemical solution of the proper precursors until its evaporation point to achieve a powder and through a subsequent thermal treatment, eliminate any kind of remnants from the precursor materials and/or achieve an appropriate crystalline structure. In this work, appropriate amounts of $Y(NO_3)_3{\cdot}6H_2O$, and of $EuCl_3$ $6H_2O$ were mixed to obtain doped phosphors, being dissolved in deionized water (18 MΩ-cm) and then the water of this solution was evaporated at ~200 °C, the remaining powder was then annealed in a an open ends hot wall tube furnace for 2 h in air to temperature up to 1100 °C. The Eu^{3+} doping concentration was 4.3 at.% in the final Y_2O_3:Eu^{3+} nano-phosphor (17 at.%, in relation to Y^{3+} in the precursor solution) [10]. Most of the nano-phosphors obtained with this technique were layered particles in the size range 1 × 1 microns and few nanometers thick.

The glasses were synthesized by melting method, it consists of heating a mix of the appropriated precursors until its melting point to achieve a liquid glass and through a subsequent thermal shock (in a copper bucket), it gets hard and takes the mold shape, finally a heat treatment at 300 °C is practiced on the glasses in order to eliminate internal stresses and avoid the rupture possibilities. In this particular case, 4 g of zinc oxide (ZnO) and 6 g of ammonium phosphate ($NH_4H_2PO_4$) supplied by Sigma Aldrich as well as between 0.025 and 0.15 g of europium doped yttrium oxide phosphors (above described) are placed in a crucible; then they are introduced into an electric muffle at 400 °C for 3 h to eliminate wet, next the temperature is raised to 1000 °C for 3 h to melt all the components until an homogeneous liquid is observed, this liquid is emptied in a block of copper to solidified it by a thermal shock and achieve a glass, immediately it is placed on a grill at 300 °C for 24 h. Finally the glasses are polish and cut in order to be characterized.

Luminescence spectra were obtained with an Edinburgh Inst. M. 960 S spectrophotometer. CL measurements were performed in a stainless steel vacuum chamber with a cold cathode electron gun (Luminoscope, model ELM-2 MCA, RELION Co.). In this case, the emitted light was collected by an optical fiber and fed into a SPEX Fluoro-Max-P spectrophotometer. All luminescent measurements were carried out at room temperature. The crystalline structure was analyzed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with 1.540 Å (Cu K) operating at 30 keV. Energy dispersive spectroscopy (EDS) and Scanning Electron Microscopy (SEM) measurements were performed using a Leica Cambridge model Stereoscan Electron Microscope equipped with a detector 440 X-ray beryllium window using an accelerating voltage of 20 kV and amplification higher than × 5000. The morphology of the powders were confirmed by STEM in a JEOL JEM-ARM200F microscope operating at 200 kV using an accelerating voltage of 20 kV and amplification higher than × 5000. The UV–vis measurements of the glasses were made with a Spectrometer PerkinElmer Lambda 25. The analyzed with the glass are analyzed with Raman confocal and Leica TCS-SP8 DM 6000 confocal microscope, with a halide lamp metal of 120 W, equipped with lassers CW (405 nm) 50 mW; Ar (458, 488 y 514 nm) 100 mW; DPSS (561 nm) 20 mW and He-Ne (633 nm) 10 mW; with four spectral detectors for fluorescence and reflection, with a minimum step of 20 nm and its path range of 1500 µm, a Speed 10 mm/s, its resolution 0.02–0.04 µm and a reproducibility < 1 µm.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms for undoped and Eu^{3+} doped

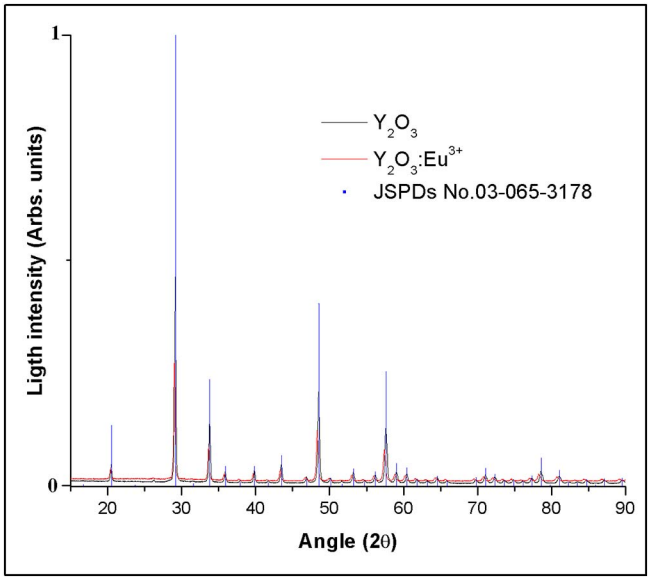

Fig. 1. XRD spectra for non-doped and europium doped yttrium oxide phosphors.

(4.3% as determined by EDS) yttrium oxide nanophosphors, annealed in air at 1100 °C, also shown in this figure is the cubic yttrium oxide phase according to JSPDS 03-065-3178 data card. At 1100 °C, the diffraction pattern peaks at the angles 20.42, 29.04, 33.64, 35.88, 39.86, 43.34, 48.44 and 57.5, corresponding to the planes (2,1,1), (2,2,2), (4,0,0), (4,1,1), (3,3,2), (1,3,4), (4,4,0) and (6,2,2) respectively, of the Y_2O_3 body centered cubic structure. The high intensity of the diffraction peaks indicates good crystallinity of the powders annealed at 1100 °C. Table 1 lists the average values of grain sizes calculated from different reflection angles, for both doped and undoped phosphors, according to the Scherer's formula:

$$T = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ = 1.5406 Å is the wavelength of the X-ray radiation used, β is the full halfwidth maximum (FWHM) of the diffraction peak in the XRD patterns in radians, θ is the Bragg diffraction angle. According to this formula the average particle size was estimated. Due to the difference in the ionic radii of Eu^{3+} (1.07 Å) and that of Y^{3+} ion (1.02 Å) the replacement of Y^{3+} by Eu^{3+} ions in Y_2O_3 lattice causes a rearrangement between the neighbors that give rise to a deformation of the lattice that produce strains by the difference of the ionic radii [11].

Fig. 2 shows SEM images for undoped and europium doped yttrium oxide annealed at 1100 °C, a layered rectangular structure is observed with occasional rectangular holes due to multiple layered geometry of the aggregates formed by this material. Table 2 lists the EDS results for undoped Y_2O_3 and for 17% europium doped phosphors. The undoped powders of Y_2O_3 present the stoichiometric values of 60% oxygen and 40% yttrium, and in the doped sample the oxygen content is approximately the same (60%) but the content of yttrium is reduced as the amount of europium is increased, thus the Y + Eu/O stoichiometry is maintained. Therefore, europium ions are introduced in substitution of Y ions in the Y_2O_3 matrix.

Fig. 3 shows representative TEM images at three magnifications of

Table 1
Average grain size values for non-doped and europium doped Y_2O_3 nano phosphors.

Temperature	Y_2O_3	Y_2O_3:Eu^{3+}
	Grain Size (nm)	Grain Size (nm)
1100 °C	39.28 ± 1.34	37.82 ± 1.24