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Photophysical characterization of $La_{1-x}Eu_xBO_3$ and $La_{1-x}Tb_xBO_3$ nanopowders synthesized by sol–gel Pechini method

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ABSTRACT

Lanthanum orthoborates doped with Eu^{3+} or Tb^{3+} were obtained by a modified Pechini method using ethylene glycol and citric acid as chelating and cross-linking reagents. Crystal structure, morphology and grain size of the obtained nanopowders were determined using XRD (X-ray diffraction), EDX (Energy-dispersive X-ray spectroscopy) and TEM (transmission electron microscopy) analysis. Photophysical properties of the nanopowders obtained were studied by luminescence excitation and emission spectra, luminescence decay curves and calculated Judd–Ofelt parameters. In an attempt to optimize the conditions of synthesis, the dependence of physicochemical properties on calcination temperature was analysed.

1. Introduction

Over the last few years, a dynamic development of technologies for obtaining efficient nanophosphors, desirable in many areas of science and industry has been observed. Among the most promising and suitable matrices are rare earth orthoborates ($REBO_3$) doped with Eu^{3+} or Tb^{3+} ions offering exceptional physicochemical properties, such as efficient emission of visible light under vacuum ultraviolet (VUV) [1–5], ultraviolet (UV) [6–8] or infrared (IR) [9] excitation, chemical and thermal stability [10]. Orthoborate materials are applied to get color picture in plasma display panels and in Hg-free fluorescent lamps thanks to their exceptional optical damage threshold [11,12]. Rare earth orthoborates doped with Eu^{3+} and Tb^{3+} ions exhibit red or orange-red and green luminescence under UV excitation, respectively. Additionally, the charge-transfer process (CT) that enhances the intensity of luminescence is observed between O^{2-} ions in borate anion and Eu^{3+} [13].

Many routes have been proposed for nanopowder synthesis, among them the sol–gel methods. They can provide nanocrystals, glasses, ceramics or films [14–18]. A specific sol–gel method is the Pechini one [19]. This type of sol–gel process starts with polymerization reaction between α-hydroxycarboxylic acids (e.g. citric acid) and polyhydroxylic alcohols (e.g. ethylene glycol). The polymerization process is carried out in a solution containing metal salts, which are incorporated into the gel (resin) structure thanks to the complexation by citric acid. Then, the precursor prepared is subjected to thermal decomposition, in order to obtain nanocrystalline powders. This method ensures obtaining a homogenous product exhibiting high crystallinity, purity, and small particle size. It is also a simple, fast and repetitive route of synthesis, which does not require the use of advanced and expensive equipment. Recently, we have reported the structural and spectroscopic properties of the new monoclinic $Gd_{1-x}Eu_xBO_3$ nanopowders, synthesized using the Pechini method. This way of synthesis provided high-quality nanophosphors of a new structure, exhibiting high values of the quantum efficiency [20].

In 1961 Levin et al. proposed three fundamental crystal structures of $REBO_3$, doped with Ln^{3+}, in analogy to the three crystalline forms of $CaCO_3$, related to the ionic radius of the rare earth. These are aragonite, calcite, and vaterite representing the orthorhombic, trigonal, and hexagonal crystal systems, respectively. The orthoborates of rare earths from La to Nd have aragonite type structures, while the ones of smaller ions (Sm to Yb) and yttrium, crystalize in the vaterite-type form. $LuBO_3$ could be obtained in both forms – a low-temperature calcite and a high-temperature vaterite form [21].

In this study, the influence of calcination temperature and dopant concentrations on crystal structure and hence spectroscopic properties is analysed through the analysis of excitation and emission spectra, luminescence lifetimes, quantum yields and values of Judd–Ofelt intensity parameters. $La_{1-x}Eu_xBO_3$ and $La_{1-x}Tb_xBO_3$ nanopowders were synthesized by a modified sol–gel Pechini method.

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2. Experimental

2.1. Synthesis

In the present work $La_{1-x}Eu_xBO_3$, $La_{1-x}Tb_xBO_3$ ($0 \leqslant x \leqslant 0.2$) phosphors were successfully synthesized by a modified Pechini method. Lanthanum La_2O_3 and europium Eu_2O_3 or Tb_4O_7 terbium oxides (Stanford Materials 99.99%), nitric acid HNO_3 (POCh S.A., ultra-pure), orthoboric acid H_3BO_3 (POCh S.A., p.a. grade), citric acid monohydrate (CHEMPUR, p.a. grade), ethylene glycol (CHEMPUR, p.a. grade) were used as precursors in the experiment. The detailed procedure is described below.

Appropriate amounts of rare earth nitrate solutions were obtained by dissolving lanthanide oxides in HNO_3. An excess amount of acid was removed by a few times repeated evaporation of solutions. Then, the stoichiometric amounts of lanthanide salts were mixed in deionized water together with appropriate amount of orthoboric acid, citric acid and ethylene glycol. Large excess of citric acid (12 g per 1 g of product) and ethylene glycol (1 ml per 1 g of product) were added. Citric acid and ethylene glycol were employed as the chelating and cross-linking reagents, respectively. The homogenous solution obtained was heated at 80 °C for 24 h. The precursors in the form of gels were annealed at different temperatures, such as 800, 900 and 1000 °C at air for 3 h.

2.2. Characterization

XRD patterns were recorded on a Bruker AXS D8 Advance X-ray diffractometer in the Bragg–Brentano geometry, with Cu k_α radiation (λ = 1.5418 Å) in the 2θ range from 6° to 60°. The XRD results were assigned to the standards from the Joint Committee on Powder Diffraction Standards (JCPDS) database. The IR absorption spectrum was recorded in the range between 400 and 4000 cm^{-1} on an FTIR spectrophotometer, Bruker FT-IR IFS 66/s. The material was mixed with KBr and then pressed to disks. TEM images were taken at an FEI Tecnai G2 20 X-TWIN transmission electron microscope, at accelerating voltage of 200 kV.

The excitation and emission spectra and luminescence decay curves were recorded on a Hitachi F-7000 spectrophotometer at room temperature (300 K) with the 150 W xenon excitation source. Excitation and emission spectra were corrected for the instrumental response.

3. Results and discussion

3.1. Structural analysis

Lanthanum orthoborates obtained with different amounts of H_3BO_3 added into the mixture of the reagents revealed different purity. On the basis of XRD patterns the optimum quantity of H_3BO_3 that ensures getting $LaBO_3$ doped with Eu^{3+} or Tb^{3+} ions of desired structure, was 50% excess in relation to the stoichiometric amount (Fig. 1). The stoichiometric amount of H_3BO_3, 25% excess and larger than 50% excess of boric acid led to the formation an additional phase, which is monoclinic LaB_3O_6 (JCPDS No.73-1150). Obviously, the excess of H_3BO_3 was employed to equalize its loss on evaporation.

The Ln^{3+} ions have similar radius, thus conversion of La^{3+} ions to Eu^{3+} or Tb^{3+} does not destroy the crystal structure [22–24]. Fig. 2 shows the XRD patterns of the $La_{1-x}Eu_xBO_3$ nanocrystals obtained by the Pechini method. It can be well seen that all diffraction peaks can be well indexed to the orthorhombic aragonite $LaBO_3$ phase (JCPDS. No. 12-0762, space group: *Pnam*) [25]. The best purity of the materials produced was achieved when the temperature of annealing was 1000 °C. On the other hand, when the temperature

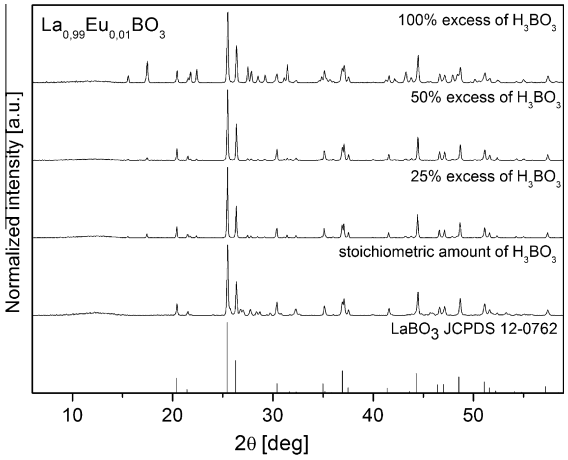

Fig. 1. XRD patterns of $La_{0.99}Eu_{0.01}BO_3$ calcined at 900 °C for 3 h.

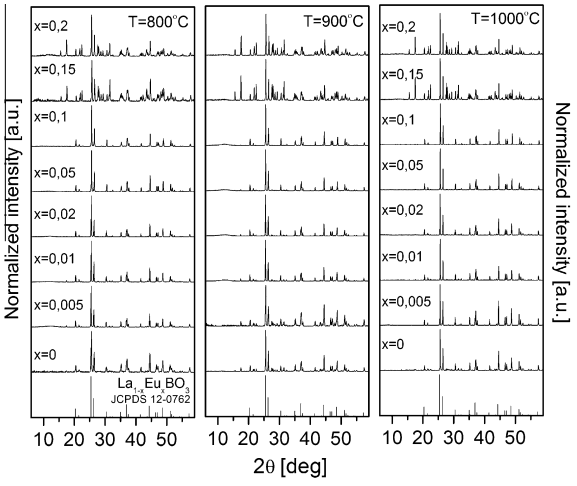

Fig. 2. XRD patterns of $La_{1-x}Eu_xBO_3$ calcined at 800, 900, 1000 °C for 3 h.

was lower than 1000 °C, XRD patterns of selected samples presented extraneous reflexes connected with monoclinic LaB_3O_6, which means that not all powders were annealed enough leading to the contamination. The samples composed of more than 10% of Eu contained some impurities due to the LaB_3O_6 presence. Once more, the strong and sharp peaks indicate that the materials obtained are well crystallized and the sol–gel Pechini method is appropriate for the synthesis of $LaBO_3$ phosphors.

Fig. 3 shows the XRD patterns of the $La_{1-x}Tb_xBO_3$ nanocrystals obtained by the sol–gel method. On the basis of XRD analysis, for $La_{1-x}Tb_xBO_3$ nanocrystals similar conclusions can be drawn as for $La_{1-x}Eu_xBO_3$. The products diffraction patterns can be easily indexed as an orthorhombic aragonite structure (JCPDS. No. 12-0762, space group: *Pnam*) [25]. However, doping with Tb^{3+} in the amount above x = 0.1 caused the formation of a new phase, monoclinic LaB_3O_6. The purity of the materials produced was the highest for the calcination temperature 1000 °C. Only four, the lowest-doped samples were white powders after calcination at 800 °C for 3 h. Finally, the intense and sharp peaks proved a high degree of crystallinity of the nanopowders obtained.

A TEM image of the synthesized $La_{0.9}Eu_{0.1}BO_3$ annealed at 900 °C for 3 h is presented in Fig. 4a. This sample is composed of flake-like and slightly agglomerated particles. The average grain size is of about 200 nm in the crystal length and 125 nm in the crystal width. The EDX spectrum in Fig. 4b shows the evidence of