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Synthesis and luminescent properties of trivalent rare-earth (Eu^{3+}, Tb^{3+}) ions doped nanocrystalline $AgLa(PO_3)_4$ polyphosphates

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ABSTRACT

The $AgLa(PO_3)_4$ phosphors activated with trivalent rare-earth (Eu^{3+}, Tb^{3+}) ions were prepared by a sol–gel synthesis method. The crystal structure of the compound was studied by X-ray diffraction patterns and found to be crystallized in the monoclinic system with a space group $P2_1/c$, indicating the calculated lattice parameters of a = 10.08 Å, b = 13.12 Å, and c = 7.314 Å. The Fourier-transform infrared spectrum, photoluminescence excitation/emission spectra, and decay curves were examined to study the optical properties. The analysis of the Eu^{3+} ions related emission spectrum revealed the presence of highly symmetric sites for the activator ions. The Tb^{3+} ions related emission spectrum exhibited a $^5D_3$ emission due to the prolonged calcination at high temperatures, which reduces the residual hydroxyl ions. The optical properties show that this host material is suitable for phosphor materials and laser crystals.

1. Introduction

In recent years, search for new luminescent and other materials which can be employed in lasers [1], photo catalysts [2], fiber optics [3], sensors [4], and photoluminescent devices [5], etc. is growing. Owing to this fact, many researchers have been working on the mixed rare-earth inorganic compounds [6–8]. Of these mixed rare-earth inorganic compounds, the condensed polyphosphate materials of general formula $M^IM^{III}(PO_3)_4$ containing mono (M^I = Li, Na, K, ...) and trivalent (M^{III} = La, Ce, Nd, ...) cations are of particular interest. The interesting chemical features of these polyphosphates are that they are stable under normal conditions of humidity and temperature and can sustain a perfect state of crystallinity for many years [9,10]. These materials are classified into two categories based on their structures: cyclic and chain structures. Cyclic structures contain polyphosphate anions in a ring of four PO_4 tetrahedra linked by bridging oxygens and chain structures have elongated chains of four PO_4 tetrahedra [11,12]. These materials also show interesting optical properties [13,14].

In this context, devoted research work is continuing in synthesizing rare-earth polyphosphates, observing their optical, structural, and catalytic properties, for various applications [15,16]. Typically, solid-state reaction method is preferred for synthesis of phosphors. This process requires a high-temperature and time-consuming heating process followed by grinding. This procedure also causes several impurity phases in the resultant product due to the poor mixing and low reactivity of raw materials and, as a result, particles come in the micrometer range of sizes. However, nowadays, several solution based chemical synthesis methods such as hydrothermal, solvothermal, co-precipitation, spray-pyrolysis, and sol–gel processes were utilized to prepare phosphors. Among these methods, the sol–gel process is a promising technique for obtaining novel chemical compositions with unique properties and ultra-fine uniform ceramic powders with excellent purity at relatively low reaction temperatures.

To date, only few reports have been found on double phosphates containing silver and rare-earth cations: $AgGd(PO_3)_4$, $AgPr(PO_3)_4$, $AgCe(PO_3)_4$, $AgNd(PO_3)_4$, $AgLa(PO_3)_4$, etc. In this work, nanocrystalline $AgLa(PO_3)_4$ powders were prepared by a sol–gel synthesis method. This polyphosphate is a member of chain family with four crystallographically independent $(PO_3)^-$ groups. The phosphate atoms are coordinated with four oxygen atoms in a tetrahedron and each P tetrahedron is connected by two common corners in *cis* position to other P tetrahedral, leading to a twisted chain of general formula $(PO_3)_n^-$ [17]. This compound was further characterized by the Fourier-transform infrared (FTIR) spectrum and the optical properties were studied by doping with different rare-earth (Eu^{3+} and Tb^{3+}) ions.

2. Experimental procedure

The sol–gel synthesis of $AgLa(PO_3)_4$:RE^{3+} (RE = Eu, Tb) nanocrystalline phosphors was carried out using high-purity grade silver nitrate ($AgNO_3$), lanthanum nitrate hydrate ($La(NO_3)_3 \cdot xH_2O$), ammonium phosphate dibasic ($(NH_4)_2 \cdot HPO_4$),

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europium nitrate pentahydrate ($Eu(NO_3)_3{\cdot}5H_2O$), terbium nitrate pentahydrate ($Tb(NO_3)_3{\cdot}5H_2O$), and citric acid ($HOC(COOH)(CH_2COOH)_2$), purchased from Sigma–Aldrich. The solution was prepared by mixing 1 mM of silver nitrate, $(1-x)$ mM of lanthanum nitrate, 4 mM of ammonium phosphate, x mM of rare earths (Eu^{3+}/Tb^{3+}), and 12 mM of citric acid (1:2 ratio of metal to citric acid) in 200 ml of de-ionized (DI) water. The solution was mixed well with the help of magnetic stirrer until a homogenous solution was formed. Once a homogenous solution was formed, the solution was heated and the solution temperature was maintained at 80 °C on a hotplate. For 1 h, the beaker was covered with a lid to give a uniform temperature to the solution. After 1 h, the lid on the beaker was removed, which made the solution evaporate slowly until a blackish wet gel was formed. The wet gel was collected and dried at 120 °C in an oven, which yields porous solid matrices called xerogel. The drying process usually causes syneresis (expulsion of liquid from gel) and substantial matrix shrinkage, often leading to cracks (mainly due to the capillary pressure). This precursor was decomposed to give black-colored flakes of extremely fine particles when heated at 400 °C for 4 h. The resulting sample was further annealed at 700 °C for 10 h. For Tb^{3+} doped samples, the powders were again heated in a CO reduced atmosphere to obtain the characteristic green emission. The samples were characterized structurally by using an X-ray diffractometer (XRD: M18XHF-SRA, Mac Science) using Cu-Kα radiation at a wavelength of 1.5406 Å. The size and shape of the particles were determined by using a transmission electron microscope (TEM: JEM-2100F, JEOL). Room-temperature photoluminescence (PL) was studied by using a spectrofluorometer (QM-4/2005SE, PTI) equipped with a xenon arc lamp.

3. Results and discussion

The morphologies of $AgLa(PO_3)_4$ phosphors prepared by the sol–gel synthesis method were observed from the TEM image. Fig. 1(a) shows the TEM image of the samples, which confirms that the particles are in the nanometer range. The high-resolution TEM (HR-TEM) image showed clear lattice fringes as shown in Fig. 1(b). The lattice spacing calculated from the HR-TEM image ($d = 2.145$ Å) corresponded to the (060) plane and was well indexed to the data in XRD. The inset of Fig. 1(b) shows the selective area electron diffraction (SAED) pattern. The SAED pattern showed the ring and dot patterns, indicating a nanocrystalline nature of the compound [18]. The structural characteristics of the samples were evaluated by the XRD patterns. The diffraction patterns taken for the samples were similar and perfectly matched with the JCPDS #37-0589, as can be seen in Fig. 2(a). There were no other impurity peaks found in the diffraction patterns and the powders were crystallized in the monoclinic system with space group $P2_1/c$. The unit cell dimensions were calculated by taking high intensity diffraction peaks and found to be $a = 10.08$ Å, $b = 13.12$ Å, and $c = 7.314$ Å. As the host and dopant ions do not have much difference in the ionic radii, there are no major changes or shifts in the diffraction peaks, suggesting that the ions are perfectly doped into the host lattice.

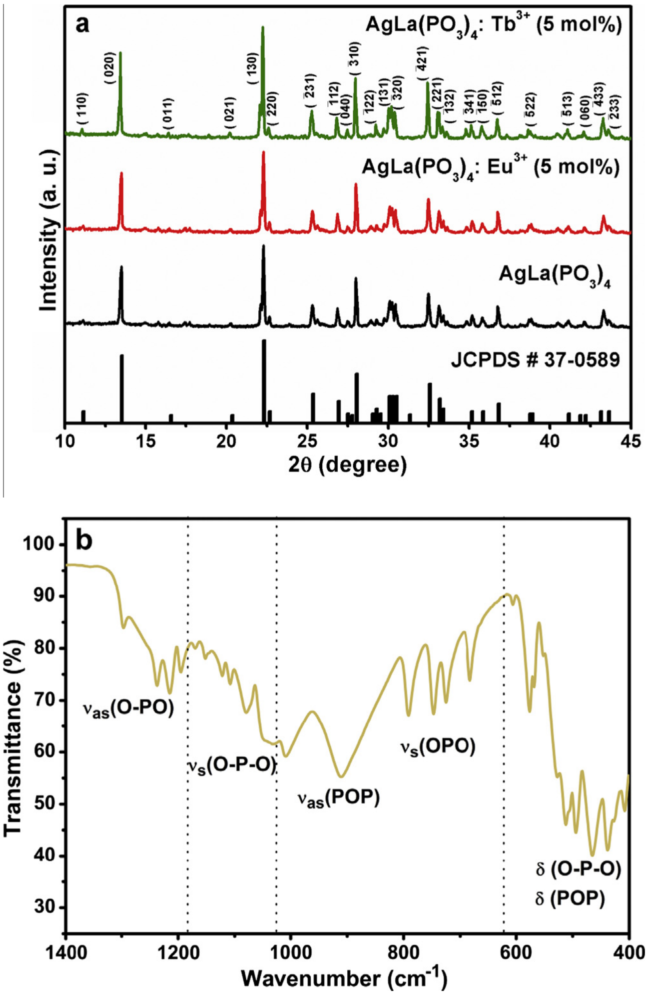

Fig. 2. (a) XRD patterns of the as-prepared and rare-earth activated $AgLa(PO_3)_4$ phosphors, and (b) FTIR spectrum of the $AgLa(PO_3)_4$ host lattice in the 1400–400 cm^{-1} range.

The FTIR spectrum of the $AgLa(PO_3)_4$ compound was taken on a Perkin-Elmer spectrum 100 series spectrometer in the range of 4000–400 cm^{-1}. The spectrum range pertinent to the present compound is 1400–400 cm^{-1}. Substantially, a large number of bands were observed in the 1400–400 cm^{-1} range due to the presence of four crystallographically different PO_4 tetrahedra [19] as shown in Fig. 2(b). Few bands above 1180 cm^{-1} are due to the anti-symmetric vibrations (υ_{as}) of PO_2 groups. Weak bands in the 1180–1050 cm^{-1} range are due to the symmetric vibrations (υ_s) of P–O stretching in the PO_2 group and these vibrational frequencies are comparable with reported ones [7,17]. The strong band centered at 910 cm^{-1} is due to the anti-symmetric vibrations (υ_{as}) of P–O–P [12]. Sharp peaks present at 792, 747, 724, and 682 cm^{-1} are assigned to the symmetric vibrations (υ_s) of O–P–O. Multiple splitting bands below 620 cm^{-1} are allocated for the anti-symmetric or

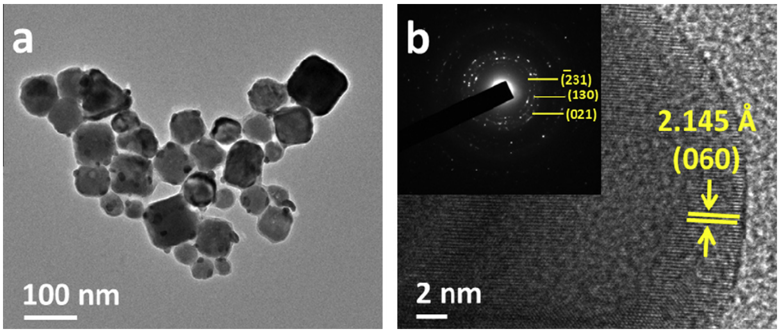

Fig. 1. (a) TEM and (b) HR-TEM images of the $AgLa(PO_3)_4$ host lattice prepared by the sol–gel synthesis method. The inset of (b) shows the corresponding SAED pattern.