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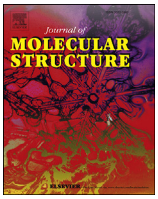

Photoluminescence studies on holmium (III) and praseodymium (III) doped calcium borophosphate (CBP) phosphors

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Using solid state reaction method, Ho^{3+} and Pr^{3+} doped calcium borophosphate (CBP) phosphors were prepared. These phosphors were characterized using XRD, SEM, FT-IR, ^{31}P solid state NMR, photoluminescence (PL) and decay profiles. Structural details were discussed from XRD and FT-IR spectra. From ^{31}P NMR spectra of these phosphors, mono-phosphate complexes Q^0-(PO_4^{3-}) were observed. Photoluminescence spectra were measured for both Ho^{3+} and Pr^{3+} doped calcium borophosphate phosphors and the spectra were studied for different concentrations. Decay curves were obtained for the excited level, $^5F_4$+$^5S_2$ of Ho^{3+} and $^1D_2$ level of Pr^{3+} in these calcium borophosphate phosphors and lifetimes were measured. CIE color chromaticity diagrams are drawn for these two rare earth ions in calcium borophosphate phosphors. Results show that Ho^{3+} and Pr^{3+} doped CBP phosphors might be served as green and red luminescence materials.

1. Introduction

Nowadays, the phosphors have been extensively used in the development of wide variety of display, lighting applications and other related communication technologies like UV–Visible light emitting diodes, solid state lasers and various photoluminescence materials [1,2]. Among various host materials, phosphate is an excellent host for preparation of phosphors due to various advantages such as low synthesis temperature, ease of preparation, good thermal and chemical stability and high emission brightness for solid state lighting applications. Among different emission materials, orthophosphates have good fundamental properties such as high band gap, high absorption of PO_4^{3-} in UV–visible region, low phonon energy and exceptional optical damage threshold [3,4].

Rare earth ions doped phosphors have been utilized in modern lighting and display field devices such as FED, PDP, VFDs and WLEDs [5,6]. The generation of white light is easily realized either by incorporation of tricolor phosphors (blue, green and red) with UV-emitting chips or by combination of phosphors (green and red) with blue GaN chips [7]. The pure rare earth ions have not so far been extensively used in practical applications as tunable solid state lasers or phosphors devices mainly because of their drawbacks such as low thermal and photo stability and poor mechanical properties. As a result, increasing attention has been focused on the design and synthesis of organic-inorganic hybrid composites owing to their good mechanical, thermal and chemical properties [8].

Among all rare earth ions, Ho^{3+} and Pr^{3+} ions are good luminescent centers since their energy levels have several metastable multiplets, which can emit light from the level $^5F_4$+$^5S_2$ (green emission) for Ho^{3+} ion and $^1D_2$ level (red emission) for Pr^{3+} ion in visible region [9,10]. Ho^{3+} and Pr^{3+} ions exhibit interesting energy level schemes and the energy levels are well separated, thus radiative transitions are favoured through the energy separation between the respective levels, which give a suitable combination for many up and down conversion processes [11].

Recently, Zhou et al. [12] initiated a study on multi-parametric thermal sensing based on NIR emission of Ho^{3+} doped $CaWO_4$ phosphors and reported the thermometry effect of $CaWO_4$:Ho^{3+} phosphors through the near infrared emission intensity of Ho^{3+}: $^5I_6 \rightarrow {}^5I_8$ transition at ~1190 nm. Wang et al. [13] observed luminescence properties of novel bluish green long-lasting phosphor $LiBaPO_4$:Eu^{2+}, Ho^{3+} and achieved good persistent luminescence in $LiBaPO_4$ phosphor with co-doped Eu^{2+}, Ho^{3+} without changing the emission band. Singh et al. [14] studied defects and optical

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properties of $CaAl_{12}O_{19}$:Ho^{3+} phosphor material and also studied thermoluminescence (TL) at different temperatures and defect centres induced by gamma irradiation. Juache et al. [15] reported luminescence properties of Pr^{3+} doped $SrZrO_3$ phosphors and observed that luminescence increased remarkably with higher sintering temperatures. Xiong et al. [16] studied luminescence properties of novel red-emitting phosphors $LaBMO_6$: Pr^{3+} and reported the photoluminescence properties of novel red emitting $LaBMO_6$: Pr^{3+} phosphor for the application in white LEDs. Boronat et al. [17] investigated on cathodluminescence emission of Pr^{3+} doped $LaAlO_3$ phosphors reported the results obtained from the cathodoluminescence (CL) properties of undoped $LaAlO_3$ and $LaAlO_3$:RE^{3+} (RE = Dy, Pr and Eu).

In this paper, an attempt is made to report the influence of different concentrations of Ho^{3+} and Pr^{3+} ions on the photoluminescence properties in $2CaO$-B_2O_3-P_2O_5 (CBP) phosphors. Changes in spectroscopic properties as a function of concentration were observed and are discussed in terms of local environment of the Ho^{3+} and Pr^{3+} ions. Different concentrations of Ho^{3+} and Pr^{3+} doped CBP phosphors were synthesized using solid state reaction method and investigated the structural and luminescence properties. Together with the concentration dependent luminescence, the color perception and photoluminescence decay of $^5F_4$+$^5S_2$ level of Ho^{3+} and $^1D_2$ level of Pr^{3+} ions were also studied. The measured lifetimes (τ_{meas}), CIE color coordinates (x, y) and absolute quantum efficiencies (Q_E) were calculated for these two ions in the CBP phosphors. The luminescence properties indicated that these phosphors were good candidates for green (Ho^{3+}) and red (Pr^{3+}) emission applications.

2. Experimental

Using solid state reaction method, Ho^{3+} and Pr^{3+} doped $2CaO$-B_2O_3-P_2O_5 (CBP) phosphors ((2-x)CaO-B_2O_3-P_2O_5-xRE (where RE = Ho_2O_3 and Pr_6O_{11}, x = 0.2, 0.4, 0.6, 0.8 and 1.0 mol%)) were prepared using raw materials, $CaCO_3$, H_3BO_3, $NH_4H_2PO_4$, Ho_2O_3 and Pr_6O_{11} with 99.9% purity. A batch of 10 gm of raw material was weighed as per the composition given. These materials were taken in an agate mortar and after grinding they are preheated at 650 °C for 2 h in porcelain crucible and then cooled to room temperature. The preheated batches were again ground and heated at 950 °C for 4 h in an electrical furnace. The obtained phosphor powders were used for various characterizations and analysis.

Crystal structure and phase purity of Ho^{3+} and Pr^{3+} doped CBP phosphors were characterized by X-ray diffraction (XRD) with Rigaku D/Max-2400 instrument, using Ni filtered Cu tube with K_α radiation. SEM morphology of Ho^{3+} and Pr^{3+} doped CBP phosphors were taken by Carl Zeiss EVO-MA15 scanning electron microscope. Fourier transform infrared spectra were recorded at room temperature with 4 cm^{-1} spectral resolution between 400 and 4000 cm^{-1} using BRUKER FTIR spectrometer. Solid state ^{31}P NMR spectra of host, Ho^{3+} and Pr^{3+} doped CBP phosphors were obtained at 400 MHz using a JEOL ECX400 DELTA2 NMR spectrometer with a 4 mm probe. Excitation, photoluminescence and decay lifetimes of Ho^{3+} and Pr^{3+} doped CBP phosphors were acquired using FLS-920 Edinburg-fluorimeter (Horiba FL3- 22iHR320). The absolute photoluminescence quantum efficiencies of the prepared samples were measured by using an integrating sphere which is connected to the fluorescence spectrometer (Horiba FL3- 22iHR320). The integrating sphere was mounted on the side of the fluorescence spectrometer sample chamber, opposite to the excitation source. The CIE 1931 chromaticity coordinates of all the present phosphors were obtained by a color analyzer equipped with a CCD detector (HAAS-2000).

3. Results and discussion

3.1. X-ray diffraction spectra (XRD)

X-ray diffraction patterns of host material, $0.6Ho^{3+}$ and $0.6Pr^{3+}$ doped CBP phosphors in the range, 10°–80° are shown in Fig. 1. It is observed that, all the samples showed similar diffraction peaks reported in JCPDS card No: 0-018-0283 and they are in good agreement. It was also found that, with the variation of doping concentration, no changes in JCPDS structure, thus implying the formation of pure crystalline phase of Ho^{3+} and Pr^{3+} doped CBP phosphors. A well crystallized hexagonal symmetry with group space *P*6*cc* (184) was observed.

3.2. SEM morphology

SEM morphologies are shown in Figs. 2(a–e) and 3(a-e) for different concentrations of Ho^{3+} and Pr^{3+} doped CBP phosphors. From the figure, it is found that the particle size has increased as the Ho^{3+} and Pr^{3+} concentration increased from 0.2 to 1.0 mol% and the particles have more irregular morphologies. The luminescence properties of phosphors depend on the particle size, shape, crystallinity and defects. In the present work, the sizes of the particles are in the range between few microns and several tens of microns and they are suitable for use in the WLEDs applications.

3.3. FT-IR spectra

Fourier transform infrared spectrum of CBP phosphor is measured in the range 500–3600 cm^{-1} and is shown in Fig. 4. From the figure, it is observed that the spectrum consists of eight bands centered at ~570, ~1029, ~1511, ~1702, ~2337, ~3119, ~3241 and ~3601 cm^{-1}. The bands at 570, 1029 and 1511 cm^{-1} are attributed to the $(PO_4)^{-3}$ vibrational bands [18] and correspond to asymmetric stretching vibrations. The band at 570 cm^{-1} is due to O—P—O asymmetric bending vibrations, while the band at 1029 cm^{-1} is due to O—P—O asymmetric stretching vibrations of $[PO_4]^{3-}$ tetrahedrons [18]. The band at 1511 cm^{-1} is attributed to the asymmetric stretching of C—O bonds [19]. The bands observed between the energy range 1702–3601 cm^{-1} are assigned to the H—O—H bending vibrational mode of the H_2O molecule.

3.4. ^{31}P solid state NMR spectra

^{31}P solid state NMR is one of the important techniques in characterizing the structures of phosphate-type phosphors due to the chemical shifts being sensitive to the phosphorus environment. The phosphate bonding is described via Q^n species, where the superscript n refers to the number of bridging oxygens per tetrahedron [20]. ^{31}P NMR spectra of CBP and CBP: $0.6Ho^{3+}$ and CBP: $0.6Pr^{3+}$ phosphors are shown in Fig. 5. The component band of the phosphate group corresponding to the chemical shift located in the positive frequency region is assigned in line with literature data, to the presence of mono-phosphate complexes Q^0 -(PO_4^{3-}), while the line corresponding to the chemical shift in the negative frequency region is attributed to the presence of di-phosphate complexes (PO_7^{4-})-Q^1 [21]. In the present work, the obtained spectrum (from Fig. 5) shows single, symmetric Gaussian peak and the positions of lines for CBP and CBP: $0.6Ho^{3+}$ and CBP: $0.6Pr^{3+}$ phosphors are at +3.9 ppm. This value indicates the presence of mono-phosphate complexes Q^0-(PO_4^{3-}) (phosphate tetrahedral with zero bridging oxygens) in CBP and CBP: $0.6Ho^{3+}$ and CBP: $0.6Pr^{3+}$ phosphors network [22,23].