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Structural and luminescent properties of cerium-ion doped barium borophosphates

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The effects of synthesis conditions on the luminescence characteristics of Ce^{3+} in barium borophosphate phosphors are investigated in the present study. Synthesis of cerium-ion doped $BaBPO_5$ in the oxidizing atmosphere results in partial reduction of Ce^{4+} to Ce^{3+}. The dominant emission at 320 nm arises due to Ce^{3+} located at Ba^{2+} sites without local charge compensation; while, the relatively weak emission at 380 nm is ascribed to Ce^{3+} substituting at Ba^{2+} sites in association with charge compensatory vacancy. The complete reduction of Ce^{4+} to Ce^{3+} occurs for the samples heated in the reducing atmosphere. The increased luminescence of $BaBPO_5$ codoped with cerium and sodium ions is attributed to the reduction in non-radiative energy transfer. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

The rare earth ions activated materials are widely used as lamp phosphors, cathode ray tube phosphors and scintillator phosphors, because of their unique spectroscopic properties [1, 2]. New hosts doped with rare earths are getting much attention owing to their potential for applications. The crystalline alkaline earth borophosphates are reported to be isostructural with mineral stillwellite, which are built up with BO_4 and PO_4 tetrahedra. The ions are coordinated with nine oxygen ions with C_2 symmetry [3, 4]. The structure of these phosphors suggests that $MBPO_5$ ($M = $ Ca, Sr, Ba) is a potential host for the luminescence of rare earth ions. The luminescence properties of rare earth ions in the host $MBPO_5$ ($M = $ Ca, Sr, Ba) are reported, focusing on the luminescent properties of Eu^{2+} and Ce^{3+} in $SrBPO_5$ and $CaBPO_5$ and VUV and UV-excited luminescence of Eu^{2+} and Sm^{2+} in $MBPO_5$ ($M = $ Ca, Sr, Ba) [4–7]. These investigations have revealed that divalent ions, such as Eu^{2+} and Sm^{2+}, can be easily stabilized in these hosts and Stokes' shifts are comparatively small owing to the restrictions imposed by host matrix on the relaxation of excited state.

Cerium ions doped materials are of great importance because of their possible applications to the lighting industry. Cerium ions can exist in the oxidation states +3 and +4 in the phosphors. The luminescence efficiency is greatly affected by the existence of Ce^{4+}, as it provides a non-radiative pathway and reduces the number of Ce^{3+}. In the case of europium and samarium doped phosphors, formation of divalent ions of these dopants during synthesis in the oxidizing atmosphere was reported in some borates and borate phosphate hosts [8–12]. These studies were mostly restricted to the reduction behavior of trivalent rare earth dopant ions in the oxidizing atmosphere. Ce^{3+} doped $BaBPO_5$ has not been investigated in detail, except for one published report [13]. In the present study, the effects of synthesis conditions on the stabilization of Ce^{3+} in $BaBPO_5$ and the effects of codoping sodium ions on the structural and luminescence properties of $BaBPO_5$ based phosphors are investigated.

2. Experimental

$Ba_{1-x}Ce_xBPO_5$ (where $x = 0.005$–0.1) phosphors were prepared via solid-state reactions at elevated temperatures. Reagent-grade $BaCO_3$, $(NH_4)_2HPO_4$ and CeO_2, and H_3BO_3 were thoroughly mixed according to the designed composition by grinding. Boric acid was added in excess by 1 at% to compensate the evaporation loss at high temperatures. The synthesis of $BaBPO_5$ phosphors codoped with cerium and sodium ions ($Ba_{1-m-n}Ce_mNa_nBPO_5$, where $m = 0.005$–0.1 and $n = 0$–0.05) was carried out via direct solid-state reactions using reagent- grade $BaCO_3$, $(NH_4)_2HPO_4$, CeO_2, Na_2HPO_4 and H_3BO_3. Initially all the mixtures were heated at 200, 400 and 600°C for 2 h. After each stage of heating, the powders were cooled to room temperature and thoroughly mixed by grinding for 30 min.

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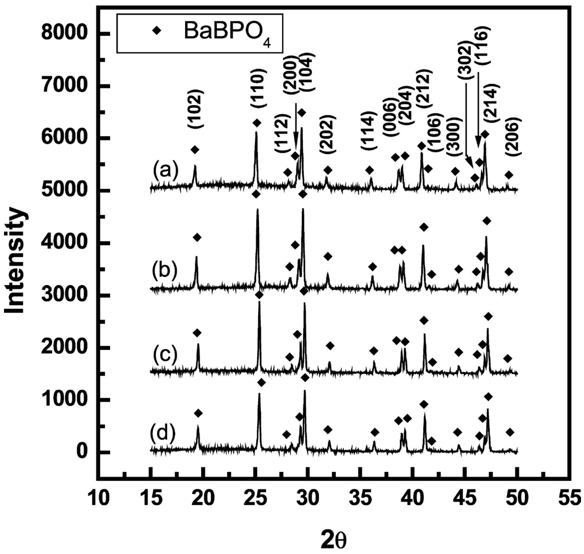

Figure 1 XRD patterns for (a) 900°C-heated $Ba_{0.995}Ce_{0.005}BPO_5$ (air), (b) 900°C-heated $Ba_{0.995}Ce_{0.005}BPO_5$ (reducing atmosphere), (c) 900°C-heated $Ba_{0.9}Ce_{0.1}BPO_5$ (air), and (d) 900°C-heated $Ba_{0.9}Ce_{0.1}BPO_5$ (reducing atmosphere).

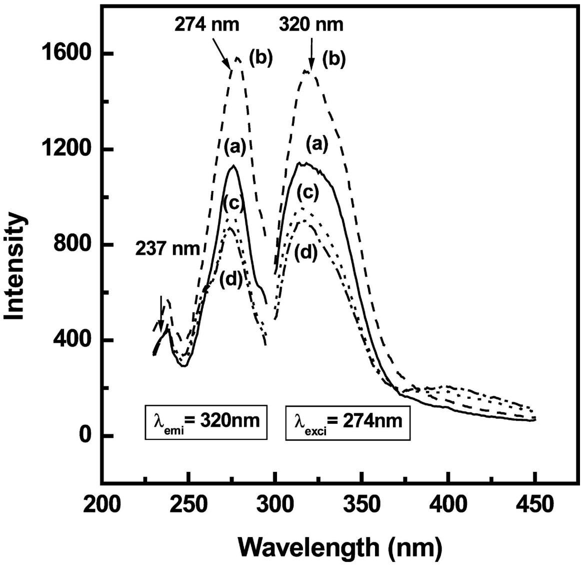

Figure 2 Excitation ($\lambda_{em.}$ = 320 nm) and emission ($\lambda_{exc.}$ = 274 nm) spectra for 900°C-heated $Ba_{1-x}Ce_xBPO_5$ phosphors synthesized in air for different cerium ions substitutions, (a) x = 0.005, (b) x = 0.01, (c) x = 0.05, and (d) x =0.1.

The samples were further heated at 900°C in air for 4 h to obtain the phosphors. Then these samples were subjected to the reducing treatment at 900°C for 4 h in the mixed gas (N_2 (95 vol%) and H_2 (5 vol%)) to achieve total reduction of Ce^{4+}. The phosphors were characterized by XRD using an X-ray diffractometer (MAC M03 XHF). Photoluminescence studies were conducted using a fluorescence spectrometer (Hitachi F-4500).

3. Results and discussion

3.1. Luminescence investigations of $BaBPO_5$ doped with cerium ions

The XRD patterns of the representative samples heated under various conditions are illustrated in Fig. 1. The XRD patterns of $Ba_{0.995}Ce_{0.005}BPO_5$ heated at 900°C for 4 h in air and later in the reducing atmosphere are depicted in curves a and b, respectively. Curve c and d show the XRD patterns of $Ba_{0.9}Ce_{0.1}BPO_5$ heated at 900°C for 4 h in air and in the reducing atmosphere, respectively. All diffraction patterns shown in Fig. 1 match with the reported XRD pattern of $BaBPO_5$ (ICDD file No. 19–0096). No additional diffraction peaks are observed for any of the phosphors. These findings suggest that monophasic phosphors can be synthesized via 900°C-heating with cerium ions replacing barium ions up to 10%. The products obtained via solid-state reactions at 900°C in the reducing atmosphere (95 vol% N_2 and 5 vol% H_2) exhibit identical diffraction patterns.

The excitation and emission spectra recorded for $Ba_{1-x}Ce_xBPO_5$ synthesized in air are illustrated in Fig. 2. The excitation spectra obtained by monitoring the emission at 320 nm reveal two excitation peaks at 237 and 274 nm. The emission spectra excited at 274 nm reveal an emission peak at 320 nm. It is also observed in Fig. 2 that Ce^{3+} luminescence intensity increases with increasing the contents of cerium ions only up to 1 at% (curve b) and drops thereafter for the samples doped with higher amounts of cerium ions (curve c and d). For cerium substitution above 1 at%, a very weak emission around 380 nm is also observed.

Fig. 3 illustrates the excitation and emission spectra recorded for $Ba_{1-x}Ce_xBPO_5$ treated in the reducing atmosphere. The excitation peaks at 237 and 274 nm along with a main emission peak at 320 nm are observed. In contrast

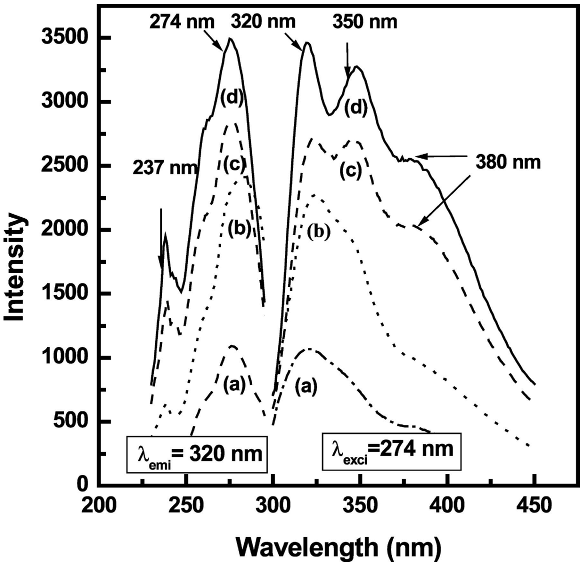

Figure 3 Excitation ($\lambda_{em.}$ = 320 nm) and emission ($\lambda_{exc.}$ = 274 nm) spectra for 900°C-heated $Ba_{1-x}Ce_xBPO_5$ phosphors synthesized in reducing atmosphere for different cerium ions substitutions, (a) x = 0.005, (b) x = 0.01, (c) x = 0.05, and (d) x =0.1.

to the phosphors prepared in air (Fig. 2), the luminescence intensity of the phosphors prepared in the reducing atmosphere increases up to 10 at% of cerium-ion substitution (Fig. 3). In comparison with $Ba_{0.99}Ce_{0.01}BPO_5$ prepared in air (Fig. 2b), a 1.4-fold increase in the luminescence is noted for $Ba_{0.99}Ce_{0.01}BPO_5$ prepared in the reducing atmosphere (Fig. 3b). This is clearly due to the complete reduction of Ce^{4+} during the synthesis of $Ba_{1-x}Ce_x BPO_5$ in air followed by heating in reducing atmosphere.

The emission peak at 350 nm is clearly observed for $Ba_{0.95}Ce_{0.05}BPO_5$ and $Ba_{0.9}Ce_{0.1}BPO_5$ prepared in the reducing atmosphere (Fig. 3c and d); while, a broad peak at 320 nm with a shoulder around 350 nm is noticed for $Ba_{0.995}Ce_{0.005}BPO_5$ and $Ba_{0.99}Ce_{0.01}BPO_5$ (Fig. 3a and b). Further another weak peak is also observed at 380 nm for the samples (curve a-d) similar to the case of samples prepared in air. Emission from Ce^{3+} can occur at wavelengths corresponding to UV and visible regions, depending upon the structure and the crystal field of the host crystal [14]. Two emission peaks separated by 2000 cm^{-1} are expected (320 and 350 nm in the present case) due to two terminating levels $^2F_{5/2}$ and $^2F_{7/2}$ of the 4f electronic configuration of Ce^{3+} [15]. The additional emission at 380 nm observed prominently in the samples prepared in the reducing atmosphere can arise from Ce^{3+} occupying different sites. It may be noted that Liang et al. [13] have also reported a composite emission consisting of 3 peaks at 309, 332 and 363 nm in Ce^{3+} (1 mol%) doped $BaBPO_5$ phosphor synthesized via heating in air followed by calcining in the reducing atmosphere for VUV-UV excitation.

To ascertain the origins of different emission peaks, the excitation spectra were recorded by monitoring emission at 350 and 380 nm for these samples. No differences are observed in the excitation spectra recorded for 320 and 350 nm emission; however, the excitation spectra obtained by monitoring 380 nm emission reveal different excitation peaks, as shown in Fig. 4. This figure illustrates the typical emission ($\lambda_{exc.} = 315$ nm) and excitation ($\lambda_{em.} = 380$ nm) spectra for $Ba_{0.95}Ce_{0.05}BPO_5$ treated in the reducing atmosphere. While the excitation spectrum shows peaks at 315, 280 and 238 nm, the emission spectrum recorded for the excitation at 315 nm consists of a broad emission peaking at 380 nm.

The alkaline earth borophosphates are isostructural with mineral stillwellite and possess only a single site corresponding to alkaline earth ions in the unit cell [3–6]. XRD studies reveal that no secondary phases are formed in the samples prepared in the reducing atmosphere. Therefore, our observation of 274 nm excited emission peaks at 320 and 350 nm along with 315 nm excited emission at 380 nm suggests that these emissions might have their origin from two types of environments for Ce^{3+} in the host. The incorporation of Ce^{3+} in the barium borophosphate matrix by substitution of Ba^{2+} sites can lead to two different types of sites because of ionic charge differences. Ce^{3+} can substitute for Ba^{2+} in the matrix, with the required charge balance provided by the incorporation of two Ce^{3+} ions along with one vacancy of Ba^{2+} at three Ba^{2+} sites. The luminescent properties of Ce^{3+} can vary depending upon whether Ce^{3+} are in association with the vacancy or not.

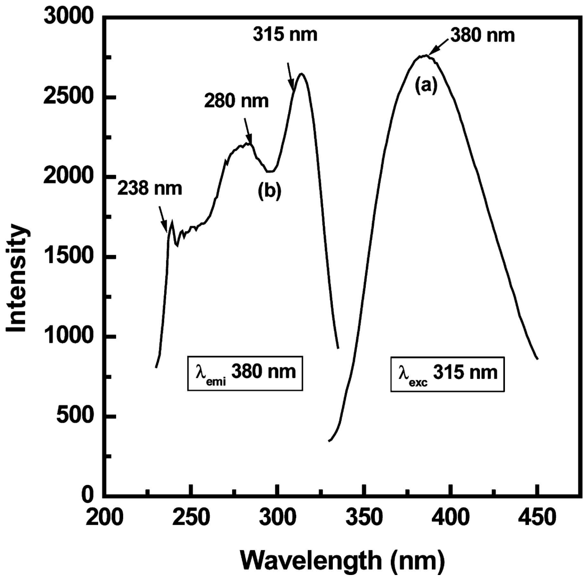

Figure 4 Excitation ($\lambda_{em.} = 380$ nm) and emission ($\lambda_{exc.} = 315$ nm) spectra for 900°C-heated $Ba_{0.95}Ce_{0.5}BPO_5$ phosphors synthesized in reducing atmosphere.

Luminescence investigations of Ce^{3+} in strontium borate, haloborates, and borophosphates have revealed the presence of two types of sites for Ce^{3+} due to charge differences [16–18]. Ce^{3+} taking up divalent-ion sites without any associated vacancy exhibit a small Stoke's shift; while, Ce^{3+} in association with vacancy lead to a large Stoke's shift and lower energy position in the excitation spectra. The emission occurring at 320 and 350 nm (Fig. 3) is attributed to Ce^{3+} occupying Ba^{2+} sites without any associated charge compensatory vacancy (called 'site I'); while, the 315 nm excited emission occurring at 380 nm (Fig. 4) is assigned to emission from Ce^{3+} occupying Ba^{2+} sites with associated vacancy (called 'site II').

3.2. Effects of codoping Na^+ on the emission characteristics of Ce^{3+}

The effects of codoping sodium ions along with trivalent cerium ions in the host of $BaBPO_5$ were investigated for samples containing 10 at% of cerium ions. The content of sodium ions was varied in the range of 0–5 at%. No major changes are noticed in emission and excitation peak positions of Ce^{3+} with the codoping of Na^+ and Ce^{3+} in the host of $BaBPO_5$. Fig. 5 illustrates the 274 nm excited emission spectra for the 900°C-heated $Ba_{0.9}Ce_{0.1}BPO_5$, $Ba_{0.895}Ce_{0.1}Na_{0.005}BPO_5$, $Ba_{0.89}Ce_{0.1}Na_{0.01}BPO_5$, and $Ba_{0.85}Ce_{0.1}Na_{0.05}BPO_5$ samples synthesized in the reducing atmosphere. The emission peaks at 320 and 350 nm are mainly characteristic of Ce^{3+} occupying site I. Due to the higher emission in-

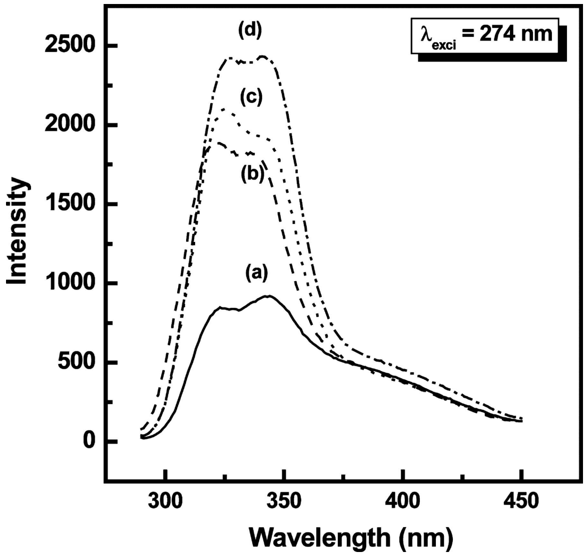

Figure 5 Emission spectra ($\lambda_{exc.}$= 274 nm) for 900°C-heated (a) $Ba_{0.9}Ce_{0.1}BPO_5$, (b) $Ba_{0.895}Ce_{0.1}Na_{0.005}BPO_5$, (c) $Ba_{0.89}Ce_{0.1}Na_{0.01}BPO_5$, and (d) $Ba_{0.85}Ce_{0.1}Na_{0.05}BPO_5$ synthesized in the reducing atmosphere.

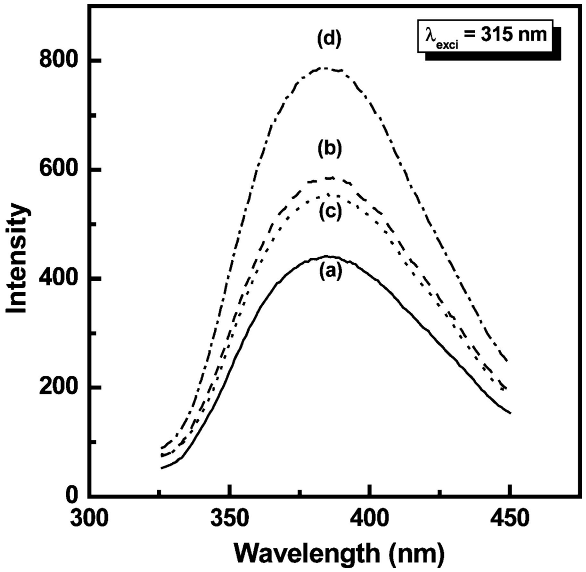

Figure 6 Emission spectra ($\lambda_{exc.}$ = 315 nm) for 900°C-heated (a) $Ba_{0.9}Ce_{0.1}BPO_5$, (b) $Ba_{0.895}Ce_{0.1}Na_{0.005}BPO_5$, (c) $Ba_{0.89}Ce_{0.1}Na_{0.01}BPO_5$, and (d) $Ba_{0.85}Ce_{0.1}Na_{0.05}BPO_5$ synthesized in the reducing atmosphere.

tensity in these samples, the spectra were recorded with an arrow emission slit-width compared to spectra shown in Fig. 3. It is clear from Fig. 5 that with constant Ce^{3+} concentration, the emission intensity of Ce^{3+} (occupying site I) rises with an increase in codopant Na^+ ions. Fig. 6 illustrates the 315 nm excited emission spectra of these samples corresponding to luminescence of Ce^{3+} ions occupying site II. It is clear that the intensity of Ce^{3+} occupying site II also increases due to codoping of Na^+ with Ce^{3+} in $BaBPO_5$ lattice. Since the incorporation of Na^+ as codopants with Ce^{3+} leads to an increase in the intensities of Ce^{3+} occupying both sites (site I and II) in the host, the observed luminescence enhancement cannot be associated with changes in site occupancy as a result of codoping in the samples.

The enhanced Ce^{3+} emission can be due to many factors, such as increased reduction of Ce^{4+} to Ce^{3+}, energy transfer, redistribution of sites, and changes in non-radiative energy transfer. Addition of sodium ions is not expected to influence the reduction of Ce^{4+}, since the Na^+ and Ce^{3+}-co-doped $BaBPO_5$ samples showing enhanced luminescence were prepared in reducing atmosphere. Ions such as Li^+, Na^+, K^+, Ca^{2+}, and Sr^{2+} as the codopants cannot directly involve in the energy transfer process. In the case of $LaPO_4$: Ce^{3+} samples, it is shown that codoping with Li^+ enhances the energy transfer from Ce^{4+} to Ce^{3+} [19]. Similar energy transfer possibility is ruled out in the present case, since Ce^{4+} will be absent in the samples prepared in the reducing atmosphere.

Selective increase in the emission intensity of Ce^{3+} occupying site I can occur due to shifting of Ce^{3+} occupying site II to site I as a result of Na^+ codoping. In such a case, an increase in intensity of emission generated by Ce^{3+} at site I should be accompanied by a reduction in emission intensity of Ce^{3+} at site II. However, emission intensity corresponding to site II also increases due to sodium codoping in the samples (Fig. 6). Therefore, the luminescence enhancement associated with the codoping of Na^+ and Ce^{3+} in $BaBPO_5$ lattice is not related to redistribution of Ce^{3+} amongst these two sites. On the other hand, reduction in non-radiative transitions can possibly enhance the luminescence of Ce^{3+} occupying both sites in the matrix, regardless of the synthesis conditions. The reduction in non-radiative transitions may be explained as due to the better spatial distribution of Ce^{3+} in the $BaBPO_5$ lattice due to the presence of Na^+, or due to better crystallinity of the co-doped samples. This can lead to the observed luminescence enhancement upon codoping Na^+ along with Ce^{3+} in $BaBPO_5$ lattice.

4. Conclusions

The structural and luminescent properties of Ce^{3+} doped in the host of $BaBPO_5$ are reported in this paper. The luminescent characteristics reveal that Ce^{3+} occupy two types of sites in the host. The different anionic environments associated with Ce^{3+} in the host of $BaBPO_5$ arise from the charge compensation for Ce^{3+} substituting for Ba^{2+}. Ce^{3+} situated at Ba^{2+} sites without associated charge compensatory vacancies reveal a small Stoke's shift with characteristic emission and excitation peaks at 320 and 274 nm, respectively. On the other hand, for Ce^{3+} in association with vacancies the typical emission and excitation peaks are observed at 380 and 315 nm respectively. These observations reveal that large Stoke's shift and low excitation energy for Ce^{3+} located at Ba^{2+} sites in association with vacancy. The incorporation of sodium ions as codopants leads to increased luminescence. The luminescence enhancement due to codoping of sodium ions is probably associated with the reduction in non-radiative energy transfer.

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