Solid state synthesis and luminescent properties of bright blue-emitting $\text{Ba}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$ phosphor

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Received: 29 December 2019 / Accepted: 25 February 2020 / Published online: 5 March 2020
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Abstract

Eu^{2+} -activated $\text{Ba}_2\text{P}_2\text{O}_7$ pyrophosphates were successfully synthesized by the solid-state reaction under reduced atmosphere and were characterized by X-ray diffraction (XRD) and Nuclear magnetic resonance and infrared (IR)/Raman spectroscopy. The luminescence properties of $\text{Ba}_{2-x}\text{P}_2\text{O}_7: x\text{Eu}^{2+}$ ($x = 0.01, 0.05$) phosphors were investigated in ultraviolet (UV) and vacuum ultraviolet (VUV) regions. Under 131 or 320 nm excitation, the phosphors exhibit a blue emitting band ranging from 350 to 500 nm, which is provided corresponding to the $5d-4f$ transition of Eu^{2+} . The as-synthesized phosphors present good thermal luminescence stability on temperature quenching and high color purity with the CIE coordinate (0.172, 0.031) for $\text{Ba}_2\text{P}_2\text{O}_7:1\%\text{Eu}^{2+}$ phosphor. These results suggest that the $\text{Ba}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$ pyrophosphate might be a promising blue-emitting phosphor for near ultraviolet (n-UV) light-emitting diodes (LEDs).

Keyword Pyrophosphate · Phosphors · Blue-emitting · Eu^{2+} · Luminescence

1 Introduction

Recently, phosphors for LED applications have received considerable attention with the rapid development of white light emitting diodes (LEDs). Blue emitting phosphors combined with a red and green emitting phosphors to produce white light is the most commonly adopted method for white LED applications due to higher luminous efficiency and lower fabrication cost [1–5]. Phosphate-based phosphors have attracted much attention in recent years as they have excellent thermal stability and good charge stability due to rigid tetrahedral three-dimensional matrix of phosphate [6–9]. In particular, Eu^{2+} -doped pyrophosphates belonging to the $\text{A}_2\text{P}_2\text{O}_7$ and ABP_2O_7 families (where A and B are divalent cations) are one class of desirable blue phosphors as they possess a few interesting characteristics such as high luminescence efficiency upon blue or near-UV LED excitation,

good thermal and chemical stability [9–17]. Browsing the literature, we found that the co-doping blue emitting ions as co-activators into any matrix was extensively studied by numerous scientists. Pang et al. reported that $\text{Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}, \text{Y}^{3+}$ and $\text{Sr}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}, \text{Y}^{3+}$ pyrophosphates show bright blue long-lasting phosphorescence [18, 19]. It is found that the phosphors emitted blue light that was related to the $4f^65d^1 \rightarrow {}^8\text{S}_{7/2}$ transition of Eu^{2+} and the co-doping of Y^{3+} enhanced the intensity and persistent time of the long-lasting phosphorescence. Co-doping Eu^{2+} in $\text{Ba}_2\text{P}_2\text{O}_7: \text{Tb}^{3+}$ lattice is also found to improve emission from Eu^{2+} [20]. To the best of our knowledge, little research on Eu^{2+} -mono-activated alkaline-earth-metal pyrophosphates with the general formula $\text{A}_2\text{P}_2\text{O}_7$ (A being an alkaline earth cation), which could have a blue light emitting property, have been published. Recently, Kolay et al. reported the luminescence properties of 2% Eu^{2+} -doped $\text{Ca}_2\text{P}_2\text{O}_7$ and $\text{Ba}_2\text{P}_2\text{O}_7$ -particles synthesized at

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low temperatures [21]. Strong blue emission has been observed upon heating the as prepared samples under argon environment and this has been attributed to the formation of Eu^{2+} ion in the lattice brought about by the partial conversion of Eu^{3+} to Eu^{2+} .

Therefore, in this present work, xEu^{2+} -doped $\text{Ba}_{2-x}\text{P}_2\text{O}_7$ was developed as a potential blue-emitting phosphor for n-UV-pumped white LEDs. This was synthesized by the solid-state reaction under reducing atmosphere. The crystal structure, photoluminescence properties and the thermal stability of the blue phosphor were investigated in detail.

2 Experimental

2.1 Powder synthesis

The compounds $\text{Ba}_{2-x}\text{P}_2\text{O}_7 \cdot \text{xEu}^{2+}$ were prepared by the solid-state reaction method under reductive atmosphere. The raw materials used for the synthesis were BaCO_3 (Aldrich, 99.9%), $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ (Acrös Organics, 99 + %) and Eu_2O_3 (Aldrich, 99.99%). These starting materials were weighted in stoichiometric amount and thoroughly mixed in an agate mortar. Thereafter, the mixtures were pre-sintered under air atmosphere at 400 °C for 4 h to remove volatile gas and then annealed twice at 900 °C for 5 h under slightly reducing atmosphere (5% H_2 + 95%Ar) with intermediate grindings. The twice anneal under a reducing atmosphere is used in order to cause the total reduction reaction $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ in the host matrices. Finally, the samples were cooled down to room temperature and grounded for further characterizations.

2.2 Characterization techniques

X-ray diffraction powder patterns were recorded with a Philips X-Pert Pro diffractometer operating with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) was carried out at 121.5 MHz with a Bruker Advance 300 spectrometer operating in a static field of 7.1 T.

The infrared absorption spectra were recorded with a Nicolet 55X-FTIR spectrometer equipped with diamond micro-ATR accessory and working with OMNIC software. Raman spectra of samples were recorded at room temperature with a T64000 JOBINYVON spectrometer equipped with a CCD detector cooled with liquid nitrogen.

The photoluminescence spectra in the range UV–visible were measured using a Jobin–Yvon set-up consisting of a Xe lamp operating at 400 W. For the temperature measurement, the setup was equipped with a homemade heating cell connected to a temperature controller. The VUV

excitation spectra and corresponding emission spectra were recorded at room temperature using specific system built by Jobin–Yvon allowing excitation in the range 112–300 nm. The commission International de l'Eclairage (CIE) chromaticity coordinate values are measured by a PMS-80 Plus-UV-Vis-near-IR Spectrophotometer colorimeter.

3 Results and discussion

3.1 Phase structure

The XRD patterns of undoped and Eu^{2+} -doped $\text{Ba}_2\text{P}_2\text{O}_7$ compounds are depicted in Fig. 1. It can be seen that the main reflections of the entire samples match well with the $\text{Ba}_2\text{P}_2\text{O}_7$ phase (ICSD 80101) [22]. No impurity phase is observed, implying that, the incorporation of Eu^{2+} ions into the $\text{Ba}_2\text{P}_2\text{O}_7$ lattice does not cause any significant change to the crystal structure of the host matrix.

The $\sigma\text{-Ba}_2\text{P}_2\text{O}_7$ pyrophosphate crystallized as a hexagonal crystal system with P6₂m space group [22]. As shown in Fig. 2, Ba ions have two different types of coordination environments, in which one is coordinated by seven oxygen atoms and the other is coordinated by ten oxygen atoms. In the crystal structure, two crystallographically distinct P sites exist in the lattice, to form two kinds of PO_4 tetrahedra linked to the bridging oxygen ions on inversion centers.

The ^{31}P MAS NMR, Raman and infrared spectra of $\text{Ba}_2\text{P}_2\text{O}_7$ pyrophosphate illustrated in Fig. 3a, b and c respectively. The examination of the NMR spectrum of this compound (Fig. 3a) shows broad band, which consist of two lines, is observed in the Q^1 range (−10/−20 ppm) [23–26]. Q-Typing is used to describe the environment of

Fig. 1 XRD powder patterns of pure and Eu^{2+} -doped $\text{Ba}_2\text{P}_2\text{O}_7$ pyrophosphates

Fig. 2 Schematic views of the $\text{Ba}_2\text{P}_2\text{O}_7$ structure along a-direction. Coordination environment around Ba (1) and Ba (2) sites

a phosphorus atom in a condensed phosphate, denoted as Q^n where n is the number of bridging oxygen atoms connected to that particular phosphorus atom. The two peaks shown in the NMR spectra confirm the presence of two crystallographically distinct phosphorus sites with two different PO_4 tetrahedra. This is in good agreement with the crystal structure which was two inequivalent phosphorus [22].

The assignment of Raman lines (Fig. 3b) and infrared bands (Fig. 3c) were done by comparison with the spectra of the pyrophosphates in the literature [27, 28]. The bands observed in the range $1240\text{--}1020\text{ cm}^{-1}$ are due to the symmetric and asymmetric stretching frequencies of PO_3 in $\text{P}_2\text{O}_7^{4-}$ groups. The bands observed in the regions $985\text{--}800$ and $780\text{--}690\text{ cm}^{-1}$ are attributed respectively to the asymmetric and symmetric P–O–P group [29]. The bands due to the deformation and rocking modes of PO_3 are also identified in the low frequency regions.

3.2 Photoluminescence properties

3.2.1 Excitation and emission spectra

The UV excitation spectra of $\text{Ba}_{2-x}\text{P}_2\text{O}_7: x\text{Eu}^{2+}$ ($x = 0.01, 0.05$) monitored at 413 nm are shown in Fig. 4. A broad excitation band in range $250\text{--}400\text{ nm}$ is observed which can be attributed to the $4f\text{--}5d$ transition of Eu^{2+} ions. Obviously, the excitation spectra from 250 to 400 nm means the phosphor $\text{Ba}_2\text{P}_2\text{O}_7: \text{Eu}^{2+}$ can be excited effectively by UV LEDs. The VUV excitation spectra of $\text{Ba}_2\text{P}_2\text{O}_7: (1\%, 5\%)\text{Eu}^{2+}$ pyrophosphates in $100\text{--}400\text{ nm}$ region

are presented in Fig. 5. Monitored at about 417 nm , these spectra reveal two different areas: one for the lower energy corresponding to the direct absorption in the dopant (originated from $4f^7(^8\text{S}_{7/2})\text{--}4f^65d$ transitions of Eu^{2+}) and one for the higher energy due to the lattice absorption [30]. This last area shows a group of bands peaking at about $140, 163$ and 191 nm . The bands at 140 and 163 nm correspond to the absorption of $(\text{P}_2\text{O}_7)^{4-}$ groups in the host crystal. According to the structure, there are two different $(\text{P}_2\text{O}_7)^{4-}$ anionic groups in the $\text{Ba}_2\text{P}_2\text{O}_7$ host, which can explain the two absorption bands displays in Fig. 5. The band peaking at 191 nm is related to the charge transfer band (CTB) of $\text{Ba}^{2+}\text{--}\text{O}^{2-}$ [31]. The excitation band with the maximum at 228 nm could be assignable to charge transfer (CT) absorption of $\text{Eu}^{2+}\text{--}\text{O}^{2-}$ [32, 33].

Figure 6a displays the photoluminescence emission spectra of $\text{Ba}_2\text{P}_2\text{O}_7: (1\%, 5\%)\text{Eu}^{2+}$ under the excitation at 320 nm . The emission spectra exhibit a broad blue emission band ranging from 350 to 500 nm , which assigned to the $4f^65d^1 \rightarrow 4f^7$ allowed electronic transition of Eu^{2+} ions. No other characteristic emission peaks of Eu^{3+} exist near the profiles, which prove that Eu^{3+} ions were reduced to Eu^{2+} completely in our experiments. The asymmetry nature and broadness of the emission spectra of blue phosphors demonstrates the presence of different emission centers. Structurally, there are two crystallographically different Ba^{2+} sites in the $\text{Ba}_2\text{P}_2\text{O}_7$ host. So the broad asymmetric emission band can be well deconvoluted into two

Fig. 3 **a** ^{31}P MAS NMR, **b** raman and **c** IR/ATR spectra of $\text{Ba}_2\text{P}_2\text{O}_7$ pyrophosphate

Gaussian profiles peaked at 412 and 435 nm as depicted in insert Fig. 6a.

To understand the origin of the observed emission center, the Van Uitert equation was employed to

Fig. 4 Excitation spectra of $\text{Ba}_2\text{P}_2\text{O}_7:\text{xEu}^{2+}$ ($\text{x}=0.01, 0.05$) recorded at 300 K, by monitoring the emission wavelength at 413 nm

Fig. 5 VUV excitation spectra of $\text{Ba}_2\text{P}_2\text{O}_7:\text{xEu}^{2+}$ ($\text{x}=0.01, 0.05$) under excitation wavelength $\lambda_{\text{em}}=417$ nm

quantitatively analyze the site occupancy of Eu^{2+} in the Ba^{2+} sites on the basis of the following empirical formula [34]:

$$E = Q \left[1 - \left(\frac{V}{4} \right)^{1/V} 10^{-(n \cdot E_a \cdot r)/80} \right] \quad (1)$$

where E (cm^{-1}) is the position of the emission band of Eu^{2+} , Q is the position in energy for the lower d-band edge for the free ion ($34\,000\,\text{cm}^{-1}$ for Eu^{2+}), V represents the valence of the activator ($V=2$ for Eu^{2+}), E_a is the constant electron affinity of the atoms that form anions. Here, E_a is approximately 2.19, as reported in other phosphates structures [1, 35], n is the coordination number of the “active” ion (Eu^{2+}),

Fig. 6 **a** Emission spectra of $\text{Ba}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$ (1%, 5%) recorded at 300 K, upon UV excitation at 320 nm. **b** Emission spectra of $\text{Ba}_{2-x}\text{P}_2\text{O}_7:x\text{Eu}^{2+}$ ($x=0.01, 0.05, 0.07$ and 0.10) with inset showing the emission intensity with Eu^{2+} concentrations

r is the effective radius of the host cation replaced by the Eu^{2+} ion. Here, the radius of Ba^{2+} is $1.52 \text{ \AA}$ when the coordination number is 10, whereas that is $1.38 \text{ \AA}$ when the coordination number is 7. Therefore, the values of E calculated by the above equation are $25,266 \text{ cm}^{-1}$ (412 nm) and $18,859 \text{ cm}^{-1}$ (435 nm) respectively, corresponding to ten and seven for the coordination number of Ba sites. As could be seen, the experimental values agree well with the calculated values and the blue emission bands at 412 and 435 nm are assigned to activators Eu^{2+} occupied the site of Ba(1) (10-coordinated) and Ba(2) site (7-coordinated), respectively. It could be found that the emission intensity tends to increase with an increase in the Eu^{2+} doping concentration and it reaches the maximum at $x=0.05$, as indicated in the inset of Fig. 6b which plots the emission intensity of $\text{Ba}_{2-x}\text{P}_2\text{O}_7:x\text{Eu}^{2+}$ ($x=0.01, 0.05, 0.07, 0.10$)

Fig. 7 VUV emission spectra of $\text{Ba}_2\text{P}_2\text{O}_7:x\text{Eu}^{2+}$ ($x=0.01, 0.05$) under **a** 131 nm and **b** 163 nm excitation

phosphors as a function of the Eu^{2+} content. Consequently, the concentration quenching occurs as the Eu^{2+} contents are beyond 0.05, namely, the emission intensity declines dramatically as the content of Eu^{2+} exceeds 5 mol%.

The VUV-excited emission spectra of $\text{Ba}_2\text{P}_2\text{O}_7:(1\%, 5\%) \text{Eu}^{2+}$ are illustrated in Fig. 7. Under the VUV excitation at 163 nm and 131 nm, these photoluminescence spectra show nearly the same spectral characteristics, no significant changes except for the emission intensity. They exhibit a blue emission band peaking at 416 nm due to the electric-dipole allowed $5d-4f$ transition of Eu^{2+} ions.

3.2.2 Dependence of luminescence on temperature

Generally, the thermal stability of phosphor is of great significance for its application in white LEDs. Then, the temperature dependence of phosphors is important since it has a considerable influence on the light output as well

as color-rendering index [36, 37]. Usually, the phosphors employed in LED devices are expected to operate above 150 °C. Thus, the temperature-dependent emission spectra of selected phosphor $\text{Ba}_{1.99}\text{P}_2\text{O}_7:1\%\text{Eu}^{2+}$ was investigated in the temperature region 28–220 °C under UV radiation ($\lambda_{\text{exc}} = 320$ nm) and are displayed in Fig. 8a. The variation curve of the emission intensity as a function of temperature was also displayed in Fig. 8b. It is clearly observed that the relative emission intensity decreases gradually with increase in temperature. This behavior is expected due to the loss of energy by means of non radiative transitions at higher temperatures.

At 150 °C, the emission intensity of phosphors decreases about 77% of its initial value for $\text{Ba}_{0.99}\text{Eu}_{0.01}\text{P}_2\text{O}_7$. This result suggests that the phosphor have a good thermal stability and can be used as a promising blue-emitting phosphor for near-UV LED application. To further investigate the luminescence behavior at different temperatures, the activation energy (E_a) for thermal quenching can be estimated using the modified Arrhenius equation as follows [38]:

$$I_T = I_0 / 1 + c \exp \left(- \left(\frac{E_a}{k_B T} \right) \right) \quad (2)$$

where I_0 and I_T are the luminescence intensity of $\text{Ba}_{1.99}\text{P}_2\text{O}_7:0.01\text{Eu}^{2+}$ at room temperature and testing temperature, respectively; c a constant and k_B Boltzmann's constant (8.617×10^{-5} eV/K). According to the equation, the thermal activation energy E_a can be calculated by plotting $\ln[(I_0/I_T)-1]$ versus $1/k_B T$, where the straight slope equals $-E_a$. As shown in Fig. 8c, the value of the activation energy E_a of the as-prepared $\text{Ba}_{1.99}\text{Eu}_{0.01}\text{P}_2\text{O}_7$ phosphor is calculated to be 0.157 eV, which is similar to another report on the $\text{NaAlP}_2\text{O}_7:0.03\text{Eu}^{2+}$ phosphor [13]. The relatively high activation energy indicating that thermal quenching is not easy to take place and the synthesized phosphors are thermal stable.

3.2.3 CIE chromaticity

Figure 9 shows the CIE chromaticity coordinates of the $\text{Ba}_{1.99}\text{P}_2\text{O}_7:0.01\text{Eu}^{2+}$ phosphor under the excitation of

Fig. 8 **a** Temperature dependent emission spectra of $\text{Ba}_{1.99}\text{P}_2\text{O}_7:0.01\text{Eu}^{2+}$ ($\lambda_{\text{exc}} = 320$ nm). **b** Temperature dependent relative emission intensity of $\text{Ba}_2\text{P}_2\text{O}_7:0.01\text{Eu}^{2+}$ sample. **c** A $\ln[(I_0/I)-1]$ versus $1/k_B T$ activation energy graph for thermal quenching of $\text{Ba}_2\text{P}_2\text{O}_7:1\%\text{Eu}^{2+}$ phosphor

Fig. 9 CIE chromaticity coordinates of $\text{Ba}_2\text{P}_2\text{O}_7:0.01\text{Eu}^{2+}$ phosphor

320 nm. The CIE (x, y) coordinates are (0.172, 0.031), indicating that the pyrophosphate has high color purity. Besides, under 365 nm UV lamp, the digital photograph of $\text{Ba}_2\text{P}_2\text{O}_7:0.01\text{Eu}^{2+}$ phosphor emits bright blue emission, which can be clearly observed by the naked eyes as displayed in the inset of Fig. 9. Thus, suggest that phosphor may serve as a promising blue-emitting candidate for w-LEDs application.

4 Conclusions

Blue-emitting phosphors $\text{Ba}_{2-x}\text{P}_2\text{O}_7: x\text{Eu}^{2+}$ ($x=0.01, 0.05$) were successfully synthesized by a solid-state reaction method in H_2/Ar reducing atmosphere. The luminescence properties under UV and VUV excitation are investigated for potential applications in white LEDs. The pyrophosphate phosphor offered a broad excitation band extending from 250 to 400 nm and a broad blue emission band peaking at 416 nm upon 320 nm excitation light that was ascribed to the characteristic $d-f$ emission of Eu^{2+} . It was indicated that Eu^{2+} randomly substituted two Ba^{2+} crystallographic sites with different coordination environments. The CIE coordinate is determined to be (0.172, 0.031) for $\text{Ba}_2\text{P}_2\text{O}_7:1\%\text{Eu}^{2+}$ phosphor with high blue color purity. Therefore, $\text{Ba}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$ phosphor achieved in this work is a kind of potential

blue-emitting component for near-UV white light-emitting diodes.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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