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Investigation of Eu^{2+} luminescence in barium tetraphosphate $Ba_3P_4O_{13}$ polycrystalline ceramics

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Abstract

In this paper, $Ba_3P_4O_{13}$:Eu^{2+} phosphor was synthesized by a solid-state reaction. The photoluminescence (PL) emission spectrum and luminescence decay kinetics confirm that the doped Eu^{2+} ions can occupy two different Ba^{2+} sites. The PL excitation spectrum shows a broad band matching well with the emission of near-UV chip. $Ba_3P_4O_{13}$:Eu^{2+} is a promising phosphor for near-UV chip excited white LEDs. The doped Eu^{3+} ions can also be reduced to Eu^{2+} ions in air atmosphere at high temperature. Charge compensation mechanism is applied to explain this kind of abnormal reduction.

Keywords: A. Powder: solid state reaction; B. Spectroscopy; C. Optical properties

1. Introduction

Recently, more and more attention is focused on phosphor converted white light-emitting-diodes (White LEDs) because of their advantages, such as high efficiency, long lifetime, energy saving and environment-friendly [1–3]. Developing the excellent phosphor materials matching well with near-UV or blue chips is the research focus in the field of solid-state-light (SSL) industry [4–6].

Up to now, Eu^{2+} ion has been widely investigated as an efficient activator in phosphors for display and lighting due to its intense broad excitation and strong emission band [7]. The excellent luminescent properties can be attributed to the allowed inter-configurational 4f→5d transitions with high oscillator strength [8,9]. In general, the 5d→4f emissions of Eu^{2+} depend strongly on the host composition, crystal structure and lattice symmetry [5,10,11]. So the colors of the Eu^{2+} emission can vary from long-wavelength ultraviolet to red. In addition, its emission peak can easily shift and its full width at half maximum will broaden if electron–phonon interaction is stronger [12].

Phosphates are a large family of compounds. The luminescent properties of rare earth doped materials have been investigated widely due to their application in the field of display and lighting [13]. For $Ba_3P_4O_{13}$ crystal, the structure has been reported by Gatehouse in 1991[14]. The luminescent properties of $Ba_3P_4O_{13}$:Eu^{2+} phosphor has only been investigated simply by Lagos in 1968 [15]. In this paper, the PL emission spectrum at lower temperature and luminescence decay kinetics have been utilized to confirm that the doped Eu^{2+} ions can occupy two different Ba^{2+} sites. At the same time, it is found that the Eu^{3+} can be reduced to Eu^{2+} in $Ba_3P_4O_{13}$ host in air at high temperature. Charge compensation mechanism is applied to explain this kind of abnormal reduction.

2. Experimental

$Ba_3P_4O_{13}$:Eu^{2+} phosphor was synthesized by a solid-state reaction. The stoichiometric amounts of materials $BaCO_3$ (Aldrich, 99.9%), $(NH_4)_2HPO_4$ (Aldrich, 99.9%) and Eu_2O_3 (Aldrich, 99.99%) were well mixed. The materials were prefired at 600 °C for 2 h in air to pyrolyze phosphate; then

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the raw materials were re-ground and calcined at 750°C for 8 h in air atmosphere.

The crystalline structure of the final product was examined by using a Philips XPert/MPD diffraction system with CuKα ($\lambda = 1.5405$ Å) radiation. The photoluminescence (PL) excitation and emission spectra were measured with a Fluorescence Spectrophotometer (PTI) with a 150 W Xe lamp as an excitation source. The PL emission spectrum at 18 K was obtained by 355 nm pulsed Nd/YAG (yttrium aluminum garnet) laser (Spectron Laser Systems SL802G). The sample was placed at cold finger in a He gas recycled cryostat. The decay curves were recorded by the 500 MHz digital oscilloscope (LeCroy 9350A).

3. Results and discussion

3.1. Identification of crystalline phase of the sample

$Ba_3P_4O_{13}$ compound crystallizes in triclinic space group $P1^-$ with lattice constants of $a = 5.691$ (5), $b = 7.238$ (7) and $c = 8.006$ (5) Å; $\alpha = 83.65$ (5), $\beta = 75.95$ (8) and $\gamma = 70.49$ (7)° [14]. Fig. 1 shows X-ray diffraction pattern of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ sample. The XRD pattern of $Ba_3P_4O_{13}$ crystal (JCPDS, no. 79-1530) is also shown for comparison. The diffraction peaks are in good agreement with data given in JCPDS 79-1530, which indicates that doped Eu^{2+} ions do not change the crystal structure of $Ba_3P_4O_{13}$. Because the electric charges of Ba^{2+} and Eu^{2+} are identical and the radii of them are similar ($r_{Ba(+2)} = 0.142$ nm, $r_{Eu(+2)} = 0.125$ nm CN = 8) [16], we argue that the doped Eu^{2+} ions prefer to occupy Ba^{2+} sites.

3.2. PL properties of $Ba_3P_4O_{13}$:Eu^{2+} prepared in air

It is well known that Eu^{2+} usually gives broadband emission due to d → f transition, and the spectral position of the emission band depends strongly on the crystal structure of host [13]. The coordination numbers for the barium ions in $Ba_3P_4O_{13}$ crystal have been taken to be eight for Ba(1) and seven for Ba(2) (the crystal structure of $Ba_3P_4O_{13}$ emphasizing the coordination environment of Ba(1) and Ba(2) cations is shown in the inset of Fig. 1). The mean distance of Ba(1)–O bond is 2.82 (13) Å and that of Ba(2)–O bond is 2.76 (7) Å [14]. As discussed above, the doped Eu^{2+} ions will substitute Ba^{2+} ions sites in $Ba_3P_4O_{13}$. Two different Ba sites [Ba(1) and Ba(2)] can be partially occupied by Eu^{2+} ions. According to the above structure analysis, the mean distance of Ba(1)–O is longer than that of Ba(2)–O, so the Eu^{2+} ions substituting Ba(1) sites experience weaker crystal-field strength which is inversely proportional to R^5 (R: chemical bond length between a cation with d orbital electrons and the coordinating anion) [17].

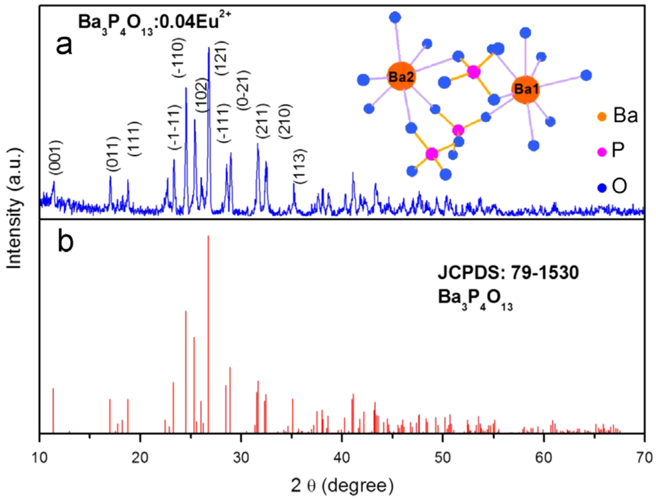

Fig. 1. XRD pattern of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ phosphor, the XRD pattern of $Ba_3P_4O_{13}$ crystal (JCPDS, no. 79-1530) is also shown for comparison (the inset shows the crystal structure of $Ba_3P_4O_{13}$ emphasizing the coordination environment of Ba1 and Ba2 cations).

Room temperature excitation and emission spectra of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ are depicted in Fig. 2. The excitation spectra show broadband in the near-UV region. Although the two excitation spectra show some difference when monitored by different emission wavelengths, they should be ascribed to the $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} ions. The 5d levels of Eu^{2+} that are not shielded from the outside environment are split under different ligand field strengths and the number of split levels is determined by the local symmetry around Eu^{2+} ions [18]. For $BaCl_2$:Eu^{2+} phosphor, Eu^{2+} ions occupy the Ca^{2+} site having O_h symmetry. So the 5d orbitals of Eu^{2+} are split into two levels, t_{2g} and e_g [19]. In the case of $CaSr_{1-x}Eu_xSi_5N_8$, the excitation spectrum is broadband and cannot be exactly resolved because Eu^{2+} could occupy two different Sr sites [20]. In the present case, the relative complicated environment of the Ba^{2+} also results in a broad excitation band, which is similar to $CaSr_{1-x}Eu_xSi_5N_8$ sample. Because the PL excitation spectra show strong absorption in the range of near-UV, $Ba_3P_4O_{13}$:Eu^{2+} could be a potential phosphor for white LEDs.

The broad emission band of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ sample is assigned to the allowed $4f^65d \rightarrow 4f^7$ transition of Eu^{2+}. It is found that the no Eu^{3+} emission (f–f transition) is observed within the sensitivity of our Fluorescence Spectrophotometer,

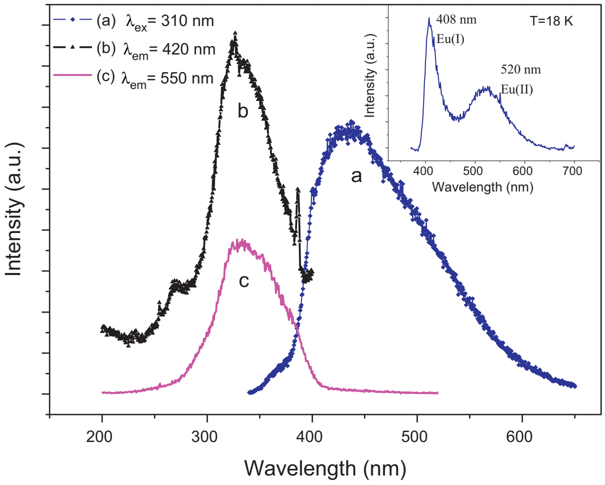

Fig. 2. Photoluminescence excitation ($\lambda_{em} = 420$, 550 nm) and emission ($\lambda_{ex} = 310$ nm) spectra of $Ba_{2.96}Eu_{0.04}P_4O_{13}$.

which indicates that the doped Eu^{3+} ions can be reduced to Eu^{2+} ions in $Ba_3P_4O_{13}$ host in air atmosphere at high temperature (750°C) successfully. Moreover, it is found from Fig. 2 that the emission spectrum is not symmetric. The emission spectrum consists of a peak at 430 nm and a shoulder at longer wavelength side. The chromaticity coordinate is calculated to be ($x=0.17$ and $y=0.20$). Considering the two crystallographic Ba sites in the $Ba_3P_4O_{13}$, two emission bands are expected to be observed. However, only one asymmetric emission band is presented in $Ba_{2.96}Eu_{0.04}P_4O_{13}$ system at room temperature, which indicates that two sites could have similar environment, eventually leading to the impossibility of separating the overlap of two emission bands. In order to confirm that the asymmetric emission band originates from two different Eu^{2+} ions, emission spectrum at low temperature ($T=18$ K) is measured and the result is shown in the inset of Fig. 2. It is clearly seen that two distinct emission bands peaking at 408 and 520 nm are observed. The 408 nm emission band is assigned to the $4f^65d\rightarrow4f^7$ transition of Eu^{2+}[Ba(1)], while the 520 nm emission band is assigned to the $4f^65d\rightarrow4f^7$ transition of Eu^{2+}[Ba(2)].

Luminescence decay curves for d→f transition of Eu^{2+} in $Ba_{2.96}Eu_{0.04}P_4O_{13}$ phosphor with pulsed excitation at 355 nm are measured at different temperatures, and the results are shown in Fig. 3. The decay curves can be fitted by single exponential equation: $I(t)=I_0+A\exp(-t/\tau)$, where I and I_0 are the luminescence intensities, A is a constant, t is the time, τ is the decay time for the exponential components. The values of τ extracted from the fitted curve are in the order of micro-second, and they are depicted in Fig. 3. The lifetime of Eu^{2+}[Ba(2)] is longer than that of Eu^{2+}[Ba(1)]. The lifetimes of Eu^{2+}[Ba(2)] do not show obvious change at different temperatures (i.e., 18 K and 300 K) while the lifetime of Eu^{2+}[Ba(1)] at low temperature is shorter than that at room temperature. In most cases, the lifetime of excited state decreases with increasing temperature as a result of a substantial increase in non-radiative relaxation rate. The abnormal vary of lifetime being similar to Eu^{2+}[Ba(1)] in $Ba_3P_4O_{13}$ has been reported in many systems, for example, $Sr_5(PO_4)_2(SiO_4)$:Eu^{2+} [21], $NaCaPO_4$:Eu^{2+} [22], $Na_2CaMg(PO_4)_2$:Eu^{2+} [23], (Sr,Ca,Ba)$Si_2O_2N_2$:Eu^{2+} [2], CaF_2:Eu^{2+} [24,25], $Ba_5SiO_4Cl_6$:Eu^{2+} [26] and so on. However, the reason for this unusual temperature dependence of Eu^{2+} fluorescence lifetime in these crystals is not clear.

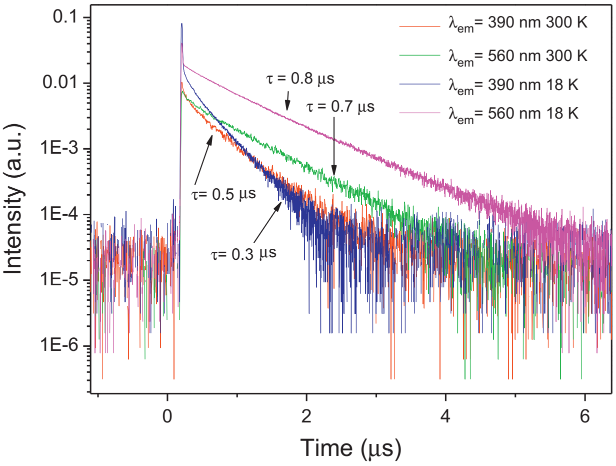

Fig. 3. Decay curves of $Ba_{2.96}Eu_{0.04}P_4O_{13}$ phosphor.

3.3. Europium reduction mechanism in $Ba_3P_4O_{13}$:Eu^{2+} prepared in air

Su and his co-workers have studied the abnormal reduction of $Eu^{3+}\rightarrow Eu^{2+}$ in a lot of systems [27–30]. They have drawn a conclusion that four conditions are necessary to realize the reduction of $Eu^{3+}\rightarrow Eu^{2+}$ in solid state compounds when they are prepared in air at high temperature [30], i.e., (1) there is not oxidizing ions in the host compounds; (2) the doped Eu^{3+} ion substitutes divalent cation sites; (3) the substituted cation and the Eu^{2+} ion have similar radii; and (4) the host has an appropriate structure, i.e., having tetrahedral anion groups (BO_4, SO_4, PO_4, SiO_4 or AlO_4). For the compound $Ba_3P_4O_{13}$, Ba^{2+} is not an oxidizing ion, which meets condition (1). An acceptable percentage difference in ion radii between doped and substituted ions cannot exceed 30% [31]. The calculations of the radius percentage difference between doped ions (Eu^{3+}, Eu^{2+}) and substitute ions (Ba^{2+}) in $Ba_3P_4O_{13}$ are summarized in Table 1, based on the equation ($D_r=100\times[R_m(\mathrm{CN})-R_d(\mathrm{CN})]/R_m(\mathrm{CN})$, where D_r is the radius percentage difference; CN is the coordination number; R_m(CN) is the radius of the host cation, and R_d(CN) is the radius of doped ion)[28] and the data of the effective ionic radii [16].

It can be seen from Table 1 that the doped Eu^{3+} ions and the reduced Eu^{2+} ions will substitute Ba^{2+} sites, which meet conditions (2) and (3). The skeleton structure of $Ba_3P_4O_{13}$ comprises Ba^{2+} ions and non-centrosymmetric $[P_4O_{13}]^{6-}$ polyanions consisting of four corner-shared P–O tetrahedra with a P–P–P–P torsion angle of 180° [14], which matches condition (4). Therefore, four conditions for the reduction of Eu^{3+} to Eu^{2+} in $Ba_3P_4O_{13}$:Eu prepared in air condition are satisfied, and we may expect the reduction of Eu^{3+} to Eu^{2+} in $Ba_3P_4O_{13}$:Eu prepared in air will take place. In fact, this goal has been achieved and the Eu^{3+} ions have almost been reduced to Eu^{2+} ions. This is the first time that this complete reduction has been observed in a solid state compound.

The reduction of Eu^{3+} to Eu^{2+} in $Ba_3P_4O_{13}$:Eu when prepared in air at high temperature can be explained by charge compensation mechanism [27,28,32]. When Eu^{3+} ions are doped into $Ba_3P_4O_{13}$, they will substitute Ba^{2+} ions. To keep the electroneutrality of the compound, it is necessary that two Eu^{3+} ions substitute three Ba^{2+} ions; therefore, one vacancy defect of V_{Ba}'' with two negative charges, and two positive defects of

Table 1
Ionic radii difference percentage (D_r) between matrix cation and doped ions.

Doped ion	Radius/Å (CN)	D_r	
		Ba 1.42 (8)	Ba 1.38 (7)
Eu^{3+}	1.066 (8)	24.93	
	1.01 (7)		26.81
Eu^{2+}	1.25 (8)	11.97	
	1.20 (7)		13.04

$Eu^{\bullet}_{Ba}$ will be created. Then the vacancy V_{Ba}'' will act as a donor of electrons while the two $Eu^{\bullet}_{Ba}$ defects become acceptors of the electrons. Consequently, the negative charges in the vacancy defects of V_{Ba}'' will transfer to the Eu^{3+} sites and reduce Eu^{3+} to Eu^{2+} through thermal stimulation. Because the reduced Eu^{2+} ions are closely surrounded by the network of PO_4 tetrahedra and can effectively avoid the attack of oxygen.

4. Conclusions

The reduction of Eu^{3+} to Eu^{2+} has been achieved successfully in $Ba_3P_4O_{13}$:Eu phosphor prepared in air at high temperature. This kind of reduction can be explained by the charge compensation mechanism. The PL emission spectrum consists of two broad bands, which can be attributed to d–f transition of Eu^{2+} ions occupying two different Ba^{2+} sites. The PL excitation spectrum also shows a broad band matching well with the emission of near UV chip. $Ba_3P_4O_{13}:Eu^{2+}$ is a promising phosphor for near-UV chip excited white LEDs.

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