



CERAMICS INTERNATIONAL

Ceramics International 37 (2011) 3697–3702

www.elsevier.com/locate/ceramint

The luminescence and structural characteristics of Eu³⁺-doped NaBaPO₄ phosphor

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> Received 9 May 2011; accepted 16 June 2011 Available online 23 June 2011

Abstract

 Eu^{3+} -doped NaBaPO₄ was prepared by a high-temperature solid-state reaction. The phase formation was confirmed by X-ray powder diffraction measurements. The laser site-selective excitation and emission spectra have been investigated in the $^5D_0 \rightarrow ^7F_0$ region by using a pulsed, tunable and narrowband dye laser. The excitation spectra corresponding to the $^7F_0 \rightarrow ^5D_0$ transition consist of two transitions at 579.6 nm Eu(I) and 578.9 nm Eu(I), indicating the Eu^{3+} ions occupy two crystallographic sites of Ba^{2+} ions. The decay lifetimes of the two Eu^{3+} sites were measured. Two crystallographic sites for Eu^{3+} ions doped in NaBaPO₄ lattice were assigned from the luminescence characteristic and structure features. Meanwhile, the charge compensation mechanism of Eu^{3+} doping in NaBaPO₄ was discussed.

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Keywords: Phosphate; Structural occupation; Luminescence; Europium

1. Introduction

Eu³⁺ has a simple electronic energy level scheme and its transitions are hypersensitive, i.e. they depend strongly on the chemical surroundings [1]. Because of these hypersensitive transitions, Eu³⁺ has been used as a local structure probe in determining the microscopic symmetries of different sites available in various host lattices. Usually, the local structures, e.g., coordination numbers (CNs) and degree of distortion by defects, have an important inuence on the spectroscopic properties of Eu³⁺ ions doped in a host [2]. As the most important emitter in the red region of the visible spectrum, Eu³⁺ has gained considerable interest and been widely investigated to be the efficient red-emitting phosphors [3–10].

The phosphates with $ABPO_4$ formula (A and B are monoand divalent cations, respectively) are in a large family of monophosphates with the different structure types strictly depending on the relative size of the A and B ions [11]. The variety in these structures makes it possible to tailor the

physical and chemical properties of the ABPO₄ family

Recently, RE-doped phosphors in NaBaPO₄ matrix have been extensively reported. $ABaPO_4$:Eu (A = Na, K) [13] exhibit a mixed-valence europium state (Eu³⁺ and Eu²⁺) and the photoluminescence (PL) results show that the NaBaPO₄:Eu and KBaPO₄:Eu phosphors emit a strong blue light under UV excitation. NaBaPO₄:Eu³⁺ [14] and NaBaPO₄:Tb³⁺ [15] have been reported to be potential red-emitting and green-emitting W-LEDs phosphors, respectively. Upadeo and Moharil [16] investigated radiation-induced valence changes (Eu³⁺ \rightarrow Eu²⁺ conversion) in Eu-doped NaBaPO₄. However, the structural occupation of Eu³⁺ sites in NaBaPO₄ phosphor has not been reported in the present work yet.

In this work, NaBaPO₄:Eu³⁺ was synthesized by a conventional high temperature solid-state reaction. The excitation and site-selective emission spectra have been investigated under pulsed dye laser excitation in the $^5D_0 \rightarrow ^7F_0$ region of Eu³⁺-doped NaBaPO₄. The site occupancy and the charge

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materials. As an important family of luminescent materials, orthophosphates have been paid intense attention because of their excellent properties, e.g., the large band gap and the high absorption of PO₄³⁻ in VUV region, moderate phonon energy, the high thermal and chemical stability, and the exceptional optical damage threshold [12].

Recently, RE-doped phosphors in NaBaPO₄ matrix have

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compensation mechanism of Eu³⁺ ions in the NaBaPO₄ lattices were discussed. This is helpful for the luminescence investigation of RE ions doped in this kind of phosphate host.

2. Experimental

The preparation of NaBaPO₄:Eu³⁺ was carried out by solid state synthesis. The raw materials were high-purity (4 N) Na₂CO₃, BaCO₃, NH₄H₂PO₄ and Eu₂O₃. The doping level of Eu³⁺ is 3.0 mol%. The starting materials with stoichiometric amounts were ground together in an agate mortar. The mixture was firstly heated up to 350 °C and kept at this temperature for 5 h. After a second homogenization in the mortar, the sample was heated up to 650 °C and kept at this temperature for 10 h. After that, the sample was mixed and heated at 900 °C for 10 h. The products were quenched to room temperature.

The X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max-2000 diffractometer operating at 40 kV, 30 mA with Bragg–Brentano geometry by using Cu K_{α} radiation ($\lambda=1.5418~\text{Å}$) and analyzed using Jade-5.0 software. The optical excitation and emission spectra were recorded by a Perkin-Elmer LS-50B luminescence spectrometer and a Hitachi F-4500 fluorescence spectrophotometer.

For the excitation and site-selective emission measurements, the excitation source was a dye laser (Spectron Laser Sys. SL4000) pumped by the second harmonic (532 nm) of a pulsed Nd: YAG laser (Spectron Laser Sys. SL802G). The pulse energy was about 5 mJ with 10 Hz repetition rate and 5 ns duration. The samples were placed in a liquid helium flow cryostat for measurements at low temperatures. The luminescence was dispersed by a 75 cm monochromator (Acton Research Corp. Pro-750) and observed with a photomultiplier tube (Hamamatsu R928). Suitable filters were used to eliminate the intense laser scattering.

3. Results

3.1. The crystal phase formation

The XRD pattern of NaBaPO₄:Eu³⁺ was compared with Joint Committee on Powder Diffraction Standards (JCPDS card No. 33-1210) (Fig. 1). By a comparison between them, the position and intensity of the main peaks are the same. No impurity lines were observed, and all the reflections could be well indexed to a NaBaPO₄ single phase. The lattice parameters of the sample were fitted by Jade.5.0 program to be a = b = 5.612 Å, c = 7.24 Å, $V = 197.5 \text{ Å}^3$ and Z = 2. These results well agree with the reported data of pure NaBaPO₄, i.e. a = b = 5.622 Å, c = 7.259 Å, $V = 198.7 \text{ Å}^3$ [17].

Fig. 2 presents the three-dimensional framework of NaBaPO₄ crystal structure with space group $P\bar{3}m1$. The schemes were modeled using the Diamond Crystal and Molecular Structure Visualization software on the basis of the atomic coordinates data reported in Ref. [17]. The structure is isotypic with that of glaserite. There are three different cation sites in the three-dimensional framework. Na and Ba lie at sites of 3 m symmetry and are coordinated to 6 and 12 oxygen atoms,

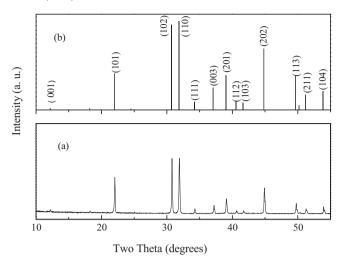


Fig. 1. XRD patterns of NaBaPO₄:Eu³⁺ (a) and JCPDs card No. 33-1210 (b).

respectively. The remaining cation site has 3 m symmetry, a coordination number of 10, and contains equal amounts of Na⁺ and Ba²⁺ [18]. Na⁺, Ba²⁺ and Y cation ions alternate in the chains along the c axis as shown in Fig. 2. The main characteristic of NaBaPO₄ structure consists in a statistical occupation of the Y sites by Na⁺ or Ba²⁺ [17].

3.2. Photoluminescence spectra

The photoluminescence excitation and emission spectra of NaBaPO₄:Eu³⁺ 3.0 mol% are shown in Fig. 3. In the excitation spectrum (Fig. 3(a)), the broad band ranging from 200 to 300 nm with a maximum at 256 nm are the charge transfer (CT) transition from the 2p orbital of the O^{2-} to the 4f orbital of the Eu³⁺. The dominated sharp lines in the wavelength region of 350–500 nm are from the f–f transitions within $4f^9$ configuration of Eu³⁺ ions. Obviously, the excitation spectrum (Fig. 3(a)) indicates that NaBaPO₄:Eu³⁺ 3.0 mol% can be efficiently excited by the radiation of near UV-emitting InGaN based LED chips (around 400 nm).

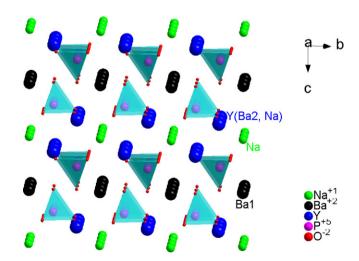


Fig. 2. Schematic crystal structures of two unit cells, revealing a well-ordered array of Na, Ba1, and Y (Ba2, Na) atoms.

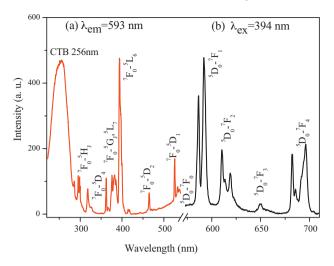


Fig. 3. The photoluminescence excitation and emission spectra of NaBa- PO_4 : Eu^{3+} .

The emission spectra under the excitation of 394 nm are shown in Fig. 3(b). The spectra consist of a number of sharp lines ranging from 575 to 710 nm, which are associated with the transitions from the excited state 5D_0 to ${}^7F_I(J=0, 1, 2, 3 \text{ and } 4)$ levels of Eu³⁺. The red emission at 612 nm is an electric dipole transition, while the orange emission range at 593 nm is a typical magnetic dipole transition. The emission spectra are dominated by the transitions of ${}^5D_0 \rightarrow {}^7F_1$. According to the Judd–Ofelt theory, the magnetic dipole transition is permitted. However, the electric dipole transition is allowed only when the europium ion occupies a site without an inversion center and the intensity is significantly affected by the symmetry in local environments around Eu³⁺ ions. If the Eu³⁺ ions occupy an inversion symmetry site, the o-red emission, magnetic transition ${}^5D_0 \rightarrow {}^7F_1$ is the dominant transition. On the contrary, the electric dipole transition $^{5}D_{0} \rightarrow {}^{7}F_{2}$ is the dominant transition [19].

3.3. The excitation spectra of ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ transition

Eu³+ (4f6 configuration) is largely used as a probe of the surrounding symmetry because the emission and excitation lines between 5D_0 and 7F_0 levels are the non-degenerate and they cannot be split by a crystal field surrounding the Eu³+ions. This reveals the presence of crystallographic nonequivalent sites in a given host matrix [2]. In order to examine the site-distributions of Eu³+ ions in NaBaPO4, the excitation spectra and site-selective emission spectra were measured. Fig. 4 shows the excitation spectra corresponding to the $^7F_0 \rightarrow ^5D_0$ transition at 10 K and 300 K obtained by monitoring the total luminescence from NaBaPO4:Eu³+.

It is found that the excitation band appears to be asymmetric on the short wavelength side in Fig. 4, this implies that Eu³⁺ ions occupy more than one site in the NaBaPO₄ lattice. To investigate the relation between the coordinative environment and photoluminescence properties of Eu³⁺ ions, the excitation spectrum at 10 K was deconvoluted into two Gaussian components peaked at the low-energy component of 579.6 nm (referred to as Eu(I)) and the high-energy component

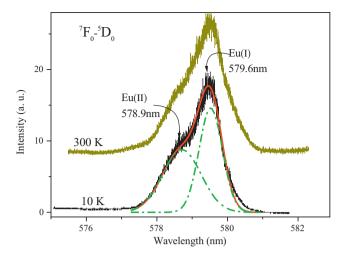


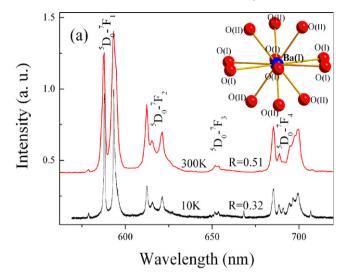
Fig. 4. The excitation spectra for $^7F_0 \rightarrow ^5D_0$ transition of Eu³+ in NaBa-PO₄:Eu³+ at 10 K and 300 K by monitoring the total luminescence, of which the spectrum at 10 K was deconvoluted to two Gassian components.

of 578.9 nm (referred to as Eu(II)), as shown in Fig. 4. No other line corresponding to ${}^7F_0 \rightarrow {}^5D_0$ transition was detected. It can be seen that the occupation probability of the major site Eu(I) is dominant. The minor site Eu(II) is weakly occupied due to its weak excitation intensity. The observation of two excitation bands is in agreement with the results of two crystallographic sites available in NaBaPO₄ [17,18]. Tang and Chen [13] recently have reported that there are two Eu²⁺ emission bands in NaBaPO₄, which can be ascribed to Eu²⁺ ions on the two crystallographic sites.

3.4. The site-selective emission spectra

The site-selective emission spectra under the Eu(I)- and Eu(II)-line excitations at 10 and 300 K for NaBaPO₄:Eu³⁺ are shown in Fig. 5. The different emission spectra due to the ${}^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3 and 4) transitions were observed. According to the emission spectra at 10 K, the wavelengths and energies of the ${}^5D_0 \rightarrow {}^7F_J$ (J=0, 1, 2, 3 and 4) transitions within each Eu³⁺ site were derived and listed in Table 1. It can be seen that the emission intensity of ${}^5D_0 \rightarrow {}^7F_1$ transition under the Eu(I)-line excitation is stronger than that of ${}^5D_0 \rightarrow {}^7F_2$ transition in Fig. 5(a), however, the emission intensity of ${}^5D_0 \rightarrow {}^7F_1$ transition under the Eu(II)-line excitation is weaker than that of ${}^5D_0 \rightarrow {}^7F_2$ transition in Fig. 5(b). The intensity ratio of $R = I({}^5D_0 \rightarrow {}^7F_2)/I({}^5D_0 \rightarrow {}^7F_1)$ is a measure of Eu³⁺ ion's site symmetry. A higher symmetry of the crystal field around Eu³⁺ will result in a smaller value [2].

In the site-selective emission spectra of Eu(I) site in Fig. 5(a), the magnetic-dipole transition $^5D_0 \rightarrow ^7F_1$ is the most prominent group, while the $^5D_0 \rightarrow ^7F_2$ transitions are very weaker. By means of calculation, the intensity ratios R are 0.32 and 0.51 at 10 K and 300 K, respectively. However, the R are 3.33 and 3.14 at 10 K and 300 K respectively in the site-selective emission spectra of Eu(II) site in Fig. 5(b). Obviously, the intensity ratios R values in Eu(I) site excitation are very smaller than that in Eu(II) site. So the symmetry of Eu(I) site could be higher than that of Eu(II) site.



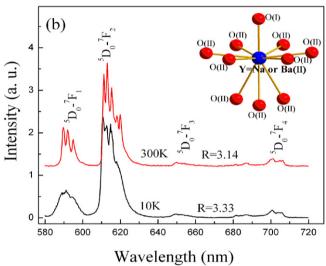


Fig. 5. The emission spectra of ${}^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3 and 4) under the site-selective excitation into Eu³⁺(I) at 579.6 nm (a) and Eu³⁺(II) at 578.9 nm (b) at 10 K and 300 K. The R values in figure are the integrated intensity ratio of $({}^5D_0 \rightarrow {}^7F_2)/({}^5D_0 \rightarrow {}^7F_1)$ and the insets represent crystal structures of Ba(I) (a) and Ba(II) (b).

Inset in Fig. 5(a) exhibits the crystallographic structure of Ba²⁺ site in NaBaPO₄. It is noticed that Ba²⁺ shares six O(I) and six O(II). The six apical oxygen atoms, O(I)s, are nearly coplanar and they together with the Ba2+ are said to lie in the equatorial plane of this cation. It is found that the distances of Ba(I)–O(I), and Ba(I)–O(II) are 3.247 and 2.788 Å, respectively, so the mean Ba(I)-O distance is 3.018 Å. The crystallographic structure of Y site, which is occupied by equal amounts of Na+ or Ba2+, is illustrated in the inset of Fig. 5(b). According to calculation, the bond lengths of Ba(II)six O(II) and Ba(II)-other three O(II) are 2.839 and 3.018 Å, respectively, while the distance of Ba(II)–O(I) is 2.416 Å, as a result, the average Ba(II)-O distance is 2.850 Å. So there are two different sites that 12 and 10 coordination occupied by Ba(I) and Ba(II) respectively in NaBaPO₄ lattices. This is clearly indicated that the symmetry of Ba (I) site is supposed to be higher than that of Ba (II) site. Based on the effective ionic

Table 1
The emission wavelengths (nm) and wave numbers (cm⁻¹) corresponding to the $^5D_0 \rightarrow ^7F_J$ (J = 1, 2, 3 and 4) transitions at 10 K in NaBaPO₄:Eu³⁺.

Transitions	Sites			
	Eu(I)		Eu(II)	
	(nm)	(cm ⁻¹)	(nm)	(cm ⁻¹)
$^{5}D_{0} \rightarrow ^{7}F_{0}$	579.52	17,256	578.9	17,274
$^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{1}$	588.3	16,998	589.6	16,961
	593.3	16,855	592	16,892
			595	16,807
$^5D_0 \rightarrow ^7F_2$	612.3	16,332	611.2	16,361
	615.5	16,247	613	16,313
	621.1	16,100	615.4	16,250
			618.1	16,179
			619.9	16,132
$^5D_0 \rightarrow {}^7F_3$	648.7	15,415	649	15,408
	650.3	15,378	649.9	15,387
	651.5	15,349	650.5	15,373
	653.5	15,302	652	15,337
	653.8	15,295	654.1	15,288
	668.4	14,961	654.7	15,274
$^5D_0 \rightarrow {}^7F_4$	685.3	14,592	685.9	14,579
	688.5	14,524	686.8	14,560
	691	14,472	688	14,535
	694.5	14,399	699.4	14,298
	696.8	14,351	701.2	14,261
	699.6	14,294	704.5	14,194
	706.7	14,150	706.3	14,158

radii of cations with different coordination numbers, it could be proposed that Eu^{3+} ions occupy preferably the Ba^{2+} sites. So this undoubtedly points to that the dominated Eu(I) is from the Eu^{3+} ion that substitutes the Ba(I) while the Eu(II) is supposed to occupy the site of the Ba(II). It is in accord with the emission spectra of Eu^{3+} ions in $NaBaPO_4$ lattices.

3.5. The luminescence decay

The luminescence decay curves of the 5D_0 emission after the Eu(I)- and Eu(II)-line excitations at different temperatures were measured. The typical decay curves at 10 K and 300 K are shown in Fig. 6. It can be seen that the decay curves are single exponential. The exponential decay curve can be fitted into a single exponential function as:

$$I = I_0 \exp\left[\frac{-t}{\tau}\right] \tag{1}$$

where I_0 is the initial emission intensity for t = 0, τ is lifetime. The luminescence lifetimes of the Eu³⁺ ions are calculated as a function of temperature. The 5D_0 luminescence lifetimes are 2.31 and 2.01 ms in Eu(I) and Eu(II) site at 10 K, respectively. However, the 5D_0 decay time of Eu³⁺ ions in Eu(I) and Eu (II) site is 2.11 ms and 1.49 ms at 300 K, respectively. It is found that with the temperature increasing; the lifetimes drop gradually, presenting a typical temperature quenching behavior. In addition, the lifetimes in Eu(I) site are longer than that in Eu(II) site. This agrees well with the excitation spectra intensity of Eu³⁺ ions in the two sites as shown in Fig. 4.

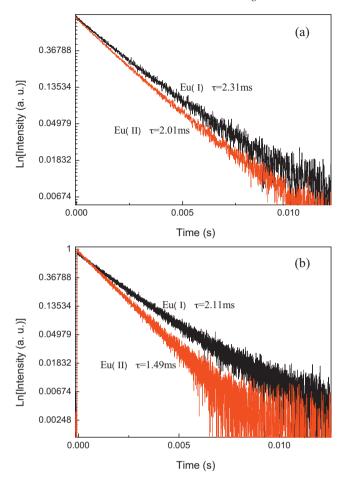


Fig. 6. The luminescence decay curves of NaBaPO₄:Eu³⁺ at (a) 10 and (b) 300 K after the excitation of 579.6 nm by monitoring $^5D_0 \rightarrow ^7F_1$ emission of 592 nm in Eu(I) and after the excitation of 578.9 nm by monitoring 612 nm in Eu(II).

4. Discussions

The uorescence spectroscopy of Eu^{3+} can give information about the sites occupied by Eu^{3+} in the lattices because each Eu^{3+} center with different crystal eld symmetry possesses a unique optical transition in the $^7F_0 \rightarrow ^5D_0$ excitation spectrum. The energy levels of Eu^{3+} centers are very sensitive to the local environment of the corresponding cation [2]. So the local structure environments around Eu^{3+} ions have an important inuence on its spectroscopic properties in a host. The following discussions were about the luminescence and site occupancy of Eu^{3+} ions in NaBaPO₄.

First, site symmetry also inuences the ${}^5D_0 - {}^7F_2 / {}^5D_0 - {}^7F_1$ intensity ratio, which corresponds to an "asymmetry" parameter. The ${}^5D_0 - {}^7F_2 / {}^5D_0 - {}^7F_1$ intensity ratio increases when the contribution of the electrical dipolar interaction in the transition probability increases. This effect is related to distortion occurring in the europium surrounding [20]. As discussed above, the intensity ratios R is 0.32 at 10 K in the site-selective emission spectra of Eu(I) site in Fig. 5(a), however, the R is 3.33 at 10 K for Eu(II) site in Fig. 5(b). The site Eu(I) with smaller values of the $({}^5D_0 \rightarrow {}^7F_2)/({}^5D_0 \rightarrow {}^7F_1)$ emission ratio, presents therefore more symmetrical than the site Eu(II). Based

on the effective ionic radii of cations with different coordination numbers, it could be proposed that Eu^{3+} ions occupy preferably the Ba^{2+} sites. This undoubtedly points to that the dominated Eu(I) is from the Eu^{3+} ion that substitutes the Ba(I) while the Eu(II) is supposed to occupy the site of the Ba(II).

Secondly, the splitting of the ${}^{7}F_{1}$ or ${}^{7}F_{2}$ levels is characteristic of the crystal eld strength [21]. As the Eu-O mean distance decreases, the crystal eld as well as the splitting of the ${}^{7}F_{1}$ and ${}^{7}F_{2}$ energy levels increase [20]. As we know, considering the 2J + 1 components for the Eu³⁺ in the crystal field, the maximum splitting number of the transition lines for ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{J} (J = 0, 1, 2)$ were 1, 3, 5, respectively, for each site. From Table 1, for resonant excitations with the site Eu(I) in Fig. 5(a), the spectra has 2 and 3 emission lines, for ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions, respectively. Under site-selective excitation into site Eu(II), emission lines for ${}^5D_0 \rightarrow {}^7F_1$ and $^{5}D_{0} \rightarrow ^{7}F_{2}$ transitions are 3 and 5, respectively. This means that the symmetry of the crystal-field in site Eu(I) is higher than that of site Eu(II). Such emission spectra are consistent with the structure description. This indicates that Eu³⁺ in site Eu(I) should occupy the position Ba(I) with C2 symmetry. This conclusion is supported by the distance of Eu(I)-O (Ba(I)-O) longer than that of Eu(II)–O (Ba(II)–O).

Thirdly, for a given emitting ion, long decay time is characteristic of the most symmetrical surrounding while short decay values are observed when site distortion occurs [20]. According to Fig. 6, the 5D_0 decay time in Eu(I) and Eu(II) site is 2.31 ms and 2.01 ms at 10 K, respectively. It is obviously found that the lifetimes in Eu(I) site are longer than that in Eu(II) site. So Eu(I) site has more symmetrical surrounding than Eu(II) site. In addition, the decay curves of two Eu $^{3+}$ sites are single exponential, and the energy could not be transferred between Eu(I) and Eu(II) site. This is because Ba(I) and Y(Ba(II)) are along the a axis and the distance between them is very long, i.e. the distance between different Eu $^{3+}$ ions is quite long too.

As discussed above, it could be proposed that Eu³⁺ ions occupy preferably the Ba²⁺ sites. The required charge compensations for the occupation of Eu³⁺ ions could be more complicated. This can most probably be achieved by the possible mechanism: the positive charge due to Eu³⁺ ion substitute for Ba²⁺ may be combined with the cation vacancy to form the dipole complexes of $[2(Eu_{Ba}^{3+})^{\bullet} - V_{Ba}^{"}]$ and $[(Eu_{Ba}^{3+})^{\bullet} - V_{Na}']$. Such a charge compensation mechanism is very common in other components, e.g., RE³⁺ doped apatite structure phosphate [22]. The possible negative charge compensation related to interstitial oxygen O_i" here is difficult because this mechanism usually occurs in the case of the heavily RE-doping. And usually, in oxides, the reaction energy to create the O_i" is higher than that of cation vacancy [23]. However, the defect compensation does not exert any obvious inuence on the luminescence of Eu³⁺ in this sample because of the low doping level. This is in agreement with the excitation spectrum of Eu³⁺ ions in Fig. 4, which presents that there is two Eu³⁺ crystallographic site ascribed to have two occupancy sites of Ba²⁺ in NaBaPO₄ lattice.

5. Conclusion

A red-emitting phosphor, Eu³⁺-doped NaBaPO₄, was prepared by a general high-temperature solid-state reaction. Structural characterizations reveal that the phosphor derives from glaserite structure with space group $P\bar{3}m1$. The excitation spectrum consists of the strong f–f transitions of Eu³⁺ ions, indicating NaBaPO₄: Eu³⁺ can be efficiently excited by the radiation of near UV-emitting InGaN based LED chips. Under the near UV excitation the phosphor shows intense orange-red emission from the electric dipole transition $^5D_0 \rightarrow ^7F_1$. The excitation spectrum corresponding to the $^7F_0 \rightarrow ^5D_0$ transition consists of the strongest line at 579.6 nm Eu(I) and a weak peak at 578.9 nm Eu(II), indicating the Eu³⁺ ions occupy two different crystallographic sites of Ba²⁺ ions, i.e. the Eu³⁺ ions occupy one intrinsic crystallographic site of Ba(I) and a probable site of Ba(II) or (Y) in NaBaPO₄ lattice.

Acknowledgments

This work was supported by Program for Postgraduates Research Innovation in University of Jiangsu Province (2010) in China, and by Mid-career Researcher Program through National Research Foundation (NRF) grant funded by the Ministry of Education, Science and Technology (MEST) (Project No. 2009-0078682).

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