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Unusual luminescence and temperature dependent decay behavior of divalent europium ion in $KBaBP_2O_8$

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ABSTRACT

The unusual photoluminescence (PL) properties and temperature dependent decay behavior of Eu^{2+} in $KBaBP_2O_8$ are reported and discussed. The emission spectrum is so complicate that it can be deconvoluted into three fitting peaks. The emission bands peaking at 380 and 444 nm can be assigned to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} centers substituting for K^+ and Ba^{2+} site, while the emission band at 497 nm may be attributed to the Eu^{2+} center on K^+ site with a nearby charge-compensated vacancy. The decay time of the $4f^65d$ emission increases with temperature. This increase can be explained by either thermal population of the $4f^7$ ($^6P_{7/2}$) level or thermal population of higher energetic $4f^65d$ states.

1. Introduction

The photoluminescence (PL) properties of Eu^{2+} in different host lattices have been investigated widely in the past [1–3]. In most cases, Eu^{2+} emission arises from $4f^65d \rightarrow 4f^7$ transitions and broader band emission is observed. Moreover, the peak position of emission band depends strongly on the Eu^{2+} sites and the crystal field environment around them. Usually the full-width of half-maximum (FWHM) is less than 100 nm if only one site is available for Eu^{2+} ion occupation or only one kind of crystal field environment felt by Eu^{2+} ion [4,5]. Recently, Dai et al. showed that in $Sr_5(PO_4)_{3\text{-}x}(BO_3)_xCl:Eu^{2+}$ two distinct Eu^{2+} centers can appear with changing the value x, resulting in a yellow emission (550 nm) and a blue emission (446 nm) [6]. The $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} is a parity-allowed transition. The decay time is in the microsecond range and usually decreases with increasing temperature [7]. The reason is nonradiation processes become more efficient at higher temperature. However, some abnormal examples have been reported in the literature [8–11].

In this paper, the PL properties of Eu^{2+} in $KBaBP_2O_8$ are reported and discussed. The PL properties of Eu^{2+} in $KBaBP_2O_8$ doped with Eu^{2+} have been investigated due to their potential application in the field of white LEDs [12]. First, we will discuss the PL properties of $KBaBP_2O_8$:6%Eu^{2+} at room temperature. Some unusual luminescence properties were observed compared to the results reported by other groups. Then the temperature dependence of the emission spectrum and decay time of the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} is reported. Just as for $BaFBr:Eu^{2+}$, $Ba_5SiO_4Cl_6:Eu^{2+}$ and other host lattices doped with Eu^{2+}, the decay time increases with increasing temperature. It will be shown that the increase for different emission bands can be explained by different models.

2. Experimental

The measurements were carried out on $KBaBP_2O_8$:6%Eu^{2+} powder sample, which was prepared by solid state reactions as described elsewhere [12]. Stoichiometric amounts of K_2CO_3 (A.R.), $BaCO_3$ (A.R.), H_3BO_3 (A.R.), $NH_4H_2PO_4$ (A.R.), and Eu_2O_3 (99.99%) were ground and pre-heated at 600 °C for 3 h in air. After ground, the mixtures were fired at a tube furnace under reducing atmosphere (95% N_2/5% H_2) at 850 °C for 6 h with heating rate of 5 °C/min.

X-ray powder diffraction (XRD) analysis was carried out on a Beijing Puxi XD-2 diffractometer with Cu Kα ($\lambda = 1.5405$ Å) operated at 36 kV and 30 mA. PL spectra at room temperature were performed on a fluorescence meter (Shimadzu, RF 5301PC) with a 150 W Xe lamp as an excitation source. The higher and lower temperature PL spectra (9–525 K) and the decay curves were recorded by the 500 MHz digital storage oscilloscope (LeCroy 9350 A) in which the signal was fed from PMT. The excitation source was 266 nm UV laser (originating from the

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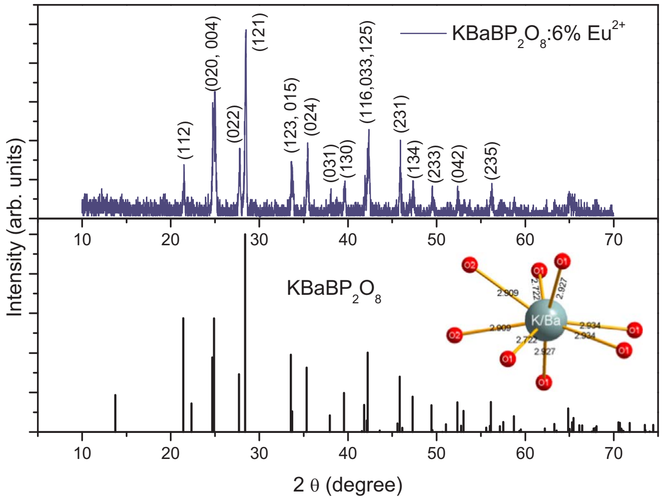

Fig. 1. XRD pattern of $KBaBP_2O_8$:6%Eu^{2+}. The standard pattern of $KBaBP_2O_8$ crystal calculated from CIF file is depicted for comparison.

fourth harmonic of a Quanta-ray DCR YAG:Nd laser). For the lower temperature measurement (9–300 K), the sample was placed at cold finger in a He gas recycled cryostat [13]. For the higher temperature measurement (300–525 K), the setup was equipped with a homemade heating cell connected to a temperature controller.

3. Results and discussion

Phase purity of $KBaBP_2O_8$:6%Eu^{2+} sample was checked by means of X-ray powder diffraction. The crystal structure of $KBaBP_2O_8$ has been investigated by Zhao et al. [14]. It represents a new kind of non-centrosymmetric borophosphate with three dimensional diamond-like framework and crystallizes in tetragonal system with space group $I\bar{4}2d$ with lattice parameters a = 7.202, c = 14.300 Å. It is impossible to separated K^+ and Ba^{2+} cations in this structure and each surrounded by eight oxygen atoms. Namely, there is only one type of site for the Ba^{2+}/K^+ ions. The XRD pattern of the $KBaBP_2O_8$ doped with Eu^{2+} sample is shown in Fig. 1. It shows similarities to the pattern assigned to $KBaBP_2O_8$ in Ref. [14], indicating that the doped Eu^{2+} ions are incorporated into the cation ions sites and forms solid solution.

PL emission spectra of $KBaBP_2O_8$:6%Eu^{2+} are shown in Fig. 2(a). It is clear that the emission spectra are super-wide bands extending from 350 to 600 nm when excited by photons of 254, 268, 282, 330, 371, 381, 391, 401 and 411 nm wavelengths. The emission spectra consist of two sub-bands peaking at about 380 and 450 nm, and the ration of them depends on excitation wavelength strongly. The emission bands are assigned to the $4f^65d^1 \rightarrow 4f^7$ transitions on different Eu^{2+} centers. Moreover, the peak at 380 nm is a symmetrical band with a FWHM of 50 nm, which is a regular emission of d→f transition of Eu^{2+} [4,5], whereas the peak at 450 nm present an asymmetrical band with a long tail at the low-energy side. We carried out excitation measurements to confirm which absorption bands are associated with each emission band. So we choose different emission wavelengths (λ_{em} = 361, 369, 380, 402, 429, 448, 470, 492 and 529 nm) as the monitoring wavelengths. The results are presented in Fig. 2(b). The excitation spectra of these bands are clearly different, although all of them are broad band absorption originating from $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+}. The excitation spectra (curves 1, 2, 3 and 4) peaking at about 280 nm correspond to one kind of Eu^{2+} center's absorption and the others (curves 5, 6, 7, 8 and 9) peaking at 335 nm are similar to each other corresponding to the other Eu^{2+} centers' absorption. The optical properties of Eu^{2+} doped $KBaBP_2O_8$ have been reported in the literatures [12,15]. However, some different results are found when compared with their works. For example, they did not observe the emission band peaking at 380 nm under UV excitation and the difference between excitation spectra of these different emission bands.

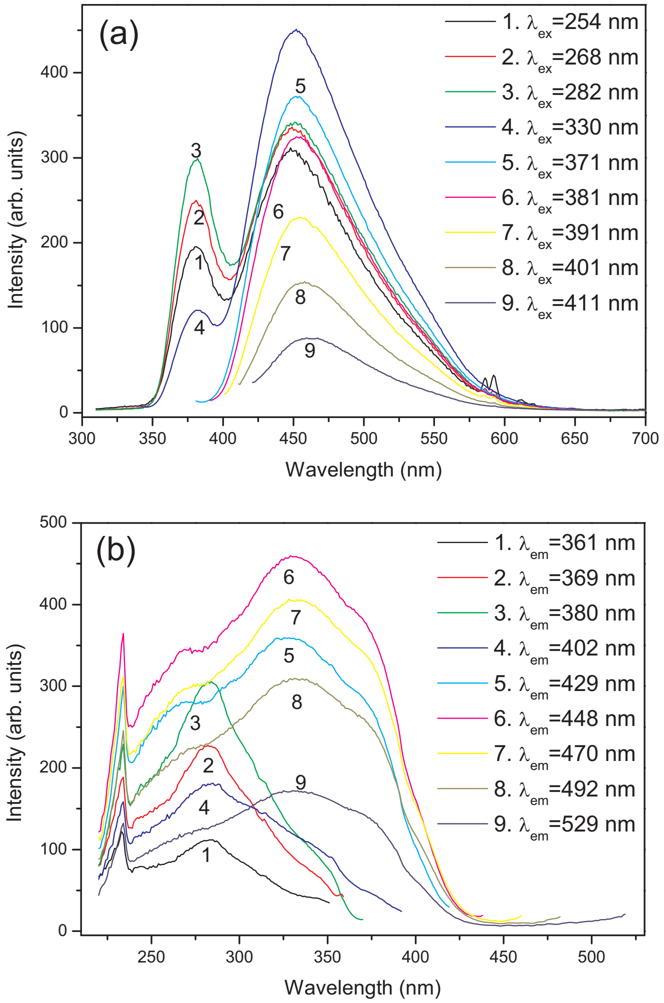

Fig. 2. PL emission spectra (a) and excitation spectra (b) of $KBaBP_2O_8$:6%Eu^{2+} sample. The excitation and monitoring wavelengths are presented in the figures.

As discussed above, the PL emission spectrum of $KBaBP_2O_8$:6%Eu^{2+} system presents super-wide band. We try to deconvolute the emission spectra into multi-peaks using Gauss function and one of the results is shown in the inset of Fig. 3. The emission spectrum can be deconvoluted into three sub-Gaussian peaks. We observe peaks at 380, 444 and 497 nm, which indicates that two or more Eu^{2+} centers are available in the $KBaBP_2O_8$ crystal. It is well known that the crystal field effect and nephelauxetic effect have great influence on the luminescent properties of Eu^{2+}. In this case, the doped Eu^{2+} ions can incorporate into not only the Ba^{2+} sites but also K^+ sites according to the ionic radius ($r_{Ba(II)} = 1.42$ Å, $r_{K(I)} = 1.51$ Å, $r_{Eu(II)} = 1.25$ Å, CN = 8) [16]. The luminescence properties of $KBaBP_2O_8$ and $KSrBP_2O_8$ activated with Eu^{2+} were reported by Sun and Wen [12,17]. $KBaBP_2O_8$ and $KSrBP_2O_8$ are isostructural and crystallize in the tetragonal system with space group $I\bar{4}2d$ [14]. The observed emission bands are situated at 445 and 462 nm for $KBaBP_2O_8:Eu^{2+}$ and $KSrBP_2O_8:Eu^{2+}$, respectively. The crystal field splitting of the Eu^{2+} 5d level will become smaller when the radius of the cation increases. So a smaller crystal field splitting of the 5d level in $KBaBP_2O_8$ crystal will shift the Eu^{2+} emission band to higher energy. Therefore, the emission band peaking at 444 nm can be assigned to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} center substituting for Ba^{2+} site, while the emission band peaking at 380 nm can be assigned to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} center substituting for K^+ site. In the crystal structure of $KBaBP_2O_8$, both Ba^{2+} and K^+ have only one