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Photoluminescence properties and efficient energy transfer of Ce^{3+}/Eu^{2+} activated $K_2Ba_7Si_{16}O_{40}$ phosphors

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ABSTRACT

Ce^{3+}/Eu^{2+} activated $K_2Ba_7Si_{16}O_{40}$ phosphors have been synthesized via a high-temperature solid-state method with CO atmosphere. Under ultraviolet (UV) light pump, the photoluminescence (PL) spectra of $K_2Ba_7Si_{16}O_{40}$: Ce^{3+} is composed of a broadband from 300 nm to 500 nm ascribed to the spin-allowed 5d–4f transition of Ce^{3+} ions. The optimal concentration is 8% for Ce^{3+} single doped $K_2Ba_7Si_{16}O_{40}$ due to the ernergy dispersion between Ce^{3+} ions and the critical distance between Ce^{3+} ions is 15.05 Å. $K_2Ba_7Si_{16}O_{40}$: Eu^{2+} emits a broad green emission peaking at 498 nm. The spectral overlap between the emission of Ce^{3+} and the excitation of Eu^{2+} suggests the resonance-type energy transfer from Ce^{3+} to Eu^{2+}, which is further demonstrated by the decay curves of $K_2Ba_7Si_{16}O_{40}$: 8 mol% Ce^{3+}, m Eu^{2+}. The critical distance between Ce^{3+} and Eu^{2+} ions is calculated to be 25.06 Å by Dexter's theory. Furthermore, the energy transfer mechanism is dipole-dipole interaction. In addition, the thermal activation energy is calculated to be 0.26 eV. The CIE coordinates can be tuned from blue to green by increasing Eu^{2+} ions. All results suggest that $K_2Ba_7Si_{16}O_{40}$: Ce^{3+}, Eu^{2+} is potentially useful for near-UV pumped white LEDs.

1. Introduction

With the implementation of the green lighting project, the fourth generation of lighting source represented by light emitting diodes (LED) is gradually used by people around the world. LED can satisfy the needs of green, energy-saving, environmental protection because of its long life, high efficiency, color variety and reliable [1–4]. The commercial method to realize white light is combining a blue emitting InGaN chip with yellow phosphor $Y_3Al_5O_{12}$: Ce^{3+} (YAG: Ce^{3+}) [5], the efficiency of which is more than 80 lm/W for 1 W devices, higher than the compact fluorescent lamps (CFLs). However, that method suffers a low color rendering index (CRI; usually less than 75) and high correlated color temperatures (CCT; usually higher than 5500 K) due to the lack of the red component [6,7]. A new way has been put forward to improve the CRI or CCT, near-ultraviolet (n-UV) or ultraviolet (UV) LED chips with blue/green/red tricolor phosphors or the single-phase full-color emission phosphors [8–10]. Therefore, new phosphors for UV pumped LEDs with good stability and high efficiency are urgently needed.

The ions which possess f-d or d-d electron configurations often emit visible broadband light due to the influence of crystal-field and nephelauxetic effects [11], which are good candidates as activators of phosphors. Due to a $4f^7$ electron configuration, the luminescence properties of Eu^{2+} ions depend on the symmetry, coordination environment and covalence of the cations in the host structure [12,13]. Similar to Eu^{2+} ions, the trivalent Ce^{3+} ions own a $4f^1$ electron configuration and the fluorescence is usually a broadband attributed to the electric dipole 4f–5d transition with decay time shorter than 100 ns. Because the 5d state of Ce^{3+} is strongly affected by crystal-field splitting [14], or nephelauxetic effects [15], the emission band ranges from ultraviolet to visible areas in different crystal structures [16]. Ce^{3+} ion is also an effective sensitizer to activators due to the effective absorption. There are many reports on the effective sensitizer Ce^{3+} ions in several hosts, like silicates, fluoride, oxyapatite, borates and sulfides [17–23]. The Ce^{3+}/Eu^{2+} co-activated $Sr_3B_2O_6$ phosphors emit the light from blue through white and eventually to yellow-orange by resonance-type energy transferred from Ce^{3+} to Eu^{2+} [22]. The resonant type energy transfer from Ce^{3+} to Eu^{2+} via a dipole-dipole interaction is validated in $Ca_8La_2(PO_4)_6O_2$: Ce^{3+}/Eu^{2+} phosphors [23]. However, there is still no knowledge on the energy transfer and its mechanism between Ce^{3+} and Eu^{2+} in $K_2Ba_7Si_{16}O_{40}$. The preparation and the

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structure of potassium barium silicate $K_2Ba_7Si_{16}O_{40}$ were first reported by Dent Glasser et al. [24]. It was solved using three-dimensional single crystal X-ray diffraction data and refined by block diagonal least squares, indicating a monoclinic unit cell and a C2/m space group with five different Ba^{2+} sites and two K sites. The Eu^{2+} single-doped $K_2Ba_7Si_{16}O_{40}$ exhibit green emission with high quantum efficiency (QE) and good thermal stability properties under the excitation of blue light reported by You et al. [25]. Herein, Ce^{3+}/Eu^{2+} single-doped and co-doped $K_2Ba_7Si_{16}O_{40}$ with various concentrations were prepared by a high-temperature solid-state method. The photoluminescence properties, decay curves, thermal stabilities and quantum efficiencies of the Ce^{3+}/Eu^{2+} co-doped $K_2Ba_7Si_{16}O_{40}$ have been investigated systematically. Ce^{3+} and Eu^{2+} single doped $K_2Ba_7Si_{16}O_{40}$ show blue and green emitting colors, respectively. Photoluminescence spectra of $K_2Ba_7Si_{16}O_{40}$: 8%Ce^{3+}, mEu^{2+} imply the energy transfer from Ce^{3+} to Eu^{2+} and the shortening lifetime of Ce^{3+} in $K_2Ba_7Si_{16}O_{40}$: 8%Ce^{3+}, mEu^{2+} demonstrates the effective energy transfer from Ce^{3+} to Eu^{2+}. Furthermore, the energy transfer mechanism is the dipole-dipole interaction between Ce^{3+} ions and Eu^{2+} ions in $K_2Ba_7Si_{16}O_{40}$. The good thermal stability has also been detected and its activation energy is calculated to be 0.26 eV. All the results show that the $K_2Ba_7Si_{16}O_{40}$: Ce^{3+}, Eu^{2+} may be an excellent color-tunable phosphor.

2. Experimental section

2.1. Materials and synthesis

All the samples $K_2Ba_7Si_{16}O_{40}$: Ce^{3+}/Eu^{2+} were synthesized by a high-temperature solid-state reaction. The highly pure starting materials K_2CO_3 (analytical reagent (A.R.)), Eu_2O_3 (4N), $BaCO_3$ (A.R.), CeO_2 (4N), and SiO_2 (A.R.) were weighed as stoichiometric amounts and grounded thoroughly in an agate mortar for 45 min. Then, the homogenous mixture was put into an aluminum crucible. Next, the crucible with powder was fired in a muffle furnace under a reducing atmosphere (CO) at 1200 °C for 4 h. The products were grounded to be fine powder for further measurement after cooled down to room temperature naturally.

2.2. Measurement and characterization

The structure and phase purity of as-synthesized samples were characterized by powder X-ray diffraction (XRD) (Bruker D8 powder diffractometer) with Cu target radiation resource (λ = 1.54078 Å). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded by using a Hitachi F-4600 fluorescence spectrophotometer, and a 150 W Xe-arc lamp used as an excitation source. The temperature-dependent luminescence was measured on the same spectrophotometer with a self-made heating attachment with a computer-controlled electric furnace. The decay curves were recorded on FLS980 and 320 nm pulse laser radiation (nano-LED) was used as the excitation source. Absolute photoluminescence quantum yield was also measured using the integrating sphere on the FLS980 fluorescence spectrophotometer (Edinburgh Instruments Ltd., U.K.).

3. Result and discussion

3.1. Crystal structure

Powder XRD was performed to verify the phase purity of the samples. Fig. 1 shows the representative XRD patterns of $K_2Ba_7Si_{16}O_{40}$: 8% Ce^{3+}. All diffraction peaks can be basically indexed to the standard data of $K_2Ba_7Si_{16}O_{40}$ (ICSD No. 31993), indicating that Eu^{2+} or Ce^{3+} ions were successfully incorporated into the $K_2Ba_7Si_{16}O_{40}$ host lattice.

Crystal structure of $K_2Ba_7Si_{16}O_{40}$ unit cell and five different crystallographic sites of Ba^{2+} with 7, 8 and 9 coordination numbers are shown in Fig. 2. The structure consists of infinite Si_2O_5 sheets parallel to

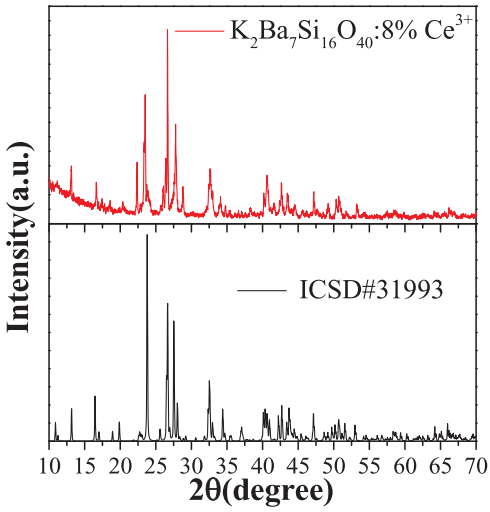

Fig. 1. XRD pattern of as-prepared sample with its reference ICSD No. 31993.

(201) linked together through eight-coordinate K and seven and nine-coordinate Ba atoms [24]. The Ba (1) and Ba (3) have a coordination number of nine O atoms; the Ba (2) has seven O atoms around it and the coordination of Ba (4) and Ba (5) is eight. The ionic radii of Ba^{2+} are 1.38 Å (CN (coordination number) = 7), 1.42 Å (CN = 8), 1.47 Å (CN = 9), respectively. Also, there are two crystallographic sites K^+ with eight O atoms and the ionic radius is 1.51 Å (CN = 8). The ionic radii of Ce^{3+} are 1.07 Å (CN = 7), 1.143 Å (CN = 8), 1.196 Å (CN = 9), and Eu^{2+} are 1.20 Å (CN = 7), 1.25 Å (CN = 8), 1.30 Å (CN = 9), respectively. Considering the ionic radii of all relative ions, the Ce^{3+} and Eu^{2+} have better chance to occupy Ba^{2+} ions sites.

3.2. Photoluminescence properties

Because of the $4f^1$ configuration of Ce^{3+}, its luminescence property is easily affected by the host structure. From Fig. 3a, the PLE spectra of $K_2Ba_7Si_{16}O_{40}$: 8% Ce^{3+} monitoring different wavelength (from 330 to 410 nm with 20 nm interval) show five obvious peaks at different positions. When monitoring 330 nm, PLE bands I (~235 nm), III (~290 nm), IV (~311 nm) is clearly shown and bands II (~264 nm), IV (~310 nm) and V (~330 nm) are obvious as monitoring 410 nm. When the sample is excited by the light with different wavelengths at five peaks respectively, the emission spectra show a broadband with the range of 300–500 nm for the 5d–4f transitions of Ce^{3+} ions. The emission peaks excited by different light with different wavelengths are totally different in shapes and intensities, as is shown in Fig. 3b. The difference can be seen more clearly in the insets, which is agreed well with the speculation that Ce^{3+} replaced five Ba^{2+} sites in the $K_2Ba_7Si_{16}O_{40}$ host.

The PL spectra of $K_2Ba_7Si_{16}O_{40}$: nCe^{3+} with varying Ce^{3+} concentrations under 330 nm excitation are depicted in Fig. 4. The PL spectra exhibit a broad blue emission band with redshift gradually from 377 nm to 390 nm (Inset) as Ce^{3+} ions increase. The redshift may be caused by the different energy around Ce^{3+} ions, which is easily affected by crystal field splitting and the nephelauxetic effect. The crystal field splitting effect describes the energy difference between the highest and lowest 5d energy levels, and the nephelauxetic effect describes the energy difference between the 4f and 5d levels. The crystal field splitting can be influenced by the coordination environment, the symmetry of activator sites, bond lengths of activator to coordinating anions and covalency between activator and its ligands. Generally, the crystal field splitting (D_q) can be determined by the equation [26–28]:

$$D_q = \frac{1}{6} Ze^2 \frac{r^4}{R^5}$$