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Luminescence properties of Eu^{2+} and Ce^{3+} in $Na_5Ca_2Al(PO_4)_4$ produced by the combustion-assisted synthesis method

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ABSTRACT

New greenish-blue luminescence Eu^{2+}/Ce^{3+} codoped $Na_5Ca_2Al(PO_4)_4$ phosphors were prepared by a combustion-assisted synthesis method. X-ray powder diffraction analysis confirmed the formation of $Na_5Ca_2Al(PO_4)_4$ host lattice.. The Eu^{2+}-doped $Na_5Ca_2Al(PO_4)_4$ sample has an efficient greenish-blue emission band that peaks at 476 nm, while Ce^{3+}-doped $Na_5Ca_2Al(PO_4)_4$ sample exhibits a strong emission band at 391 nm. Efficient energy transfer from Ce^{3+} to Eu^{2+} occurs due to the large spectral overlap between the emission of Ce^{3+} and excitation of Eu^{2+}. Co-doping Ce^{3+} enhances the emission intensity of Eu^{2+} greatly by transferring its excitation energy to Eu^{2+}, and Ce^{3+} plays a role as a sensitizer. Ce^{3+}/Eu^{2+} co-doped $Na_5Ca_2Al(PO_4)_4$ can possibly be applied as greenish-blue phosphors in the fields of lighting and display.

1. Introduction

In recent years, white light-emitting diodes (LEDs) have gained much attention as devices for display and solid state lighting [1]. White LEDs are expected to be a promising candidate to replace conventional incandescent and fluorescent lamps due to their merits of being environmentally friendly, highly efficient and having a longer lifetime. Nowadays, intensive studies have been carried out with the aim of improving the luminous efficiency and color-rendering properties of white LEDs, and especially phosphors. Eu-activated phosphors, for example, aluminates, silicates, phosphates and derivatives, have been intensively studied for their luminescent properties. As an activated ion, Eu^{2+} ion has the 5d electron unshielded from the crystal field by the 5 s and 5p electrons, and its spectral properties are strongly affected by the surrounding environment such as symmetry, covalence, coordination, bond length, site size and crystal-field strength, etc. [2]. The absorption and emission spectra of Eu^{2+} usually show a broad band due to transitions between the $4f^7$ ground state and the crystal field components of the $4f^65d^1$ excited state configuration. Thus the Eu^{2+}-emission band may be changed from blue to red in the visible spectral region. The wavelengths of excitation and emission bands strongly depend on the host crystal. So the choice of host greatly affects the optical properties of Eu^{2+} ions. Phosphate compounds are the excellent matrices to be developed for Eu^{2+}-activated phosphors. Phosphate phosphors doped with Eu^{2+} ions have excellent thermal stability and the tetrahedral rigid three-dimensional matrix of the phosphates is thought to be ideal for charge stabilization [3–5]. In addition, the low sintering temperature required for their synthesis is another reason that these phosphates are considered to be excellent hosts for preparing phosphors [6].

There are two possible ways to improve the luminescence properties of Eu^{2+} doped phosphate phosphors: to modify the crystal field of Eu^{2+} and to introduce a sensitizer that has strong absorption in the spectral range and transfers its energy to Eu^{2+}. The latter is more effective in improving photoluminescence properties of phosphors. Energy transfer by exchange interactions is often employed to sensitize an activator ion in order to achieve brighter emission. The activator Ce^{3+} ions have efficient absorption in the UV region, which can sensitize other activators such as Eu^{2+}, and so this has been utilized to enhance the emission of Eu^{2+} via energy transfer in many compounds [7–9].

Phosphates usually show a rather short wavelength of optical absorption edge, which makes them suitable as hosts to accommodate active rare earth ions [10]. Aluminum dicalcium pentasodium tetrakis(phosphate), $Na_5Ca_2Al(PO_4)_4$, crystallizes in the monoclinic space group Cc(9), as confirmed by Alkemper et al. in 1994 [11]. It has lattice parameters of $a = 11.071(3)$ Å, $b = 13.951(4)$ Å, $c = 10.511(3)$ Å, $\beta = 119.34(1)°$ and $V = 1415.2$ Å^3. However, the luminescent properties of $Na_5Ca_2Al(PO_4)_4$:Eu^{2+} have never been clearly reported. In the present work, efficient spectral conversion is obtained from Eu^{2+}-doped $Na_5Ca_2Al(PO_4)_4$ phosphors. A systematic study of the energy transfer form Ce^{3+} to Eu^{2+} in $Na_5Ca_2Al(PO_4)_4$ host has been carried out. The effects of dopant content and the codoping of Ce^{3+} ions on the luminescence efficiency of $Na_5Ca_2Al(PO_4)_4$:Eu^{2+} phosphors have been investigated systematically and are presented here.

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2. Experimental

Eu^{2+} and/or Ce^{3+} activated $Na_5Ca_{2-x-y}Al(PO_4)_4$:xEu^{2+},yCe^{3+} (NCAP:xEu^{2+},yCe^{3+}) samples were prepared as follows [12]: First, stoichiometric amounts of source materials $NaNO_3$ (A.R.), $Ca(NO_3)_2\cdot 4H_2O$ (A.R.), $Al(NO_3)_3\cdot 9H_2O$ (A.R.), and $NH_4H_2PO_4$ (A.R.) were thoroughly mixed, and an appropriate amount of $CO(NH_2)_2$ (A.R.) was added as fuel. Second, Eu_2O_3 (99.99%) was dissolved in HNO_3 to convert into $Eu(NO_3)_3$ completely. These reagents were dissolved in deionized water and introduced into a muffle furnace maintained at 500 °C for 5 min. Then the samples were reheated at 600 °C for 3 h in a H_2 atmosphere and were allowed to cool in the reducing atmosphere to room temperature. The obtained transparent glassy samples were finally ground into powder for measuring phase compositions and the photoluminescence properties.

The phase purity of the as-prepared samples was checked by powder X-ray diffraction (XRD) analysis with a Bruker D8 advanced automatic diffractometer with Cu Kα radiation operating at 40 kV and 40 mA. The measurements of emission (PL) and excitation (PLE) spectra were performed by using a Jasco FP-6500 Spectrofluorometer (Jasco Corporation, Japan), and a xenon lamp was used as the excitation source. For comparison, all measurements were performed at room temperature with the identical instrumental parameters.

3. Results and discussion

Fig. 1(a) illustrates the XRD patterns of the un-doped samples crystallized at various temperatures. Most of the diffraction peaks of the sample sintered at 550 °C can be basically indexed to the corresponding standard data for the monoclinic phase of $Na_5Ca_2Al(PO_4)_4$ (JCPDS Card No. 84-2464). The XRD pattern in Fig. 1(a) shows that $Na_5Ca_2Al(PO_4)_4$ is well crystallized in the sample sintered at 550 °C. However, a trace of β-$NaCaPO_4$ as a second phase (marked by arrows) can also be discerned. We can see that an increase of the sintering temperature results in a decrease of the $Na_5Ca_2Al(PO_4)_4$ diffraction peak intensity and $Na_5Ca_2Al(PO_4)_4$ seems to dissolve [13]. Meanwhile, the intensities of the peaks around 32.6°, 33.1°, and 33.7° for the phase of β-$NaCaPO_4$ become steadily higher as the sintering temperature increases. Fig. 1(b) demonstrates the typical powder XRD patterns of NCAP:0.04Eu^{2+}, NCAP:0.28Ce^{3+}, and NCAP:0.04Eu^{2+},0.28Ce^{3+} samples. All diffraction peaks were found in good agreement with that reported in the JCPDS Card No. 84-2464, regardless of the contents of the dopants, thereby indicating that the obtained samples are single-phase and the codoped Eu^{2+} and Ce^{3+} ions do not cause any significant change in the host structure. On the basis of the effective ionic radii of cations with different coordination numbers [14], we suggested that the Eu^{2+} and Ce^{3+} ions prefer to substitute the Ca^{2+} ions because the ionic radii of Eu^{2+} (1.17 Å) and Ce^{3+} (1.14 Å) are approximate to that of Ca^{2+} (1.12 Å). The small shift of the diffraction angle to the lower 2θ angle should be ascribed to the Ca^{2+} ions substituting for the Eu^{2+}/Ce^{3+} ions.

The excitation (PLE) and emission (PL) spectra of NCAP:0.04Eu^{2+} are shown in Fig. 2. The PLE spectrum, monitored at 476 nm, shows a broad band due to $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+}. Eu^{2+} ions incorporated in the $Na_5Ca_2Al(PO_4)_4$ host lattice exhibit strong absorption at about 250–450 nm, which is close to the emission wavelength (380–400 nm) of InGaN-based near UV LED. The main excitation peak is located at 354 nm, which indicates that the phosphor is very suitable for a color converter using near UV light as the primary light source. Upon the excitation of 354 nm, the PL spectrum of NCAP:0.04Eu^{2+} exhibits a broad band emission centered at 476 nm attributed to the typical $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. It can be used as a greenish blue-emitting phosphor excited by near UV LED chips and mixed with other color emission phosphors to obtain white light. Moreover, the dependence of the PL intensities of NCAP:xEu^{2+} on the content of Eu^{2+} (x) is shown in the inset of Fig. 2. The PL intensity increases with the increasing Eu^{2+} content until it reaches a maximum at $x = 0.04$, then it decreases as the content of Eu^{2+} further increases because of the concentration quenching which is caused by the energy transfer between the identical Eu^{2+} ions.

As shown in Fig. 3, the PLE spectrum of Ce^{3+} in NCAP shows a broad band from 250 nm to 350 nm, which is assigned to the allowed $4f^1 \rightarrow 5d^1$ transition of the Ce^{3+} ions. The dominant bands in the PLE spectrum are difficult to resolve due to the Ce^{3+} $5d^1$ multiplet excited states and the serious overlap between $5d^1$ levels. When excited under 319 nm, the emission of NCAP:Ce^{3+} shows one asymmetric band extending from 350 to 450 nm with a maximum at about 391 nm. The asymmetry of the emission band of NCAP:Ce^{3+} results from a splitting into two levels of the ground state due to spin orbit coupling, and it can be deconvoluted into two Gaussians centered at 388 and 409 nm that originated from the lowest 5d level to $^2F_{5/2}$ and $^2F_{7/2}$, respectively [15].

Based on the above PLE spectra of the Ce^{3+} and Eu^{2+} single-doped samples, it can be observed that Eu^{2+} activated $Na_5Ca_2Al(PO_4)_4$ samples have a broader absorption range in the UV region than that of Ce^{3+} activated samples and so Eu^{2+} activated $Na_5Ca_2Al(PO_4)_4$ sample can better satisfy the requirements of white-LEDs. However, Eu^{2+} activated $Na_5Ca_2Al(PO_4)_4$ sample has a lower luminescence intensity and a

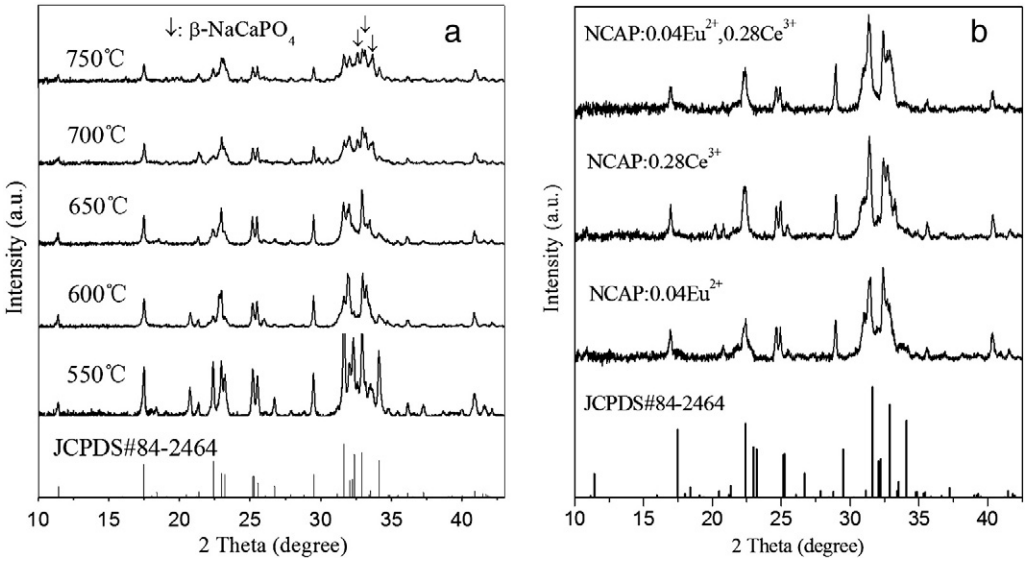

Fig. 1. XRD patterns of the un-doped samples sintered at various temperatures (a); XRD patterns of NCAP:0.04Eu^{2+}, NCAP: 0.28Ce^{3+}, and NCAP:0.04Eu^{2+},0.28Ce^{3+} sintered at 600 °C (b).