

Luminescence properties of a new green emitting Eu^{2+} -doped barium chlorosilicate phosphor

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Abstract A new intense green light-emitting phosphor, the Eu^{2+} -doped ($\text{BaO-BaCl}_2\text{-SiO}_2$) phosphor system, was synthesized at 800°C by the conventional high-temperature solid-state reaction. Its structure and luminescence properties were investigated by using thermogravimetry-differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), diffuse reflection spectra, photoluminescence (PL) and photoluminescence excitation (PLE) spectra. The photoluminescence spectrum reveals that this phosphor can be efficiently excited by near-ultraviolet (UV) light and blue light in the wavelength region covering 280 and 480 nm, which perfectly matches the emission wavelength of near-UV light-emitting diodes (LEDs). It emits an intense green light peaking at 502 nm, which is promising to develop possible applications for white LEDs.

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1 Introduction

Nowadays, the studies on red/green/blue tricolor phosphors suitable for UV excitation have attracted more and more attention because of their significant applications in solid-state lighting (SSL) [1, 2]. Up to now, many phosphors suitable for near-ultraviolet (UV) excitation have been reported,

including orthosilicates, akermanites, aluminates, sulfides, molybdates, oxynitrides/nitrides, and so on [1–4]. However, the sulfide-based phosphors have low chemical stabilities against humidity and poor resistance against irradiation from GaN chip [5, 6]. For oxynitride/nitride phosphors, the synthesis techniques are very harsh; they are commonly synthesized at high temperature and high pressure. The phosphors with better optical properties and low cost are still in development.

Divalent europium is an important activator for luminescent materials, which have been extensively studied for years. The luminescence of Eu^{2+} -activated phosphors usually results from the ground $4f^7$ levels to the excited $4f^65d$ configuration. Since the $4f-5d$ transitions are electric-dipole allowed, the absorption and emission of Eu^{2+} are characterized as very efficient broad bands in many hosts [7]. Moreover, it is well known that the $5d$ wave function has a large spatial extension; its transition line is usually broadened, and it depends on the surroundings of the Eu^{2+} ions. Thus, the different crystal-lattice environment is a critical parameter for determining the optical properties of the Eu^{2+} ions [8]. In the present work, a new kind of barium chlorosilicate phosphor system, Eu^{2+} -doped ($\text{BaO-BaCl}_2\text{-SiO}_2$), was synthesized via the solid-state reaction method, and it shows strong green emission upon the excitation of near-UV light. It will be shown that this series of materials are promising in meeting the application requirements for near-UV LEDs as green emitting phosphors.

2 Experimental

We designed the chemical composition of the Eu^{2+} -doped ($\text{BaO-BaCl}_2\text{-SiO}_2$) phosphor system as ($\text{BaO-BaCl}_2\text{-}$

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SiO_2): $x\text{Eu}^{2+}$, in which x indicated the Eu^{2+} concentration for the substitution of the Ba^{2+} sites. The so-called (BaO–BaCl₂–SiO₂) system in this paper will denote the given composition ratio, which is determined by “Ba₅Si₂O₈Cl₂”, and hereafter named the (BaO–BaCl₂–SiO₂) system. The powder was prepared using the conventional high-temperature solid-state synthesis method. The starting materials were BaCO₃ [analytical reagent, (A.R.)], BaCl₂·2H₂O (A.R.), SiO₂ (A.R.) and Eu₂O₃ with a purity of 99.99%. They were weighed by a molar ratio of BaCO₃, BaCl₂·2H₂O, and SiO₂, being equal to 4:1.1:2. A small amount of Eu₂O₃ was added in the mixture as activator. The raw materials were thoroughly mixed in an agate mortar by grinding and then placed in a corundum crucible with a lid. The samples were firstly preheated at 500°C, for the sufficient diffuse and infiltration of the starting materials, with a soaking time of 2 h in CO reducing atmosphere, and carbon grains were used as a reducing agent, by which the samples were covered during firing. Secondly, the preheated mixtures were milled sufficiently again after cooling and subsequently sintered at 800°C for 6 h in CO reducing atmosphere. Thermogravimetric analysis for the mixture of the typical starting materials were performed on a Setaram TGA92 TG-DSC instrument at a heat rate of 10°C/min from room temperature to a maximum temperature of 1200°C. The phase purity of the as-prepared phosphor was recorded by a X-ray Powder diffraction spectroscopy (XRD, Shimadzu, XRD-6000) operating at Cu K α radiation, 40 kV, 30 mA, and a scan speed of 2.0° (2 θ)/min. Diffuse reflection spectra of as-synthesized phosphor powder samples were measured on a UV-Vis-NIR spectrophotometer (UV-3600, SHIMADZU) attached to an integral sphere, using BaSO₄ as a standard measurement. The excitation and emission spectra were recorded by using a Perkin-Elmer LS-55 fluorescence spectrophotometer with a photomultiplier tube operating at 400 V, and a 150-W Xe lamp was used as the excitation lamp; the measured fluorescence spectra data were all calibrated under the same operating conditions. The above measurements were carried out at room temperature.

3 Results and discussion

Figure 1 shows the TG-DSC curves for the (BaO–BaCl₂–SiO₂) precursors, which are a mixture of the typical starting material (BaCO₃, BaCl₂·2H₂O and SiO₂) with the molar ratio of 4:1.1:2. As seen in Fig. 1, the weight loss of the precursors occurs in the TG curve up to about 1000°C with increasing temperature, and three strong endothermic peaks at about 73, 100 and 800°C, and an exothermic peak at about 990°C are shown in the DSC curve in Fig. 1. The crystallization processes of the precursors can be divided into three stages according to the TG-DSC curves. The first

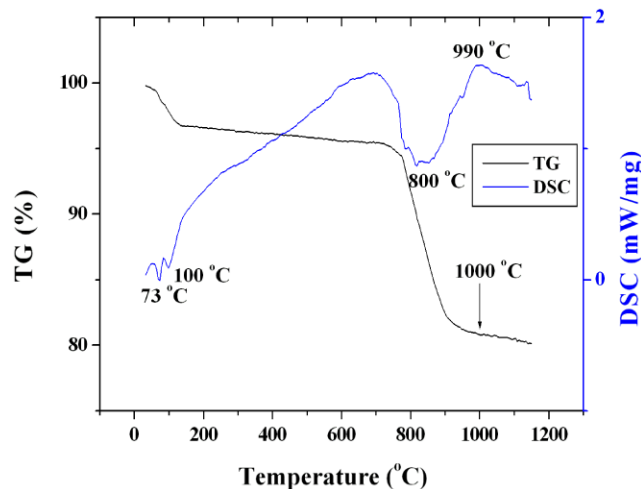


Fig. 1 TG-DSC curves for (BaO–BaCl₂–SiO₂):Eu²⁺ precursors

stage corresponds to a loss of 16.35% from room temperature (20°C) to about 140°C shown on the TG curve, which is also testified by the two sharper endothermic peaks at 73 and 100°C in the DSC curve. The first stage likely originated from the volatilization of the absorbed water and the water of the crystallization. The second stage shows a mass loss of 69.16% starting from 770 to 1000°C, which is also given by the endothermic peak at 800°C and an exothermic peak at 990°C in the DSC curve. In this stage, the mass loss should correspond to the decomposition of BaCO₃ and the partial evaporation of BaCl₂. The strong endothermic peak at about 800°C corresponds to the beginning temperature of the large weight loss region, and the strong exothermic peak at about 990°C indicates that some new crystal phase begins to form in this temperature region. In the third stage, the weight remains invariable when the temperature is over 1000°C, which implies that the processes of precursor decomposition and reaction have been completed and some stable crystal phase has formed.

Figure 2 shows the XRD pattern of the as-prepared (BaO–BaCl₂–SiO₂) system in this paper. For the obtained crystal phase, it is observed that there are no peaks of raw material impurity phase in the XRD pattern after careful comparison with the diffraction peaks of BaO, BaCl₂ and SiO₂ in the JCPDS database, and the obtained typical XRD pattern indicates that it belongs to the well-formed crystalline structure. It is also found that the main phase does not agree with any other data in the JCPDS database available. Moreover, we have measured the XRD patterns of samples with various Eu²⁺ concentrations (1–10%). The conclusion is that the different Eu²⁺ concentrations have little influence on the (BaO–BaCl₂–SiO₂) system structure. We speculate that the (BaO–BaCl₂–SiO₂) system is likely to be a kind of new structure built up with the barium chlorosilicate framework, which is similar to the former report [4]. The study of

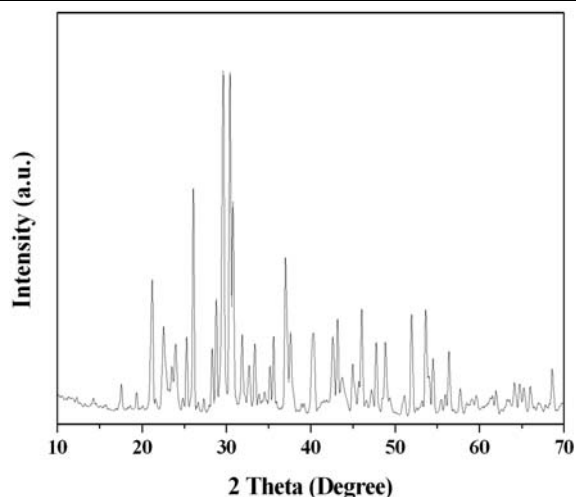


Fig. 2 XRD patterns of the $(\text{BaO-BaCl}_2\text{-SiO}_2)$ host material system at the synthesis temperature of 800°C

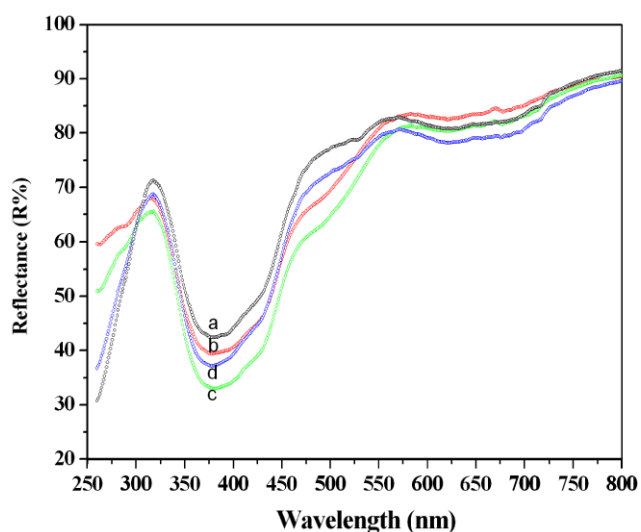


Fig. 3 The diffuse reflection spectra of $(\text{BaO-BaCl}_2\text{-SiO}_2):x\text{Eu}^{2+}$ phosphor for various Eu^{2+} concentrations. (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.1$ and (d) $x = 0.15$

its detailed structure will be further performed in our future work.

The diffuse reflection spectra of $(\text{BaO-BaCl}_2\text{-2SiO}_2):x\text{Eu}^{2+}$ ($x = 0.02, 0.05, 0.1$ and 0.15) are shown in Fig. 3. For $(\text{BaO-BaCl}_2\text{-2SiO}_2):x\text{Eu}^{2+}$, the onset of the reflectance is around 275 nm , and it increases steeply until up to 310 nm ; then a reflectance platform appears in the wavelength range of 500 to 800 nm . After careful analysis and comparison, we found that there was only one obvious absorption band, ranging from 320 to 550 nm , attributed to the transition from $4f^7$ to $4f^65d^1$ of the Eu^{2+} ions [9]. With increasing of the Eu^{2+} concentration, the absorption intensity of $(\text{BaO-BaCl}_2\text{-SiO}_2):x\text{Eu}^{2+}$ increases and it has the max-

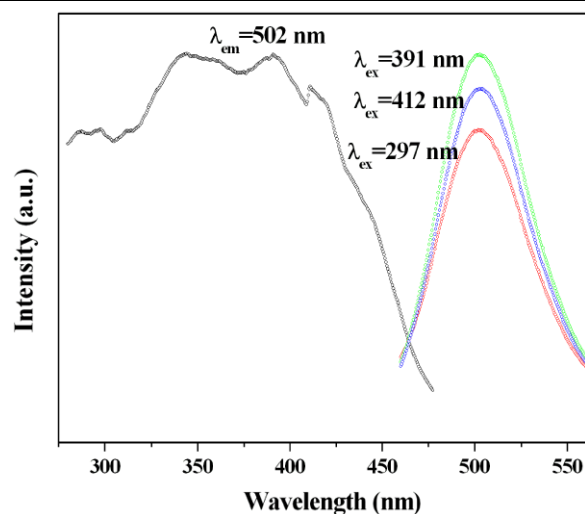


Fig. 4 PLE (left) and PL (right) spectra of $(\text{BaO-BaCl}_2\text{-SiO}_2):0.1\text{Eu}^{2+}$ ($\lambda_{\text{em}} = 502\text{ nm}$ for excitation and $\lambda_{\text{ex}} = 297, 391$ and 412 nm for emission)

imum at $x = 0.1$; then the absorption intensity decreases gradually.

The PLE spectra of $(\text{BaO-BaCl}_2\text{-SiO}_2):0.1\text{Eu}^{2+}$ phosphor, monitored at 502 nm , is shown in Fig. 4. The PLE spectra ranging from 280 to 480 nm are composed of three broad absorption bands around $341, 391$ and 412 nm , which are mainly due to $4f^7(^8S_{7/2})\text{-}4f^65d$ transitions of the Eu^{2+} ions [10]. The above analysis results also agree with the reflectance spectra. The PL spectra of $(\text{BaO-BaCl}_2\text{-SiO}_2):0.1\text{Eu}^{2+}$ are also shown in Fig. 4. Upon 391 nm excitation, the emission spectrum consists of a single green broad band with a maximum at about 502 nm and the FWHM is about 60 nm , which can be ascribed to the $5d\text{-}4f$ allowed transition of the Eu^{2+} ions. The emission band appears to be symmetric and it can be presumed that the Eu^{2+} ions occupy only one type of site in the $(\text{BaO-BaCl}_2\text{-SiO}_2)$ system lattice, which forms one corresponding emission center. With different excitation wavelengths of $297, 391$ and 412 nm , the PL spectra show no significant changes except for the emission intensity, which also is consistent with the fact that there is only one kind of Ba site in the $(\text{BaO-BaCl}_2\text{-SiO}_2)$ host material system. According to the report of Van Uitert [11], for most divalent and some trivalent rare earth ions in suitable matrices, such as sulfide, oxide, halide and aluminates, the following phenomenological equation, (1), provides a good fit to the emission peak and the excitation edge data for Eu^{2+} and Ce^{3+} . Based on this, the problem about which kind of crystallographic site is substituted by Eu^{2+} in the $(\text{BaO-BaCl}_2\text{-SiO}_2):\text{Eu}^{2+}$ system can be discussed and tested in theory. We have

$$E = Q \left[1 - \left(\frac{V}{4} \right)^{\frac{1}{V}} 10^{-\frac{\text{near}}{80}} \right]. \quad (1)$$

Table 1 The position of the d-band edge in energy for Eu^{2+} occupying the sites of Ba^{2+} with different coordination number

Coordination number of Ba^{2+}	Radius of Ba^{2+} r/nm	Position of the d-band edge E/cm^{-1}	Value of emission peak λ/nm
6	0.135	19571.31	511
7	0.138	20922.6	478
8	0.142	22251.4	449
9	0.147	23557.8	424

In (1), E represents the position of the d-band edge in energy for rare earth ions (cm^{-1}), Q is the position in energy for the lower d-band edge for the free ions, the value of Q is $34,000 \text{ cm}^{-1}$ for Eu^{2+} , V is the valence of the “active” cation; here $V = 2$. ‘ea’ is the electron affinity of the atoms that form anions, ea is taken as 2.19 eV in the $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2)$ host system [11]. n is the number of anions in the immediate shell about this ion, and r is the radius of the host cation replaced by the “active” cation. In accordance to (1), Table 1 gives the position of the d-band edge in energy for Eu^{2+} occupying the sites of Ba^{2+} with different coordination number. It indicates that there will be an emission band with a peak at 511 nm, while Ba^{2+} is substituted for by Eu^{2+} , and the value of the coordination number n of Ba^{2+} in the $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2):\text{Eu}^{2+}$ system is 6. This is consistent with the fact that the $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2):\text{Eu}^{2+}$ system has a single green broad band with a maximum at about 502 nm, as shown in Fig. 4, which also testifies the possible crystallography sites in the novel $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2):\text{Eu}^{2+}$ phosphor system.

The effect of the Eu^{2+} concentration x on the emission intensity of the Eu^{2+} -doped $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2)$ system is shown in Fig. 5, which was obtained directly from the measured value of the spectrophotometer ($\lambda_{\text{ex}} = 391 \text{ nm}$). As the Eu^{2+} concentration increases, the emission intensity increases, and it maximizes at about $x = 0.1$, which is similar to the result of the reflectance spectra. We propose that concentration quenching occurs, when the Eu^{2+} concentration is beyond $x = 0.1$. In general, concentration quenching can be caused by nonradiative energy transfer among activator ions, except for the energy transfer of activator ions to impurities, color centers or any other quenching centers. In our case, we proposed that the concentration quenching was brought about by the energy transfer among the Eu^{2+} . Considering that the energy transfer usually occurs as a result of an exchange interaction, radiation reabsorption or a multipole–multipole interaction [12], we should understand the origin of the energy transfer in the $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2):\text{Eu}^{2+}$ system, and then the reason for the concentration quenching can be revealed.

Since the fluorescent mechanism of Eu^{2+} in $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2):\text{Eu}^{2+}$ phosphor is the $4f-5d$ allowed electric-

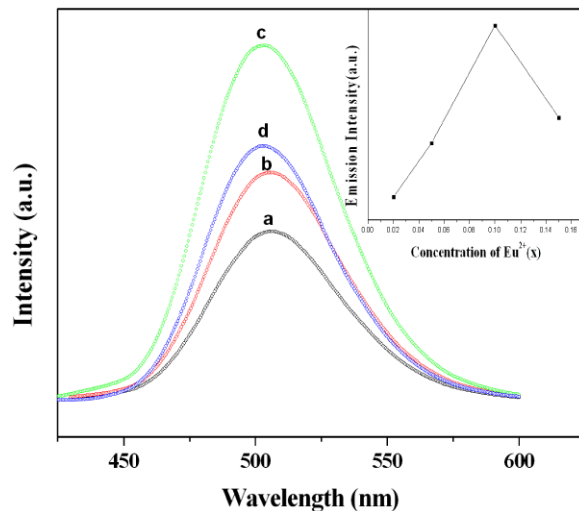


Fig. 5 The PL spectra of the $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2):x\text{Eu}^{2+}$ phosphor system for various Eu^{2+} concentrations: (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.1$ and (d) $x = 0.15$. The insert represents the Eu^{2+} emission intensities as a function of Eu^{2+} concentration (x) ($\lambda_{\text{ex}} = 391 \text{ nm}$)

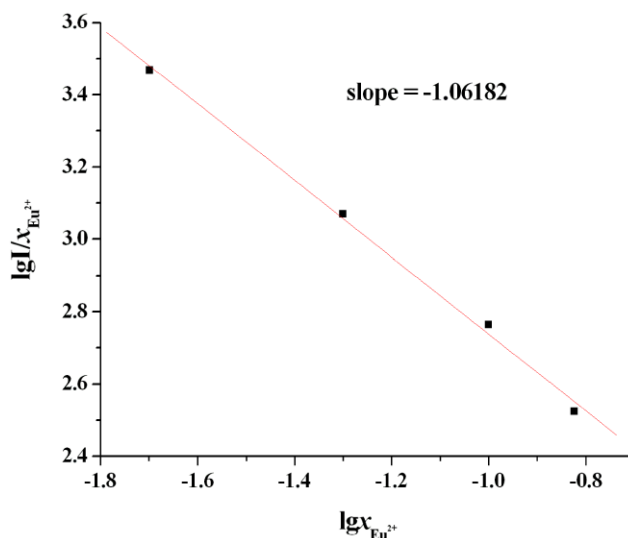


Fig. 6 The curve of $\log \frac{I}{x}$ vs. $\log x$ in $(\text{BaO}-\text{BaCl}_2-\text{SiO}_2):x\text{Eu}^{2+}$ phosphor ($\lambda_{\text{ex}} = 391 \text{ nm}$)

dipole transition, the process of energy transfer should be controlled by an electric multipole–multipole interaction [13]. According to the report of Van Uitert, the emission intensity (I) per activator ion follows the equation [14–16]

$$\frac{I}{x} = K [1 + \beta(x)^\theta]^{-1} \tag{2}$$

where x is the activator concentration, $\frac{I}{x}$ is the emission intensity (I) per activator concentration (x), and K and β are constants for the same excitation condition for a given host crystal. According to (2), $\theta = 3$ for energy transfer among

the nearest-neighbor ions, while $\theta = 6, 8$ and 10 for dipole–dipole (d–d), dipole–quadrupole (d–q), and quadrupole–quadrupole (q–q) interactions [14, 17]. To get a θ value for the emission center, the dependence of $\log \frac{I}{x}$ on $\log x$ is plotted, as shown in Fig. 6. It can be seen from Fig. 6 that the dependence of $\log \frac{I}{x}$ on $\log x$ is linear and the slope is -1.06 . The value of θ can be calculated to be 3.18 , which is approximately equal to 3 , by using (2). Since the value of θ equals 3 , it means that the quenching is directly proportional to the ion concentration, which indicates that the concentration quenching is caused by the energy transfer among the nearest-neighbor ions in the $(\text{BaO–BaCl}_2\text{–SiO}_2)\text{:Eu}^{2+}$ phosphor system.

4 Conclusion

In summary, a new green phosphor barium chlorosilicate, the Eu^{2+} -doped $(\text{BaO–BaCl}_2\text{–SiO}_2)$ phosphor system, was synthesized by the high-temperature solid-state method. It has excellent luminescence properties due to the broad excitation band extending from 280 to 480 nm. Under 391 nm UV excitation, $(\text{BaO–BaCl}_2\text{–SiO}_2)\text{:Eu}^{2+}$ shows a green emission band centered at 502 nm with FWHM of 60 nm. The possible coordination number of Ba^{2+} in the $(\text{BaO–BaCl}_2\text{–SiO}_2)\text{:Eu}^{2+}$ system is 6 , and the result of theoretical calculation suggests that the energy transfer among the nearest-neighbor ions plays a major role in the mechanism of concentration quenching of Eu^{2+} in the $(\text{BaO–BaCl}_2\text{–SiO}_2)\text{:Eu}^{2+}$ phosphor system. In view of its broad excitation band in the near-UV region, intense green emission, this phosphor is a promising candidate for near-UV LEDs.

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