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Preparation and photoluminescence properties of single-phase $Ca_2SiO_3Cl_2$:Eu^{2+} bluish-green emitting phosphor

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ABSTRACT

Using CaO/$CaCO_3$ (blend) and NH_4Cl as the respective calcium and chloride sources, we have succeeded in the synthesis of single-phase $Ca_2SiO_3Cl_2$:Eu^{2+} powder phosphor via solid-state-reaction . Indeed, two emission bands due to Eu^{2+} should be observed in $Ca_2SiO_3Cl_2$:Eu^{2+}, since there are two Eu^{2+} luminescence centers substituting for two Ca^{2+} sites. However, interestingly, only one emission band centered at 495 nm is observed. This is explained based on the uniform covalency and crystal field of two Eu^{2+} sites. The excellent thermal stability and the intense emission upon near-ultraviolet (UV) light excitation suggest that $Ca_2SiO_3Cl_2$:Eu^{2+} can be used as a potential bluish-green phosphor for near-UV white LEDs.

1. Introduction

During the past few years, white LEDs as a burgeoning lighting source for general illumination have attracted much attention due to several merits, such as high efficiency, lower energy consumption, good reliability and long lifetime. Up to now, the main strategy for producing white LEDs is to combine blue or near-UV LED chips with phosphors [1,2]. The white LEDs employing near-UV LED chips with tri-color phosphors have the advantage of less color point-shift against current as the white light is only phosphor converted rather than the case of combining blue LED chips with phosphors (e.g. YAG:Ce^{3+}). Therefore, it is necessary to develop new phosphors that are excitable by near-UV light.

Alkaline earth halo-silicate hosts activated with Eu^{2+} are well-known good candidates as LED phosphors due to their low synthesis temperature and high luminescence efficiency, such as $Ca_3SiO_4Cl_2$:Eu^{2+} [3], $Ca_{10}(Si_2O_7)_3Cl_2$:Eu^{2+} [4], $Sr_8(Si_4O_{12})Cl_8$:Eu^{2+} [5], $Ca_6Sr_4(Si_2O_7)_3Cl_2$:Eu^{2+} [6], $Ca_8Zn(SiO_4)_4Cl_2$:Eu^{2+} [7], $Ca_8Mg(SiO_4)_4Cl_2$:Eu^{2+} [8], etc. $Ca_2SiO_3Cl_2$ is another material of this type which was first reported by Golovastikov and Kazak in the form of single-crystal in 1977 [9]. Although the attempt to prepare Eu^{2+} activated $Ca_2SiO_3Cl_2$ powder phosphor has been reported [10], single-phase $Ca_2SiO_3Cl_2$:Eu^{2+} and its photoluminescence properties have not been achieved till now. Obviously, improvement of the phosphor synthesis method is urgently required. After lots of experimental works, we find that using binary mixture of CaO and $CaCO_3$ as calcium source and NH_4Cl as chloride source can permit fabrication of single-phase $Ca_2SiO_3Cl_2$ powder sample rather than using either CaO or $CaCO_3$ singly as calcium source and $CaCl_2$ as chloride source. In this letter, we report, to our knowledge for the first time, the synthesis and photoluminescence properties of single-phase $Ca_2SiO_3Cl_2$:Eu^{2+} which possesses an intense bluish-green emission suitable for near-UV based white LEDs.

2. Experimental

Syntheses of $Ca_2SiO_3Cl_2$:Eu^{2+}: $Ca_2SiO_3Cl_2$:Eu^{2+} was synthesized via solid-state-reaction . The reagent grade starting materials CaO, $CaCO_3$, SiO_2, and NH_4Cl were mixed together with a mole ratio of 1.79:0.2:1:2.2. The doping concentration of Eu^{2+} is 1 mol%. NH_4Cl is in excess by 10% to supply enough chloride. After homogenization, the mixtures were placed in a crucible and sintered at 800 °C for 4 h in CO reducing atmosphere.

Characterization: A Bruker D8-Focus X-ray diffractometer (XRD) was employed to check the crystalline phase of phosphors. The photoluminescence (PL) emission and excitation (PLE) spectra were measured by a Hitachi F-4500 spectrometer equipped with a 150 W-xenon lamp under a working voltage of 700 V. For fluorescence lifetime measurement, the third harmonic (355 nm) of Nd–YAG laser (Spectra-Physics, GCR 130) was used as the excitation source, and the signals were detected with a Tektronix digital oscilloscope (TDS 3052).

3. Results and discussion

XRD analysis: $Ca_2SiO_3Cl_2$ has two allotropic structures belonging to tetragonal and orthorhombic systems. What we are interested

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here is just thetetragonal phase of $Ca_2SiO_3Cl_2$. Fig. 1 shows the XRD patterns of $Ca_2SiO_3Cl_2:Eu^{2+}$, as well as the standard JCPDS data of $Ca_2SiO_3Cl_2$. All diffraction peaks of $Ca_2SiO_3Cl_2:Eu^{2+}$ are basically indexed to the standard JCPDS data. Due to the preferential growth effect caused by different synthesis routes, the relative intensities of diffraction peaks are different from the standard data. Similar phenomenon has been observed previously in other inorganic phosphor materials [11]. The structure of $Ca_2SiO_3Cl_2$ crystallizes in the space group *I*4(79) with lattice constants $a=10.698$ Å and $c=9.345$ Å. In $Ca_2SiO_3Cl_2$, there are two Ca^{2+} sites, both of which are surrounded by seven anion ions, i.e. three Cl^- and four O^{2-}, shown in the inset of Fig. 1. Bond lengths of Ca–O and Ca–Cl are listed in Table 1.

Photoluminescence of Eu^{2+} doped $Ca_2SiO_3Cl_2$: The PL and PLE spectra of $Ca_2SiO_3Cl_2:Eu^{2+}$ are shown in Fig. 2. According to the structure of $Ca_2SiO_3Cl_2$, there must exist two emission bands originating from two Eu^{2+} luminescent centers from substituting for two Ca^{2+} sites. In order to distinguish these two emission bands, different excitation wavelengths are chosen to measure the PL spectra and different emission wavelengths for PLE spectra. To our surprise, only a single band, not two, was observed in PL spectra with a peak at 495 nm and a bandwidth of 75 nm which is assigned to Eu^{2+} $4f^65d$–$4f^{\ 7}$ transitions. There may be two possible situations for this phenomenon. The first is that Eu^{2+} ions may prefer to occupy one of the two Ca^{2+} sites and generate only one kind of luminescence centers rather than two. This situation often occurs in those host lattices with large coordinate differences between cationic sites. The second is that coordinate environments of two cationic sites are almost the same leading to similar covalency and crystal field on Eu^{2+} ions which could result in one unresolved emission band. As for $Ca_2SiO_3Cl_2:Eu^{2+}$, the location of coordinate anion for two Ca^{2+} sites is uniform (inset of Fig. 1) and average bond lengths of Ca(I) and Ca(II) are 2.6299 and 2.6291 Å (see Table 1), respectively, indicating the minor difference between two Ca^{2+} sites. Accordingly, we consider that the two Eu^{2+} sites experience almost identical crystal field environments, resulting in one PL band. The identical PLE and PL spectra for different excitation and emission wavelengths just testify to this judgment. In addition, it can be seen that $Ca_2SiO_3Cl_2:Eu^{2+}$ is excitable by near-UV light and exhibits intense bluish-green emission of which the intensity is comparable with that of the known $Ca_3SiO_4Cl_2:Eu^{2+}$ phosphor [3] under the same measurement condition. It is believed that $Ca_2SiO_3Cl_2:Eu^{2+}$ is promising to be used for near-UV white LEDs.

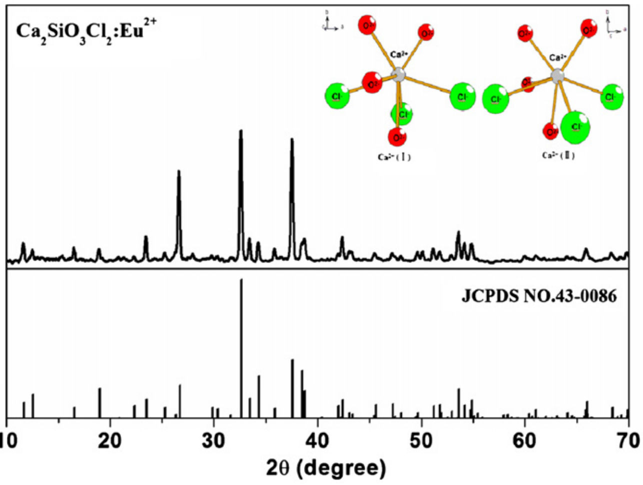

Fig. 1. XRD patterns of $Ca_2SiO_3Cl_2:Eu^{2+}$ powder sample. The inset shows the schematic coordinate environment of Ca^{2+} sites.

Table 1
Ca–O and Ca–Cl bond length of two Ca^{2+} sites in tetragonal $Ca_2SiO_3Cl_2$ [9].

Sites	Coordinate anion	Bond length (Å)	Average bond length (Å)
Ca(I)	O3	2.3190	2.6299
	O2	2.4396	
	O2	2.5717	
	O1	2.6627	
	Cl1	2.7671	
	Cl2	2.8109	
	Cl2	2.8383	
Ca(II)	O2	2.2883	2.6291
	O3	2.4535	
	O3	2.5390	
	O1	2.6664	
	Cl2	2.7565	
	Cl1	2.8243	
	Cl4	2.8755	

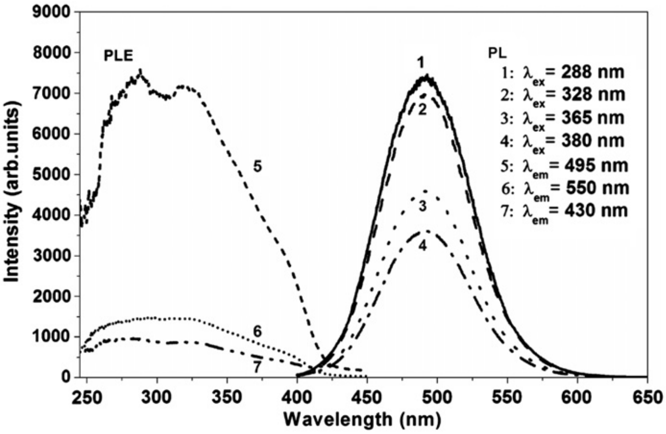

Fig. 2. PL and PLE spectra of $Ca_2SiO_3Cl_2:Eu^{2+}$.

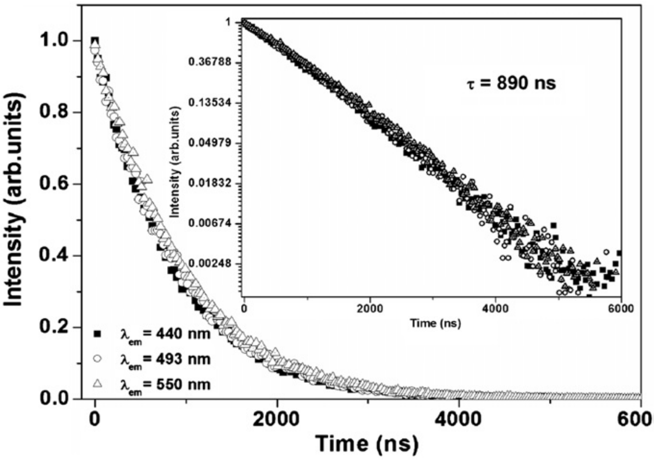

Fig. 3. Fluorescence decay curves of $Ca_2SiO_3Cl_2:Eu^{2+}$. The inset shows the linetypes obtained by taking natural logarithm of the decay curves.

Fluorescence decay curves of Eu^{2+} in $Ca_2SiO_3Cl_2$: To further investigate the photoluminescence of Eu^{2+} in $Ca_2SiO_3Cl_2$, the fluorescence decay curves of Eu^{2+} monitored at different emission wavelengths were measured. As shown in Fig. 3, all the decay curves overlap with each other and exhibit a single exponential function. By taking logarithm of those curves (inset), straight line type is observed. The exponential decay behavior of $Ca_2SiO_3Cl_2:Eu^{2+}$ further demonstrates the comparability of two Eu^{2+} luminescent centers. The fluorescence lifetime remains nearly unchanged around 890 ns which is in the same order of

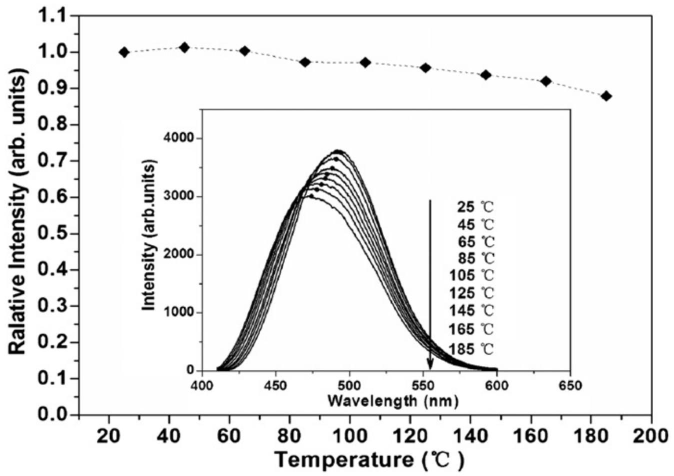

Fig. 4. The relative PL intensities of $Ca_2SiO_3Cl_2:Eu^{2+}$ at various temperatures in the range of 25–185 °C. The inset shows the temperature dependent PL spectra of $Ca_2SiO_3Cl_2:Eu^{2+}$ under 380 nm excitation.

magnitude as that of the other reported Eu^{2+} doped halo-silicate phosphors [12,13].

Thermal quenching properties of $Ca_2SiO_3Cl_2:Eu^{2+}$: Fig. 4 shows the thermal quenching of luminescence spectra of $Ca_2SiO_3Cl_2:Eu^{2+}$ at various temperatures in the range of 25–185 °C. When temperature increases, the PL intensities decrease accompanied with a blue-shift of peak and a broadening of FWHM, which can be explained in terms of configuration coordinate models [14]. The luminescence intensity at 150 °C, the usual temperature this phosphor suffers when LED is operating, remains 93% of that at 25 °C, showing the excellent thermal quenching properties of $Ca_2SiO_3Cl_2:Eu^{2+}$. It is therefore convinced that $Ca_2SiO_3Cl_2:Eu^{2+}$ can be used as a novel bluish-green emitting phosphor for white LEDs.

4. Conclusions

The single-phase $Ca_2SiO_3Cl_2:Eu^{2+}$ powder phosphor was successfully synthesized by solid-state-reaction . The photoluminescence properties were reported for the first-time . Although there should be two emission bands resulting from two Eu^{2+} luminescence centers in $Ca_2SiO_3Cl_2:Eu^{2+}$, only one emission band peaking at 495 nm was observed due to the similar coordinate environment of two Eu^{2+} sites. The excellent thermal stability and the intense emission upon near-ultraviolet (UV) light excitation suggest that $Ca_2SiO_3Cl_2:Eu^{2+}$ can be used as a potential bluish-green phosphor for near-UV white LEDs.

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