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Ce^{3+}-activated $Ca_8Zn(SiO_4)_4Cl_2$: A novel near-ultraviolet converting blue-emitting chlorosilicate phosphor for white light-emitting diodes

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ABSTRACT

A series of Ce^{3+}-activated chlorosilicate phosphors, $Ca_{8\text{-}x}Zn(SiO_4)_4Cl_2$: $x$$Ce^{3+}$, was firstly synthesized by solid-state reactions. The crystal structure and luminescence properties of the phosphors, as well as their thermal luminescence quenching capabilities and CIE chromaticity coordinates were systematically investigated. Studies revealed the incorporation of Ce^{3+} into 8-coordinated Ca site, thereby favoring the novel blue luminescence corresponding to the electric-dipole allowed $4f^05d^1$–$4f^1$ transition of the Ce^{3+} ions. Furthermore, the dipole-dipole interaction was dominantly involved in the mechanism of concentration quenching of Ce^{3+} in the phosphors, and the activation energy for thermal quenching (ΔE) was calculated to be 0.17 eV. Compared with the commercial $BaMgAl_{10}O_{17}$: Eu^{2+} phosphor, the composition-optimized $Ca_{7.97}Zn(SiO_4)_4Cl_2$: $0.03Ce^{3+}$ showed a preferable light yield with chromaticity coordinates of (0.156, 0.028) and color temperature of 1896 K. Because of the strong absorption in the near-ultraviolet region and the intense blue emission peaking at 411 nm, our developed phosphors exhibit great potential for use as the promising blue-emitting phosphors for white light-emitting diodes.

1. Introduction

Over the past few years, halosilicate-based phosphors have demonstrated remarkable potential capacity for use in phosphor-converted light-emitting diodes (LEDs) due to their outstanding chemical and physical stability, relatively low sintering temperature, and preferable luminescence properties [1,2]. Particularly, intense attention has been paid to rare-earth-activated fluosilicate/chlorosilicate phosphors such as $Ca_{5.45}Li_{3.55}(SiO_4)_3O_{0.45}F_{1.55}$: Ce^{3+} [3], $Ca_5(SiO_4)_2F_2$: Ce^{3+} [4], $SrSi_3O_8Cl_4$: Eu^{2+} [5] and $Ba_5SiO_4Cl_6$: Eu^{2+} [6]. All of these phosphors can be efficiently excited by the near-ultraviolet (n-UV) light to realize a novel blue luminescence, which makes them potential alternatives for the conventional blue-emitting phosphor $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM: Eu^{2+}). It is well-known that the Ce^{3+} ion with the 4f configuration usually has a large Stokes shift and its emission can be shifted from UV to the visible region of the electromagnetic spectrum, which is dependent on the degree of covalent bonding and the crystal field strength [3]. As the multiplex inorganic compound, the chlorosilicate is expected to be a suitable host lattice for phosphors due to the low phonon energy in chloride anions. Moreover, the minor quenching process from multi-phonon relaxation can also be realized, which will induce the efficient emission in the Ce^{3+}-activated chlorosilicate phosphors [4]. In 1989, Wu et al. firstly reported the crystal structure of $Ca_8Zn(SiO_4)_4Cl_2$ and pointed out it was of cubic system with lattice constants $a=b=c=15.07$ Å, $V=3424.04$ Å^3 [7]. Until now, however, no details regarding the luminescence properties of Ce^{3+}-activated $Ca_8Zn(SiO_4)_4Cl_2$ have been reported in the literature. Therefore, in the present work, we firstly report the synthesis, and luminescence properties and structural properties of $Ca_{8\text{-}x}Zn(SiO_4)_4Cl_2$: $x$$Ce^{3+}$ phosphors, which can be considered as the promising blue-emitting phosphors for n-UV-pumped white LEDs.

2. Experimental

The $Ca_{8\text{-}x}Zn(SiO_4)_4Cl_2$: $x$$Ce^{3+}$ (x =0.005–0.10) phosphors were prepared by solid-state reactions. The starting materials were CaO (analytical reagent, (A.R.)), $CaCl_2$ (A.R.), ZnO (A.R.), SiO_2 (A.R.), and CeO_2 (99.99%). The stoichiometric amounts of starting materials were weighed and thoroughly mixed in an agate mortar, then placed in a corundum crucible and calcined at 1373 K for 4 h in CO

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reducing atmosphere. X-ray powder diffraction (XRD, D8 Advance, Germany) patterns were employed to identify the phase structure of materials. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded on a fluorescence spectrometer (FLS920, Edinburgh Instruments, Britain). The temperature-dependent PL spectra were recorded on the same spectrophotometer which was combined with a self-made heating attachment and a computer-controlled electric furnace.

3. Results and discussion

Fig. 1a shows the XRD patterns of undoped $Ca_8Zn(SiO_4)_4Cl_2$ host and $Ca_{8\text{-}x}Zn(SiO_4)_4Cl_2$: $x$$Ce^{3+}$ phosphors. All the diffraction peaks are well indexed to $Fd\bar{3}m$ space group of cubic $Ca_8Zn(SiO_4)_4Cl_2$ phase (JCPDS No. 39-1421), indicating that the obtained phosphors are single-phase and the Ce^{3+} ions have completely dissolved in the host lattice by substituting for the Ca^{2+} ions based on their similar ionic radii. As shown in Fig. 1b, the compound $Ca_8Zn(SiO_4)_4Cl_2$ has the structure consisting of an intricate 3-dimensional framework of interconnecting $Ca(1)O_6$, $Ca(2)O_6Cl_2$, ZnO_4, and SiO_4 polyhedra [7]. There are two crystallographically distinct Ca sites in the crystal lattice. Ca(1) is coordinated by six oxygen atoms (bond length in 2.311–2.433 Å). Ca (2) has six oxygen neighbors (bond length in 2.370–2.712 Å), and the other neighbors are two chlorine atoms with bond lengths of 3.021 and 3.065 Å. The nature of Ca(1) and Ca(2) in the lattice can be further understood and assigned by the PL spectra of Ce^{3+}-activated $Ca_8Zn(SiO_4)_4Cl_2$ phosphors, which is systematically investigated as follows.

Fig. 2a shows the PL and PLE spectra of $Ca_{7.97}Zn(SiO_4)_4Cl_2$: $0.03Ce^{3+}$ phosphor. By monitoring at 411 nm, the PLE spectrum consists of four broad excitation bands around 260, 290, 331, and 360 nm, attributing to the 4f-5d transition of the Ce^{3+} ions. The asymmetric blue emission band in the PL spectrum is fitted into a good approximation with two Gaussian curves centered at 396 and 431 nm, which can be ascribed to the transitions from the lowest 5d level to the two $^2F_{5/2}$ and $^2F_{7/2}$ ground states of the Ce^{3+} ions [8]. Then, the energy gap between $^2F_{5/2}$ and $^2F_{7/2}$ associated with spin-orbit coupling is calculated to be 2051 cm^{-1}. The emission position of Ce^{3+} has a strong dependence on its local environment, which has been suggested to obey the following relation [9]:

$$E = Q\left[1 - \left(\frac{V}{4}\right)^{\frac{1}{V}} \times 10^{-\frac{n\times E_a\times r}{80}}\right] \tag{1}$$

In Eq. (1), E represents the position for the Ce^{3+} emission peak (cm^{-1}), Q is the position in energy for the lower d-band edge for the free Ce^{3+} ion (Q=50,000 cm^{-1}), V is the valence of the Ce^{3+} ion (V=3), E_a is the electron affinity of anion atom (E_a=2.19 eV), n is the number of anions in the immediate shell about the Ce^{3+} ion, and r is the radius of the host cation replaced by the Ce^{3+} ion (Å). Thus, the values of E calculated by Eq. (1) are 18,868 cm^{-1} (530 nm) and 24,155 cm^{-1} (414 nm) respectively, corresponding to 6 and 8 for the coordination number of Ca sites. It is found that the theoretical emission peak located at 414 nm is close to the experimental value of the blue emission peaking at 411 nm in the $Ca_{7.97}Zn(SiO_4)_4Cl_2$: $0.03Ce^{3+}$ phosphor, indicating that Ce^{3+} ions are more likely to occupy the 8-coordinated Ca(2) sites in the lattice. Moreover, it is accepted that the positive ion is coordinated with more negative ions as possible when they contact with each other. Thus, the polyhedral form of the structure can be determined by radius ratio of positive ion to negative ion. Providing that the value of r^+/r^- is more than 0.732, the positive ion will select 8 as the coordinated number to form the decahedron [10]. Based on this, the value of $r^+_{Ce^{3+}}/r^-_{O^{2-}}$ is calculated to be 0.745 in the $Ca_{7.97}Zn(SiO_4)_4Cl_2$: $0.03Ce^{3+}$ phosphor, which further confirms that the Ce^{3+} ions will substitute for the 8-coordinated Ca(2) sites and form the eight-top CeO_6Cl_2 decahedron. Under 360 nm excitation, the $Ca_{7.97}Zn(SiO_4)_4Cl_2$: $0.03Ce^{3+}$ phosphor shows the preferable chromaticity coordinates of (0.156, 0.028) and color temperature of 1896 K, whose color purity is better than that of the commercial BAM: Eu^{2+} phosphor (the inset of Fig. 2a).

Fig. 2(b) depicts the PL spectra of $Ca_{8\text{-}x}Zn(SiO_4)_4Cl_2$: $x$$Ce^{3+}$ phosphors. All of the PL spectra exhibit the similar profile with various relative intensities, which maximizes at x=0.03 for the $Ca_{7.97}Zn(SiO_4)_4Cl_2$: $0.03Ce^{3+}$ phosphor. Therefore, we propose that concentration quenching occurs when the Ce^{3+} concentration exceeds x=0.03. According to the Dexter theory, the PL intensity per activator of $Ca_{8\text{-}x}Zn(SiO_4)_4Cl_2$: $x$$Ce^{3+}$ phosphors is given by the equation [11]:

$$\frac{I}{x} = K\left[1 + \beta(x)^{\frac{S}{3}}\right]^{-1} \tag{2}$$

where S=6, 8, and 10 corresponding to the electric dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively, and x is the concentration of the activator and K and β

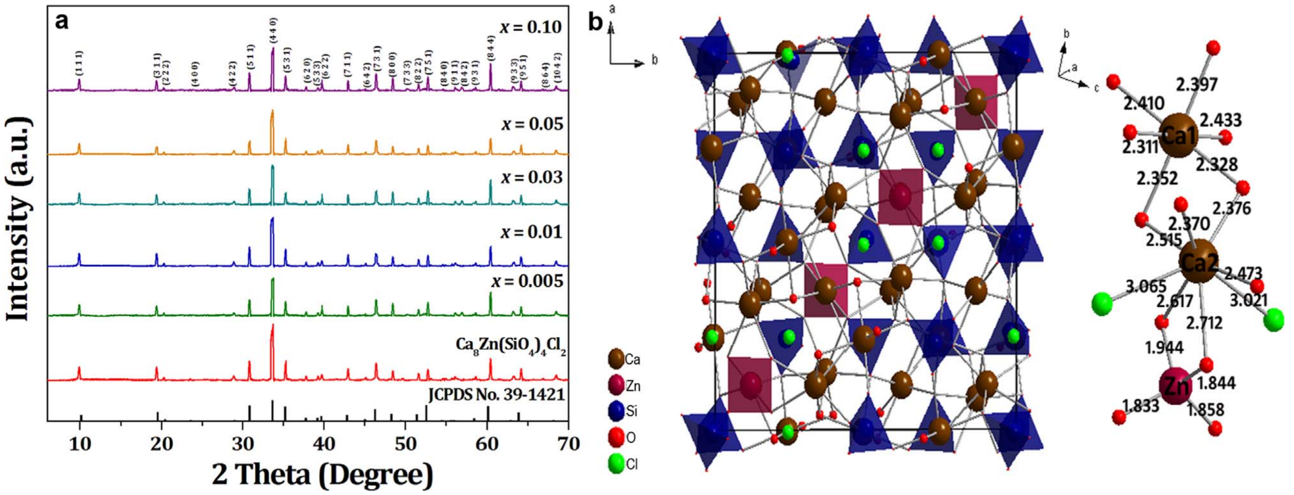

Fig. 1. (a) XRD patterns of $Ca_8Zn(SiO_4)_4Cl_2$ and $Ca_{8\text{-}x}Zn(SiO_4)_4Cl_2$: $x$$Ce^{3+}$, as well as JCPDS card (No. 39-1421). (b) The crystal structure of $Ca_8Zn(SiO_4)_4Cl_2$ lattice, and the coordination environment of metal atoms for Ca(1), Ca(2), and Zn.