The synthesis and photoluminescence of a single-phased white-emitting NaAlSiO$_4$: Ce^{3+}, Mn^{2+} phosphor for WLEDs

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ABSTRACT

A series of blue-to-white emitting phosphors NaAlSiO$_4$: Ce^{3+}, Mn^{2+} were synthesized via a high-temperature solid-state method. The obtained phosphors exhibited a broad excitation band from 250 to 400 nm peaking at 350 nm, matching well with the available UV chips. Under the excitation of 350 nm, a broad green–blue emission band peaking at 430 nm and an orange–red emission band at 590 nm were observed due to the f–d transition of Ce^{3+} and the $^4T_1$–$^6A_1$ transition of Mn^{2+}, respectively. Moreover, energy transfer process from Ce^{3+} to Mn^{2+} was verified with the mechanism to be dipole-quadrupole interaction. By varying the doping concentration of Mn^{2+}, tunable colors from blue to white were obtained in the phosphors. The results indicate that this phosphor has potential applications as a single-phased aluminosilicate phosphor for ultraviolet white light-emitting diodes (UVWLEDs).

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1. Introduction

White light-emitting diodes (WLEDs) have attracted commercial interest and extensive study for their high luminous efficiency, long lifetime, low power consumption and environmentally friendly features [1–5]. At present, the commercial WLEDs can be available by combining a blue chip with yellow-phosphor (YAG: Ce) [6]. However this approach suffers weakness such as cool white light which is uncomfortable for indoor lighting owing to the lack of a red light component [7]. Due to the deterioration of the phosphors, the poor color rendering index and low stability of the color temperature are also disadvantages. Recently, a near-UV (n-UV) LED combined with red–green–blue (RGB) tricolor multiphased phosphors has been employed to overcome the above shortcomings. However, the blue emission is poor for the strong reabsorption of red or green emissions from the blue light [8]. Thus, it is important to explore novel single-phased white-emission phosphors that can be excited by the UVLED chips.

In general, a single-phased white-emitting phosphor is produced by co-doping a sensitizer and an activator into the same host. The white light is usually attributed to different activators or one kind of activator at different crystal sites [9–12]. Recently, the single-phased color-tunable with white light-emitting phosphors have been obtained by co-doping Ce^{3+} and Mn^{2+} in proper hosts, such as Ca$_2$SrAl$_2$O$_6$ [8], NaCaBO$_3$ [13], and Ca$_2$Gd$_8$(SiO$_4$)$_6$O$_2$ [14]. As is well known that silicates have the advantages such as high chemical–physical stability and various crystal structures, which can be good candidates for WLEDs applications. More recent studies on Tb^{3+}, Eu^{3+} co-doped NaAlSiO$_4$ have been reported with a tunable color from green to red [15]; Eu^{2+} doped NaAlSiO$_4$ has been identified via a liquid phase precursor technique and the photoluminescence properties have been investigated [16]. Above researches indicate NaAlSiO$_4$ could be an excellent candidate phosphor host matrix for LEDs, in addition, Ce^{3+}, Mn^{2+} co-doped NaAlSiO$_4$ has not been studied. In this research, we have studied the photoluminescence properties of Ce^{3+}, Mn^{2+} co-doped NaAlSiO$_4$ phosphors in detail. Energy transfer process from Ce^{3+} to Mn^{2+} has been verified and the critical distance between the doped ions has been calculated as well. By appropriately adjusting the the doping concentration of Mn^{2+}, the obtained phosphors generate emission from blue to white under the UV excitation.

2. Experimental

A series of Na$_{0.97-x}$AlSiO$_4$: 0.03Ce^{3+}, xMn^{2+} (x = 0, 0.05, 0.07, 0.09, 0.12 and 0.15) phosphors were synthesized by a traditional high-temperature solid-state reaction. Na$_2$CO$_3$ (A.R.), Al$_2$O$_3$ (99.99%), SiO$_2$ (99.99%), CeO$_2$ (99.99%) and MnO$_2$ (99.99%) were employed as starting materials. The mixtures were first mixed and grind in an agate mortar for 30 min, and then sintered at 1200 °C

for 4 h under a reductive atmosphere (5% H_2 + 95% N_2). The as prepared phosphors were cooled to room temperature and reground for further research. The phases of the obtained samples were identified by X-ray powder diffraction (XRD) with Cu Kα (λ = 0.15418 nm radiation at a scanning step of 0.02° in the 2θ range from 10° to 80° operated at 36 kV and 30 mA (Rigaku Model D/max-2200).

The photoluminescence excitation (PLE) and photoluminescence (PL) spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer with a photomultiplier tube operating at 400 V, and a 150-W Xe lamp was used as the excitation lamp. The PL decay curves were measured by FLS980 fluorescence spectrophotometer.

3. Results and discussion

The XRD patterns of $Na_{0.97}AlSiO_4$: $0.03Ce^{3+}$, $Na_{0.85}AlSiO_4$: $0.15Mn^{2+}$ and $Na_{0.82}AlSiO_4$: $0.03Ce^{3+}$, $0.15Mn^{2+}$ are shown in Fig. 1a. The diffraction peaks are well assigned to the monoclinic phase of $NaAlSiO_4$ (JCPDS 35-0424), indicating that a pure hexagonal nepheline $NaAlSiO_4$ phase are obtained. The uniform diffraction patterns show that the incorporation of Ce^{3+} and Mn^{2+} didn't affect the crystal structure of the synthesized materials significantly, which indicates that both Ce^{3+} and Mn^{2+} have dissolved completely in the $NaAlSiO_4$ host. Fig. 1b shows the crystal structure of $NaAlSiO_4$ which has a structure of hexagonal nepheline with space group $P63$. The three dimensional framework structures are formed by AlO_4 and SiO_4 tetrahedra that linked to each other with sharing corner oxygen atoms. AlO_4 and SiO_4 tetrahedra are filled by Na^+ ions. There are two Na^+ sites, one is coordinated by eight oxygen atoms marked Na^+ (I) and the other is coordinated by six oxygen atoms marked Na^+ (II). Based on the effective ionic radii (r) of cations with different

coordination number (CN) reported by shannon [17], we propose that both Ce^{3+} (r = 0.101 nm when CN = 6, r = 0.114 nm when CN = 8) and Mn^{2+} (r = 0.067 nm when CN = 6, r = 0.096 nm when CN = 8) occupy Na^+ (r = 0.102 nm when CN = 6, r = 0.118 nm when CN = 8) sites preferably because both Al^{3+} (r = 0.039 nm when CN = 4) and Si^{4+} (r = 0.026 nm when CN = 4) are too small to accommodate the rare earth ions.

Fig. 2a exhibits the PLE and PL spectra of $Na_{0.97}AlSiO_4$: $0.03Ce^{3+}$. Monitored at 430 nm, the PLE spectrum clearly demonstrates that there are two absorption bands, peaked at 290 and 350 nm, which assigned to the electron transitions of Ce^{3+} from the $^2F_{5/2}$ ground state to the different components of excited 5d states split by the crystal field [18]. Under the excitation of 350 nm, the PL spectrum exhibits a broad nonsymmetrical band in the wavelength ranged at 350–600 nm with a peak centered at about 430 nm, which is attributed to the transition from the 5d level to the ground state of Ce^{3+}. As discussed above, Ce^{3+} ions are expected to occupy the sites of Na^+ ions forming two kinds of luminescent centers. It is known that Ce^{3+} usually shows two emission bands in one specific lattice, which is due to the transitions from the lowest 5d excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ spin orbit 4f ground states [19]. Therefore, there should be four emission bands when Ce^{3+} ions enter into the two different lattice sites. The dotted lines in Fig. 2a shows four bands peaking at 4 0 4 (peak A), 4 3 8 (peak B), 4 7 0 (peak C) and 519 nm (peak D), which are derived from Gaussian decomposition. The energy difference of the splitting between $^2F_{7/2}$ and $^2F_{5/2}$ of Ce^{3+} is about 2000 cm^{-1}. The energy gap between the peaks of A and B, and the peaks of C and D, are 1921 and 2009 cm^{-1}, respectively, which is in good agreement with the theoretical value. Therefore, peaks A and B could be ascribed to the emission of Ce^{3+} located at one specific site of Ce^{3+} (I) and peaks C and D are assigned to Ce^{3+} at another site as Ce^{3+} (II).
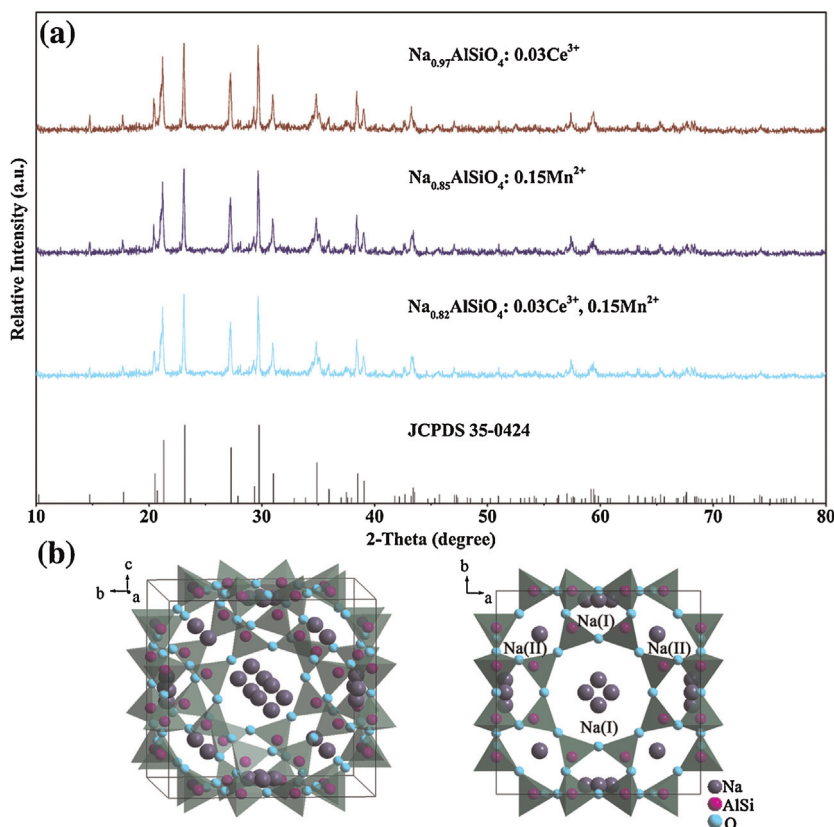

Fig. 1. (a) XRD patterns of $Na_{0.97}AlSiO_4$: $0.03Ce^{3+}$, $Na_{0.85}AlSiO_4$: $0.15Mn^{2+}$, $Na_{0.82}AlSiO_4$: $0.03Ce^{3+}$, $0.15Mn^{2+}$ and the standard pattern (JCPDS 35-0424) of $NaAlSiO_4$. (b) Crystal structures of $NaAlSiO_4$.