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Preparation and spectroscopic investigation of novel $NaAlP_2O_7:Eu^{2+}$ phosphors for white LEDs

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$NaAlP_2O_7:Eu^{2+}$ phosphors were prepared by a solid state reaction. The structure, Fourier transform infrared spectra, photoluminescence spectra and fluorescence decay curves of $NaAlP_2O_7:Eu^{2+}$ were investigated. These phosphors can be excited over a broad range and generate a greenish-blue emission band peaking at 459 nm. The critical quenching concentration of Eu^{2+} in $NaAlP_2O_7:Eu^{2+}$ phosphors is about 3 mol% and the corresponding concentration quenching mechanism is demonstrated to be dipole-dipole interactions. Meanwhile the critical distance for concentration quenching is determined to be 19.7 Å. As the temperature increases from 25 to 150 °C, the emission intensity of $NaAlP_2O_7:0.03Eu^{2+}$ still possesses 86.7% of its initial PL intensity, indicating its high thermal stability. All the results suggest that the $NaAlP_2O_7:Eu^{2+}$ phosphors are promising greenish-blue-emitting phosphors for application in white light emitting diodes.

1. Introduction

It is well-known that phosphors have attracted considerable attention because of their potential applications in white light emitting diodes (WLEDs) [1], organic light emitting diodes (OLEDs) [2], field emission displays (FEDs) [3], plasma display panels (PDPs) [4], and cathode ray tubes (CRTs) [5], etc. Among these applications, WLEDs are considered as the next generation of solid-state light source due to their high efficiency, little volume, tunable color, longer lifetime and energy conservation [6,7]. Nowadays, there are mainly two types of white light emitting diodes based on phosphor-conversion. One is blue chip and yellow-emitting phosphors (representation: $Y_3Al_5O_{12}:Ce^{3+}$), with a poor color-rendering index ($Ra < 80$) and higher correlated color temperature ($CCT > 4500$ K) which largely restrains their application. Recently, a transparent $Y_3Al_5O_{12}:Ce^{3+}$ ceramic with high quantum yield and improved thermal-quenching feature was successfully synthesized by a low temperature co-sintering technique. The phosphor is preferred to replace the conventional phosphor/organic-resin color converter [8–11]. The other one type of WLEDs contains a near-ultraviolet (NUV) LED chip and a mixture of blue-, red-, and green-emitting phosphors, resulting in better color stability and higher CRI values due to the invisibility of NUV light to the naked eye and the smoother spectral distribution of the visible range from blue to red. Therefore, it is highly desirable to find new phosphors which can be excited by the NUV LEDs.

Research and development on phosphors with phosphate groups as host lattices have been of great interest since the last few years due to their environmental friendliness, thermal and chemical stability, and easy synthesis. Hence, lots of studies with phosphates as hosts have been reported [12–15]. Recently, diphosphate compounds with the general formula as ABP_2O_7 (A = alkaline metals, B = polyvalent metals), where A and B are cations in different symmetry sites, have been extensively reported as a kind of suitable phosphor hosts in which the Stokes shift of rare earth ions can easily take place. The stokes shift is the indicator of the stiffness of host lattice [16]. It is also believed that different kinds of A or B elements may induce different crystal field environment or form different crystal structures. That is, this kind of diphosphate salts may provide lots of appropriate hosts for activator ions to regulate characteristic properties. Yuan et al. reported the spectroscopic properties of Ce^{3+} and Pr^{3+}-doped $AREP_2O_7$ phosphates (A = Na, K, Rb, Cs; RE = Y, Lu) in 2007 [17]. The lower Stokes shift of Ce^{3+} in $NaLuP_2O_7$ indicated the stiffness nature of the cage in $NaLuP_2O_7$. Yuan et al. reported the photon cascade emission of Gd^{3+}

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in the host of $RbGdP_2O_7$ and $CsGdP_2O_7$ and their VUV-UV excitation and emission spectra in 2008 [18]. Hizhnyi et al. firstly reported the electronic structure and luminescent properties of Ti-doped $NaAlP_2O_7$ phosphate, which exhibited blue-green emission in 100–150 nm (8–12 eV) involving transitions from the oxygen states (top of the VB) to titanium impurity states [19]. However, to the best of our knowledge, no investigation on rare earth doped $NaAlP_2O_7$ is reported. In this work, a series of novel blue-emitting Eu ions doped $NaAlP_2O_7$ phosphors ($NaAlP_2O_7:Eu^{2+}$) were obtained via the traditional solid-state method. Their phase formations, structures and photoluminescence properties were investigated in detail. The results indicated that $NaAlP_2O_7:Eu^{2+}$ showed bright greenish-blue emission centered at 459 nm under the excitation of 345 nm radiation, which matched well with the emission of NUV LED chips. The synthesized phosphors have significant potential for near UV LEDs.

2. Experimental section

All the Eu^{2+} doped $NaAlP_2O_7$ samples were prepared using a conventional high-temperature solid-state reaction. The raw materials were Al_2O_3 (A.R.), Na_2CO_3 (A.R.), $NH_4H_2PO_4$ (A.R.), and Eu_2O_3 (99.99%). They were mixed stoichiometrically and thoroughly in an agate mortar. According to the designed formulas, the content of Eu in the final $NaAlP_2O_7:Eu^{2+}$ samples is 0.01, 0.03, 0.05, 0.08, 0.10 and 0.15, respectively. Then, the mixtures were sintered at 850 °C for 5 h in CO reducing atmosphere. After cooling to room temperature, the samples were ground again to give the final phosphors.

The phase structures of the samples were characterized using powder X-ray diffraction (XRD) with Cu Kα radiation at 40 kV and 40 mA. The Fourier transform infrared (FT-IR) measurements were performed on a Spectrum One Paragon 1000 PC spectrometer over the 1600–400 cm^{-1} region using KBr pellet as the background.

Photoluminescence emission (PL) and photoluminescence excitation (PLE) spectra were characterized by a Hitachi F-4600 spectrometer with the photomultiplier tube operating at 600 V and a 150 W Xe lamp used as the excitation source. The temperature-dependent luminescence properties were performed by the same spectrophotometer, which was equipped with a self-made heating apparatus and a computer controlled electric furnace. The luminescence decay curves were obtained from a spectrofluorometer (HORIBA, JOBIN YVON FL3-21) with a 370 nm pulse laser radiation (nano-LED) as the excitation source, and the pulse width of the laser was 12 ns.

3. Results and discussions

The XRD patterns of the title compounds with the nominal composition of $NaAlP_2O_7:xEu^{2+}$($x = 0.01, 0.03, 0.05, 0.08, 0.10, 0.15$) are presented in Fig. 1. It is obvious that all the diffraction peaks are basically in agreement with the JCPDS card #84-2483 of $NaAlP_2O_7$ [20] except several small impurity peaks which can be matched with Al_2O_3 phase (JCPDS card 89-3072). So samples mainly composing of doped $NaAlP_2O_7$ can be received by the solid-state method. The dopant Eu^{2+} are effectively incorporated into the host as no other peaks are observed. As the radii of Eu^{2+} ($rEu^{2+}{}_{CN=6} = 1.17$ Å, $rEu^{2+}{}_{CN=7} = 1.2$ Å) is close to that of sodium ($rNa^{+}{}_{CN=7} = 1.12$ Å) compared to aluminum ($rAl^{3+}{}_{CN=6} = 0.535$ Å). Also if this kind of replacement takes place, only one sodium should be removed to compensate the produced +1 electric charge, which can be easily realised. So it is assumed the Eu^{2+} ions replace some sodium positions.

Fig. 2 shows the crystal structure of $NaAlP_2O_7$ which has a monoclinic phase with space group $P\ 2_{1/c}$. Every asymmetric unit contains 11 atomic positions including one for the Na atom, one for the Al atom, two for the P atom and seven for the O atoms. The atomic arrangement of this structure is characterized by a three dimensional framework of PO_4 tetrahedra and AlO_6 octahedra leading to narrow tunnels parallel to [010] which are occupied by Na atoms. This framework is composed by NaO_7 polyhedra, AlO_6 octahedra, and P_2O_7 diphosphate which are linked by bridges of Al–O–P and Na–O–P. Each AlO_6 octahedra is surrounded by six PO_4 tetrahedra belonging to five different P_2O_7 groups, and each of these groups shares six corners with five different AlO_6 octahedra and is bonded to one of them through bidentate bonding.

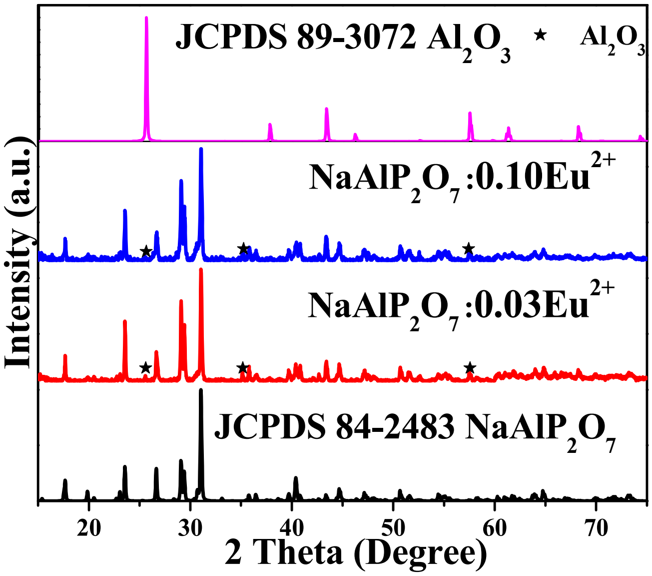

Fig. 1. XRD patterns of Eu^{2+} doped $NaAlP_2O_7$ samples.

The vibrational peaks of $NaAlP_2O_7$:0.03Eu shown in Fig. 3 were obtained from infrared spectrum measurements, which is very similar to that from other reported diphosphate compounds [21–23] and. The vibration models and assignments of FT-IR bands are summarized in Table 1. Two bands centered at 647 and 759 cm^{-1} are attributed to symmetric (ν_s) P–O–P vibrational modes, and a singlet band centered at 952 cm^{-1} is due to the asymmetric (ν_{as}) P–O–P vibrations. The wide multiple peaks in the range of 1045–1290 cm^{-1} correspond to the symmetric and antisymmetric stretching vibrations of PO_3.

Fig. 4 displays the excitation and emission spectra of the $NaAlP_2O_7$:0.03Eu^{2+} phosphors. Excited by 345 nm irradiation, the PL spectrum of $NaAlP_2O_7$:0.03Eu^{2+} shows a broad asymmetrical greenish-blue emission band peaked at 459 nm corresponding to the electric dipole allowed transition from the 5d excited state to 4f ground state of a Eu^{2+} ion. The PLE spectrum monitored at 459 nm exhibits a broad band from 200 to 400 nm originating from the electron transition from the ground state of $4f^7$ to the crystal-field split $4f^65d$ level of Eu^{2+} in the host lattice, which is essential for the excitation absorption of the n-UV LED chip.

Fig. 5 presents the emission spectra of $NaAlP_2O_7:xEu^{2+}$ phosphors with doped Eu^{2+} ($x = 0.01, 0.03, 0.05, 0.08, 0.10$ and 0.15). Upon the excitation of 345 nm, the PL spectra have similar profiles due to the 4f–5d transition of Eu^{2+}, except for the emission intensity and the peak position. It also can be seen that the PL peaks are gradually blue-shift as the concentration of Eu^{2+} increases. The dependence of the emission intensity on the concentration of Eu^{2+} is shown in the inset of Fig. 5. As the concentration of Eu^{2+} increases, the emission intensity of Eu^{2+} firstly increases and reaches the maximum when the concentration of Eu^{2+} is 0.03, and then