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The effect of electron cloud expansion on the red luminescence of $Sr_4Al_{14}O_{25}:Mn^{4+}$ revealed by calculation of the Racah parameters

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ABSTRACT

In this work, the crystal field stabilization energy (D_q) and the Racah B and C parameters were calculated quantitatively to evaluate the nephelauxetic effect of Mn^{4+} suffering from the $Sr_4Al_{14}O_{25}$ host, aiming for developing novel highly efficient red phosphor for white light-emitting diodes. The phosphor of Mn^{4+} activated $Sr_4Al_{14}O_{25}$ was synthesized via a high temperature solid reaction in air ambient. The crystallinity was investigated using the X-ray diffraction; and the photoluminescence properties were characterized with the spectrometer. The red emission was attributed to the Mn^{4+} which occupies the center of AlO_6 octahedron. Meanwhile, the Mn^{2+} and Mn^{3+} were detected by using the X-ray absorption near-edge structure spectroscopy (XANES) assisted with Electron Paramagnetic Resonance (EPR) techniques. The energy levels of $^4A_2$, $^4T_{2g}$ and $^4T_{1g}$ were determined according to excitation spectra, corresponding to the $^4A_2\,(t_2^3) \rightarrow {}^4T_1\,(^4F)$ and the $^4A_2\,(t_2^3) \rightarrow {}^4T_{2g}\,(t_2^2e)$ transitions at 330 and 450 nm respectively, whereby the calculation was carried out according to the Tanabe–Sugano diagram for octahedral complex with the d^3 electron configuration. The nephelauxetic ratio β about 0.32 suggests a strong cloud expansion of Mn^{4+} in the $Sr_4Al_{14}O_{25}$ crystal lattice with $D_q \sim 2222\ cm^{-1}$, $B \sim 794\ cm^{-1}$, $C \sim 3232\ cm^{-1}$ and $C/B \sim 4.07$. In the perspective of physics, these parameters are helpful to perceive the inter-repulsion of the outer electrons in 3d orbit of Mn^{4+} and the effect of local circumstance, in essential to understand the variant spectral configurations of Mn^{4+} luminescence observed in different hosts.

1. Introduction

The white light-emitting diodes (WLEDs) show superiorities in terms of low energy consumption, high luminescence efficiency, eco-friendship without mercury pollution, long duration, unbreakable (in contrast to glass bulbs and tubes) with solid-state encapsulation, and easy transportation and installation over than traditional incandescent and fluorescent lamps, while the red phosphor is essential to obtain warm white light with high color rendering index (CRI) and low color temperature for home lighting [1–6]. The phosphor activated by Mn^{4+} is a promising candidate for WLEDs application, because the narrow lines of Mn^{4+} emission could enhance the luminous efficacy of radiation (LER) and the CRI given in units of lumens per watt of radiometric power (lm/Wrad) [7].

Recently, several researchers have focused on the development of new phosphors activated by Mn^{4+}, such as the fluorides of $K_2TiF_6:Mn^{4+}$ [7], $K_2SiF_6:Mn^{4+}$ [7], $Na_2SnF_6:Mn^{4+}$ [8], $Cs_2SnF_6:Mn^{4+}$ [8], $Na_2SiF_6:Mn^{4+}$ [9], and $Na_2GeF_6:Mn^{4+}$ [9] as well as the aluminates of $Sr_4Al_{14}O_{25}:Mn^{4+}$ [10], $CaAl_{12}O_{19}:Mn^{4+}$ [11], and the Mn^{4+} activated non-stoichiometric $3SrO{\cdot}5AL_2O_3$ [12]. A WLED device with high CRI (Ra 90), warm-white color temperature (3088 K), and an efficiency approximate 82 lm/W has been fabricated by the scientists in the GE Global Research Centre in New York, using the Mn^{4+} activated red phosphor of $K_2TiF_6:Mn^{4+}$ [7]. Chen et al. demonstrated a white LED device prototype with chromaticity CIE (0.3291,0.3571), correlated color temperature 5639 K, CRI Ra 92.6, and an efficiency 63 lm/W using the Mn^{4+} activated non-stoichiometric $3SrO{\cdot}5AL_2O_3$ and also proposed that such kind of red phosphor is suitable to package low-power WLEDs for application

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in special circumstances with critical requirement on color rendering, such as jewelry and cosmetic sales, due to its 1 A grade (Ra 90–100) of color rendering ability [13].

Compared with the ionic nature of Metal-Fluoride (M-F) bonds, the aluminate host with strong covalence and weak polarizability are favorable to obtain red luminescence due to its strong nephelauxetic effect in decreasing the centroid of excited states, which will be helpful to obtain red luminescence. In addition, the oxide host of aluminates is very inexpensive. It will helpfully contribute to the popularization of WLEDs. However, the luminescence efficiency of the Mn^{4+} activated aluminates, such as $Sr_4Al_{14}O_{25}:Mn^{4+}$ and $CaAl_{12}O_{19}:Mn^{4+}$, still needs to be enhanced [10–14]. The relative luminescence intensity of $CaAl_{12}O_{19}:Mn^{4+}$ was enhanced about two times by doping 0.67 mol% CaF_2 and 0.7 mol% MgF_2, and the enhancement was attributed to the synergetic effect of flux and charge compensation by CaF_2 and MgF_2, respectively: CaF_2 would accelerate the crystal growth of $CaAl_{12}O_{19}:Mn^{4+}$ and Mg^{2+} ions would compensate the local charge balance surrounding Mn^{4+} ions instead of Mn^{2+} [11]. Nevertheless, both Mg^{2+} and Mn^{2+} have the +2 valence. The reason why does the replacement of the Mn^{2+} by Mg^{2+} could improve the luminescence was not elucidated. The mechanism of the enhanced luminescence of $Sr_4Al_{14}O_{25}:Mn^{4+}$ by coupling with a certain amount of $SrAl_2O_4$ phase in the non-stoichiometric $3SrO{\cdot}5AL_2O_3$ still was not clear [14].

Moreover, the spectral configuration of Mn^{4+} in the host of $Sr_4Al_{14}O_{25}$ significantly distinguishes from those reported in the K_2TiF_6 [7], K_2SiF_6 [7], Na_2SnF_6 [8], Cs_2SnF_6 [8], Na_2SiF_6 [9], Na_2GeF_6 [9], $CaAl_{12}O_{19}$ [11], and $YAlO_3$ [15]. A broad band with doublet peaks are observed in the emission spectrum of $Sr_4Al_{14}O_{25}:Mn^{4+}$ at room temperature, but several satellite peaks are observed in the others [7–15]. Besides the thermal vibration caused by the temperature, the spectral configuration is finally determined by the electronic effect and electro-magnetic interaction of the activator suffering from a certain crystal circumstance, depending on the symmetry of crystal site. When an atom has more than one electron there will be certain electrostatic repulsion between those electrons, and the amount of repulsion depends on the number and the spin of electrons and the orbitals they occupy [16–19]. The total repulsion is expressed in terms of three parameters *A*, *B* and *C*, known as the Racah parameters after Giulio Racah, who first described them [16–19]. The nephelauxetic effect, originating from the Greek known for cloud-expanding, refers to a decrease in the Racah interelectronic repulsion parameter, given the symbol *B* and *C*, which occurs when a transition metal free ion forms a complex with ligands [16–19]. The decrease in *B* indicates that in a complex there is less repulsion between the two electrons in a given doubly occupied metal *d*-orbital than there is in the respective M^{n+} gaseous metal ion, in turn implying that the size of the orbital is larger in the complex [16–19]. In order to understand the abovementioned phenomena, in this work we make an effort to evaluate the nephelauxetic effect on the spectral configuration of $Sr_4Al_{14}O_{25}:Mn^{4+}$. The Racah *B* and *C* parameters and the crystal-field parameter Δ, which equates about $10D_q$, are calculated quantitatively according to the Tanabe–Sugano diagram for octahedral complex with the d^3 electron configuration. The different valences of Mn ions existed in the $Sr_4Al_{14}O_{25}$ host are discerned out by using the Electron Paramagnetic Resonance (EPR) and the X-ray absorption near-edge structure (XANES) spectroscopy techniques.

2. Experimental

The phosphor of $Sr_4(Al_{0.999}Mn_{0.001})_{14}O_{25}$ (abbreviated as $Sr_4Al_{14}O_{25}:Mn$) was synthesized via a solid-state reaction at 1300 °C for 16 h in the air ambient from the sources of $SrCO_3$ (99.9%), $MnCO_3$ (99.9%), Al_2O_3 (99.9%), and AlF_3, where the AlF_3 was adopted as a flux. The concentration of Mn was kept at 0.001 M with respect to Al. The amount of AlF_3 was about 2.5% of total weight. The crystallinity of phosphors was examined with X-ray diffraction (XRD) analysis by using the Rigaku D/max-IIIA diffractometer with Cu Ka radiation, operated at 45 kV and 40 mA. Emission and excitation spectra were collected by using a Hitachi F-4600 spectrometer. The Mn K-edge (XANES) spectroscopies were recorded at National Synchrotron Radiation Research Center (NSRRC) in Taiwan and National Synchrotron Radiation Laboratory (NSRL) of China successively. All spectra of XANES were normalized and the standard Mn metal foils and oxide powders, MnO, Mn_2O_3 and MnO_2 were used for energy calibration and also for comparing different electronic valence states. The EPR spectra were measured by using the JES-FA200 spectrometer (JEOL).

3. Results and discussion

The dominant X-ray diffraction peaks of the crystal $Sr_4Al_{14}O_{25}$ can be identified clearly from the XRD patterns of $Sr_4Al_{14}O_{25}:Mn$, as displayed in Fig. 1, by comparing with the standard JCPDS 52-1876 [20]. The emission spectrum of the phosphor excited with 450 nm at room temperature is presented in Fig. 2, in which a broad band with doublet peaks at 652 and 665 nm are observed. The inserted picture in Fig. 2 shows the red luminescence of the $Sr_4Al_{14}O_{25}:Mn$ under the excitation of 365 nm. By monitoring the emission peaks at 652 and 665 nm, the excitation spectra of the $Sr_4Al_{14}O_{25}:Mn$ are presented in Fig. 3(a) and (b), respectively, in which a main band peaked at 330 nm and a minor one peaked 450 nm are observed. The satellite lines of Mn^{4+} emission that are clearly observed in the fluorides of Na_2SiF_6 [9] and Na_2GeF_6 [9] but are not observed here.

During high-temperature sintering process in air, the raw material of $MnCO_3$ will decompose into MnO_2 or other oxides. However, the previous research demonstrated that the Mn^{2+} existed in $CaAl_{12}O_{19}$ [11]. So, the multiple valences of Mn ions may also exist in $Sr_4Al_{14}O_{25}$. Before assigning the excitation and emission spectra in Figs. 2 and 3, the valence of Mn should be determined. The chemical shift of the main absorption edge to lower energies with a decreasing valence of transition metals is a powerful tool for probing the unknown valence of a transition metal [21]. As for Mn ions, the main absorption of X-ray is the K-edge. Herewith, we investigate the valences of Mn ions by using the XANES technique firstly. Fig. 4 displays the normalized Mn K-edge XANES spectra of the $Sr_4Al_{14}O_{25}:Mn$ phosphor and reference samples, MnO, Mn_2O_3 and MnO_2, in which a dashed line at the half absorption value has been included to elucidate the chemical shift [21]. The comparison of the K-edge XANES of the $Sr_4Al_{14}O_{25}:Mn$ phosphor with the MnO_2, Mn_2O_3 and MnO reference samples shows that the valence of Mn ions in phosphor mainly is the +4. However, the minor difference in absorption edge and the significant difference in absorption intensity suggest that a tiny of Mn^{2+} or Mn^{3+} should exist. To clarify this point, the sample is further studied by using the EPR technique. Fig. 5 presents the EPR spectra of the

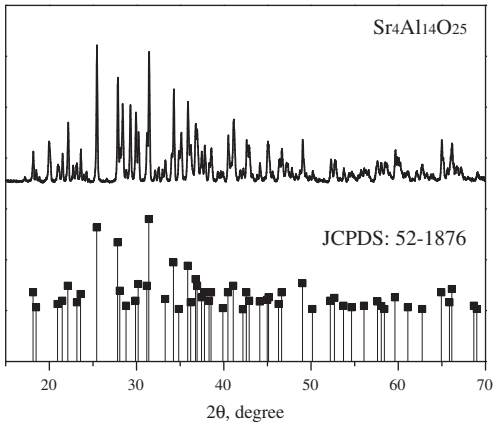

Fig. 1. The XRD patterns of the $Sr_4Al_{14}O_{25}:Mn$ phosphor compared with the standard JCPDS 52-1876.