



Letter

Preparation and luminescent properties of a new red phosphor (Sr₄Al₁₄O₂₅:Mn⁴⁺) for white LEDsY.D. Xu^{a,*}, D. Wang^a, L. Wang^{a,*}, N. Ding^b, M. Shi^a, J.G. Zhong^a, S. Qi^a^a School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China^b Bengbu Yucheng New Materials Science & Technology Ltd. Co, Bengbu 233000, China

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ABSTRACT

A new Mn⁴⁺ activated (non-RE activated) aluminate based Sr₄Al₁₄O₂₅ phosphor was prepared by a solid-state reaction. The crystal structure of Sr₄Al₁₄O₂₅:Mn⁴⁺ phosphor was characterized by XRD and emission spectrum as well as excitation spectrum of the prepared phosphor was measured. Emission spectrum shows that phosphor can be effectively excited by NUV light source. Simultaneously, emission spectrum measurement shows that the sharp emission peak at 651 nm is ascribed to the ²E → ⁴A₂ transition of Mn⁴⁺ ion and a broad band at 662 nm is attributed to the phonon sideband transition. It is found that the quenching concentration of Mn⁴⁺ in phosphor is 0.7 mol%. In the end, the emission spectra of Sr₄Al₁₄O₂₅:Mn⁴⁺, Cl⁻/Pb²⁺ were investigated. Sr₄Al₁₄O₂₅:Mn⁴⁺ phosphor is expected to be used as a red phosphor in white LEDs because phosphor can be excited by NUV chip.

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1. Introduction

White light-emitting diodes (W-LEDs) are considered to be the next generation solid-state lighting because they have many advantages over conventional lighting devices, such as high brightness, high power efficiency, low applied voltage, and long lasting life [1,2]. In 1996, Nakamura and Fasol in Nichia Company combined a blue LED chip with a yellowish phosphor of YAG:Ce to produce white light. However, the color rendering index of YAG:Ce phosphor used for W-LEDs is too low to be used in warm white LED application because of lacking a red component (color rendering index ≤85) [3,4].

Most phosphors are composed of a transparent microcrystalline host (or a matrix) and an activator, i.e., a small amount of intentionally added impurity atoms distributed in the host crystal. Among the red emitting phosphors, the most used activators are Eu²⁺ and Eu³⁺, followed by Ce³⁺ and Sm³⁺ et al. Noticeably, most of these rare earth ions are very expensive and some chlorides, citrates, and oxides of the rare earth ions are toxic and harmful, which substantially limits their wide applications in W-LEDs. On the other hand, phosphors such as 6MgO·As₂O₅:Mn⁴⁺ [5] and ZnS:Mn [6] do not include rare earth ions, however, the toxic and harmful elements such as arsenic (As) and sulfur (S) in phosphors have a long-term adverse effect on the environment. Consequently, engineers and researchers have been searching for environment

friendly and less expensive phosphors which do not contain rare earth ions.

As a transition metal ion, Mn⁴⁺ is a suitable activator for red phosphors. As far as the Mn⁴⁺-doped phosphors are concerned, the transition of Mn⁴⁺ is always ²E → ⁴A₂ [7] and the emitting of Mn⁴⁺ is always located in a red region [8]. In recent years, the luminescence of Mn⁴⁺ ions in hosts such as aluminates, silico aluminates and hexafluorostannate etc., has been reported [9–14]. Luminescence investigations of Mn⁴⁺-activated ZnAl₂O₄ phosphors suggest that the red emission results from the d–d transitions of Mn⁴⁺ ion within its 3d³ electron configuration [14]. Brik [12] and Shu [13] reported that Mn⁴⁺ doped CaAl₁₂O₁₉ is an excellent red phosphor with a broad absorption band in visible region and superior chromaticity in the deep red region, whose efficiency or intensity could be enhanced by mixing MgO and/or GeO₂, respectively. On the other hand, there are many other red emitting phosphors excited by Eu³⁺, Sm²⁺ or Ce²⁺ which have been reported in recent years [15–18].

It is reported [19,20] that the structure of orthorhombic Sr₄Al₁₄O₂₅ consists of layers made up of [AlO₆] octahedra chains interconnected by a double layer of [AlO₄] tetrahedra chains. The octahedra are connected together by sharing one edge, whereas the tetrahedra are connected by corner sharing, resulting in the presence of tricoordinated oxygen atoms and tetrahedra triclusters such as in CaAl₄O₇, SrAl₄O₇, and mullite [8]. There are six different crystallographic sites for the aluminum atoms in the Sr₄Al₁₄O₂₅ structure: three [AlO₆] octahedral sites and three [AlO₄] tetrahedral sites. Al³⁺ and Mn⁴⁺ ions have similar ion radii [21,22] and

* Corresponding author. Tel./fax: +86 0551 2901362.

E-mail addresses: drxuyudong@126.com, leiw03@126.com (Y.D. Xu).

the electron configuration of Mn^{4+} is also suitable for $[AlO_6]$ octahedral site [7,8]. Consequently, the Al^{3+} ions in the $[AlO_6]$ octahedral sites of $Sr_4Al_{14}O_{25}$ may be substituted by Mn^{4+} ions in the crystal lattice theoretically. It is also reported that Pb^{2+} or Cl^- ions can be used as an effective co-activator in the Mn-doped phosphors [23–25]. However, up to now there is no report on the existence and the luminescence properties of $Sr_4Al_{14}O_{25}:Mn^{4+}$, Pb^{2+}/Cl^- red phosphors. Based on the above studies, the authors believe that Mn^{4+} doped strontium aluminate is a very promising phosphor which can be widely used in W-LEDs owing to the low price of manganese raw materials and strontium aluminate raw materials and excellent luminescence of the phosphor.

In the present work, a series of novel luminescent materials $Sr_4Al_{14}O_{25}:Mn^{4+}$, $M(M = Pb^{2+}, Cl^-)$ red phosphors were synthesized by a solid state reaction method at high temperatures and the influences of Mn^{4+} , Pb^{2+} and Cl^- ions on the luminescent properties were studied in detail.

2. Experimental procedures

2.1. Sample preparations

The starting materials such as $SrCO_3$ (99%), Al_2O_3 (99.99%) and H_3BO_3 (99%) with molar ratio of 4:7:0.54 were ground in an agate mortar and the H_3BO_3 was added as a flux. After fully grinding the samples were put into corundum crucibles and then burned in an electric furnace for crystallization at 1300 °C for 3–7 h in the air. Similarly, the strontium aluminates with compositions of $Sr_4Al_{14-x}O_{25}:Mn_x^{4+}$ ($x = 0.0014, 0.003, 0.007, 0.014, 0.028, 0.042, 0.056$), $Sr_4Al_{14-x}O_{25}:Mn_{0.007}^{4+}Cl_y^-$ ($y = 0.044, 0.087, 0.131, 0.175$) and $Sr_4Al_{14-x}O_{25}:Mn_{0.007}^{4+}Pb_z^{2+}$ ($z = 0.0033, 0.0066, 0.01, 0.0131$) were prepared by the above method.

2.2. Sample characterization

XRD characterization was carried out on an X-ray diffractometer (D/MAX2500 V diffractometer, RIGAKU Corporation of Japan; 40 kV and 100 mA, $Cu K\alpha = 1.54056 \text{ \AA}$). Excitation and emission spectra of the powdered phosphors were measured on a HITACHI F-4500 fluorescence photometer equipped with a 150 W Xe lamp. All measurements were performed at room temperature.

3. Results and discussion

3.1. XRD characterization of the prepared phosphors

The XRD patterns of the prepared $Sr_4Al_{14}O_{25}:Mn_x^{4+}$ powders are shown in Fig. 1, which indicate that all phosphors prepared in this work are of $Sr_4Al_{14}O_{25}$ (PDF 52-1876) structure and the doped Mn^{4+} ions have little influences on the structures of the luminescence materials. The crystal structure of $Sr_4Al_{14}O_{25}$ is orthorhombic ($a = 24.791 \text{ \AA}$, $b = 8.486 \text{ \AA}$ and $c = 4.866 \text{ \AA}$) and the space group is Pmma.

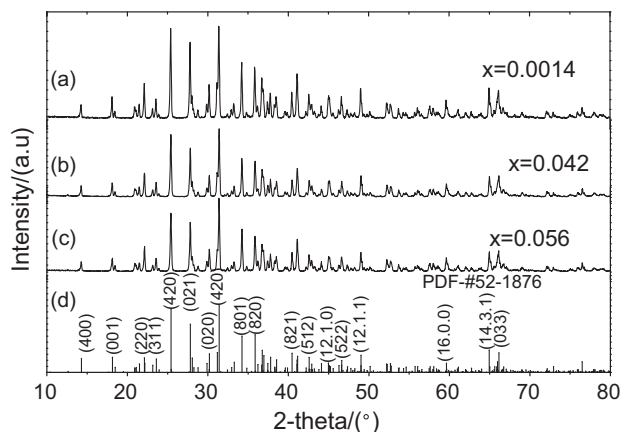


Fig. 1. XRD patterns of $Sr_4Al_{14}O_{25}:Mn_x^{4+}$ phosphors with different Mn^{4+} contents (a: $x = 0.0014$ mol.%, b: $x = 0.042$ mol.%, c: $x = 0.056$ mol.%, d: PDF #52–1876).

3.2. The excitation and emission spectra of $Sr_4Al_{14}O_{25}:Mn^{4+}$ phosphor

Fig. 2 shows the excitation and emission spectra of $Sr_4Al_{14}O_{25}:Mn^{4+}$ phosphors at room temperature. Monitored at 651 nm, two broad excitation bands ranging from 300 to 450 nm appear and the intensity at about 340 nm is the strongest, which implies that this phosphor is suitable to be excited by a NUV chip. The excitation spectra of $Sr_4Al_{14}O_{25}:Mn^{4+}$ can be tentatively divided into two parts: one is in the region of 400–450 nm, which is attributed to the transition ${}^4A_2 \rightarrow {}^4T_2$ of Mn^{4+} , as shown in the inset of Fig. 2. The other is between 300 and 400 nm, which is due to the existence of a charge transfer band (CTB) of $Mn^{4+} \rightarrow O^{2-}$. Noticeably, the excitation bands resulting from the transition ${}^4A_2 \rightarrow {}^4T_1$ of Mn^{4+} and the charge transfer bands (CTB) are normally overlapping [22]. If the $Sr_4Al_{14}O_{25}:Mn^{4+}$ phosphor is excited by a 365 nm NUV-light, the emission spectrum of the phosphor consists of a strong and broad red emission peak between 600 and 700 nm with a sharp peak at about 651 nm and a broad band at about 662 nm, which is attributed to the typical emission of Mn^{4+} [26]. Obviously, there are no emission peaks of Mn^{2+} in the spectra, indicating that the Mn^{2+} ions doped into the matrix have been completely oxidized to Mn^{4+} . As a matter of fact, the doped Mn^{2+} ions into the $Sr_4Al_{14}O_{25}$ structure are not existent as luminescence centers. Consequently, the authors believe that the sharp peak occurring at about 651 nm is ascribed to the ${}^2E \rightarrow {}^4A_2$ transition of Mn^{4+} ion (see the inset of Fig. 2). It can also be found from the emission spectra that there is only one sharp peak, indicating that the distortions of Mn^{4+} in the three different $[AlO_6]$ octahedral sites of $Sr_4Al_{14}O_{25}$ are equivalent. On the other hand, the broad band at 662 nm is attributed to a phonon sideband transition, which has been confirmed by the literature [22,26,27].

The calculative color coordinate of $Sr_4Al_{14}O_{25}:Mn^{4+}$ phosphor and the color coordinates [26] of $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2:Mn^{4+}$ phosphor and $La_2O_2S:Eu^{3+}$ phosphor are given in Table 1 and Fig. 3. Among the Mn^{4+} doped phosphors, $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2:Mn^{4+}$ phosphor is the only one currently used in practice [28], $La_2O_2S:Eu^{3+}$ phosphor has been used as a commercial red phosphor in W-LEDs [26,29]. From Table 1 and Fig. 3 it can be seen that the chromaticity (x,y) of the prepared red phosphor ($Sr_4Al_{14}O_{25}:Mn^{4+}$) is 0.72 and 0.28, respectively, which is close to that of $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2:Mn^{4+}$ phosphor. Noticeably, as far as the red fluorescence is concerned, the chromaticity of $La_2O_2S:Eu^{3+}$ phosphor is not superior to that of $Sr_4Al_{14}O_{25}:Mn^{4+}$ phosphor. Apparently, the prepared $Sr_4Al_{14}O_{25}:Mn^{4+}$ phosphor enlarges the spectral region in W-LEDs (see Table 1). Consequently, it can be said that $Sr_4Al_{14}O_{25}:Mn^{4+}$ is a suitable red phosphor used in W-LEDs.

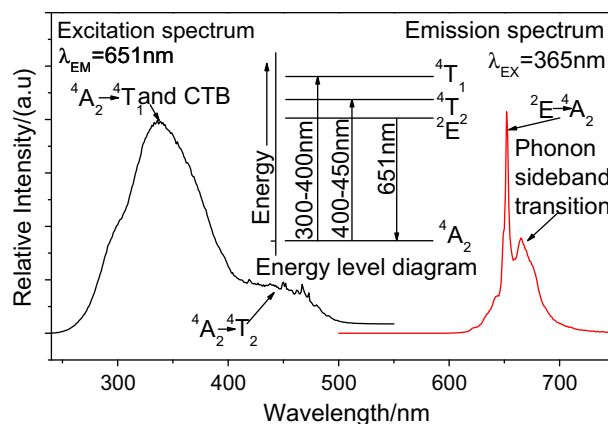


Fig. 2. Excitation spectrum and emission spectrum of $Sr_4Al_{14}O_{25}:Mn_{0.007}^{4+}$ at room temperature and energy level diagram of Mn^{4+} .

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