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# Thermally stable double perovskite $CaLaMgSbO_6:Eu^{3+}$ phosphors as a tunable LED-phosphor material

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#### ABSTRACT

A series of  $Eu^{3+}$  ions activated double perovskite CaLaMgSbO<sub>6</sub> phosphors were successfully synthesized. Crystal structure was investigated by XRD and the results showed that this double perovskite exhibited rock-salt ordering of B-site ions. High-resolution transmission electron microscopy was used to prove the existence of B-site ordering. Thereafter, luminescence properties of the as-prepared powders were discussed in detail. The phosphors could be well excited by ultraviolet, near ultraviolet, and blue light. The quenching concentration for the transition of  ${}^{5}D_{0}{}^{-7}F_{2}$  reached up to 50.0 mol%. The theoretical quenching concentration and quenching mechanism were discussed in detail. Excellent thermal stability of this double perovskite phosphor was obtained and the quenching mechanism was investigated based on the configurational coordinate diagram. The CIE coordinates showed that this double perovskite phosphor had great potential in solid state lighting.

#### 1. Introduction

White light emitting diodes (w-LEDs) have boomed in recent years due to their advantages, such as the high efficiency and positive environmental benefits in a large number of applications [1–4]. Furthermore, LED chips offer possibility to control luminescence properties and opportunity to achieve to specific requirements. Present commercial way to obtain white light is phosphor conversion method [5,6]. However, combining blue LED chip with YAG:Ce<sup>3+</sup> yellow phosphors lacks of red component and shows low color rendering index [7–9]. Therefore, red phosphors for near ultraviolet (UV) and blue chips attracted researchers' attention, such as tungstate [10,11] /molybdate [12], titanate [13,14], phosphate [15,16], and antimonate [17–19] /niobate [20] /tantalate [21].

Perovskite and perovskite-like type compounds attracted researchers' attention in many areas during the past decades [22]. Typically, double perovskites with the formula  $A_2BB'O_6$  or AA'BB'O<sub>6</sub> have been widely in mainly areas in recent years. The phosphors with the formula  $A_2BB'O_6$  show low quenching concentration. The Sr<sub>2</sub>CaMoO<sub>6</sub>:Eu<sup>3+</sup> phosphors show orange-red emission and the quenching concentration is 5.0 mol% at 615 nm [23]. The quenching concentration of La<sub>2</sub>MgTiO<sub>6</sub>:Eu<sup>3+</sup> phosphors is 10.0 mol% [14]. The phosphors with the formula AA'BB'O<sub>6</sub> exhibits high quenching concentrations. The quenching concentrations of NaLaMgWO<sub>6</sub>:Eu<sup>3+</sup> and

BaLaMgSbO<sub>6</sub>:Eu<sup>3+</sup> reach 50.0 mol% and 70.0 mol%, respectively [24,25]. As reported, the tolerance of BaLaMgSbO<sub>6</sub> is 0.958 and is rather close to 1, indicating that the symmetry of the A' site ions is high and then the electronic dipole transition is low. In this work, CaLaMgSbO<sub>6</sub> with low tolerance factor was presented. In this paper, a series of Eu<sup>3+</sup> doped CaLaMgSbO<sub>6</sub> phosphors were prepared. Luminescence properties of the phosphors were investigated in detail. Concentration quenching and thermal stability were also discussed.

#### 2. Experimental

All the samples were prepared by the solid state method. High purity CaCO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, Sb<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, and NH<sub>4</sub>Cl were used as the starting materials. The stoichiometric amounts of starting materials were intimately mixed in nylon tank for 8 h and then placed in crucibles and fired at 1450 °C for 6 h. Finally, after cooling to room temperature the samples were ground to fine powders for further characterization. Then the phosphors of CaLa<sub>1-x</sub>MgSbO<sub>6</sub>:Eu<sup>3+</sup> (x = 0.05, 0.1, 0.3, 0.5, 0.7, 0.9, and 1) were successfully synthesized.

The crystalline phases were examined by X-ray diffraction (XRD, smartlabTM 9 kW, Rigaku, Japan) using Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) in the range of 5–80° with step size 0.02° and scanning rate 5°/min. The schematic illustration of CaLaMgSbO<sub>6</sub> was obtained by the Diamond software. The morphologies of the samples were observed by

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Fig. 1. XRD pattern of  $CaLa_{1-x}Eu_xMgSbO_6$  (x = 0.05, 0.1, 0.3, 0.5, 0.7, 0.9, 1).

transmission electron microscopy (TEM, FEI G2F20) at an accelerating voltage of 220 kV. The luminescence spectra were obtained by fluorescent spectrophotometer (Lumina, America). Homemade heating cell was equipped to the spectrometer to evaluate the thermal stability of the powders.

#### 3. Results and discussion

XRD profiles of the as-prepared CaLa<sub>1-x</sub>MgSbO<sub>6</sub>:Eu<sup>3+</sup> powders are given in Fig. 1. All the diffraction peaks matched well with the monoclinic double perovskite structure of CaLaMgSbO<sub>6</sub>. Some small peaks at 25.6°, 30.1°, 34.0°, and 53.0° were belong to the impurity phase. As shown in Fig. 1, the amplified peak in the region of 32.0° and 33.0° gradually split with increasing Eu<sup>3+</sup> content, indicating that Eu<sup>3+</sup> ions had been incorporated into the lattice. Such split phenomenon is originated from the substitution of smaller Eu<sup>3+</sup> ion for La<sup>3+</sup>. Besides, the diffraction peaks at 19.1°, 37.2° and 49.5° are typical for a rock salt ordering of Mg<sup>2+</sup> and Sb<sup>5+</sup>. The tolerance factor of CaLa<sub>0.95</sub>Eu<sub>0.05</sub>MgSbO<sub>6</sub> (Ca<sup>2+</sup>, 1.34 Å; La<sup>3+</sup>, 1.36 Å; Eu<sup>3+</sup>, 1.12 Å; Mg<sup>2+</sup>, 0.72 Å; Sb<sup>5+</sup>, 0.60 Å; O<sup>2-</sup>, 1.42 Å) and was smaller than the reported [21,25].

The schematic diagram of the crystal structure of  $CaLaMgSbO_6$  is shown in Fig. 2. Obviously, this compound shows B-site ordering of



 $MgO_6$  and  $SbO_6$ .  $Ca^{2+}$  ions and  $La^{3+}$  ions occupy the A site without any ordering. Here, B ion is 6 oxygen coordination and the A ion 12 oxygen coordination. Three-dimensional net is formed by MgO<sub>6</sub> and SbO<sub>6</sub> octahedra. The TEM pattern of the selected CaLa<sub>0.95</sub>Eu<sub>0.05</sub>MgSbO<sub>6</sub> powder is shown in Fig. 3(a). The particle shape of the sample is irregular. The crystal structure of the phosphor was further verified by high-resolution TEM (HRTEM) in Fig. 3(b). In the selected areas of the sample, the obvious lattice fringes of the HRTEM image illustrate that good crystallinity was obtained. Two apparent interplanes belong to (1 0 1) and (1 1 2) according to the calculation and measurement of the adjacent lattice fringes. Moreover, the lattice spacing of the (1 0 1) plane indicated that rock-salt ordering of B-site ions indeed existed in this double perovskite. The d spacing value of  $(1 \ 0 \ 1)$  and  $(1 \ 1 \ 2)$  could be obtained by the classic Bragg equation. The normalized d spacings of (1 0 1) and (1 1 2) were calculated to be 0.448 nm and 0.268 nm, respectively.

The excitation spectra of  $CaLa_{1,x}Eu_xMgSbO_6$  are shown in Fig. 4. All the spectra are composed of a broad excitation band and several sharp lines. The broad band centered at 290 nm is ascribed to the charge transfer band (CTB) of Eu-O and Sb-O. These sharp lines in the wavelength from 360 to 470 nm presented the intra-4*f* transitions of Eu<sup>3+</sup>. The lines of Eu<sup>3+</sup> located at 465 nm, 415 nm, 395 nm, 380 nm and 363 nm were corresponding to the  ${}^7F_0 \rightarrow {}^5D_2$ ,  ${}^7F_0 \rightarrow {}^5D_4$ ,  ${}^7F_0 \rightarrow {}^5D_4$  transitions, respectively [20]. Upon increasing *x* value, the intensities of CTB and intra-4*f* transitions firstly increased and reached the maximum at x = 0.5. Continuing increasing Eu<sup>3+</sup>

Under the excitation of CTB, all the CaLa<sub>1-x</sub>Eu<sub>x</sub>MgSbO<sub>6</sub> samples exhibited emissions ranging from 580 to 640 nm, which were associated with the transitions <sup>5</sup>D<sub>0</sub> state to the <sup>7</sup>F<sub>J</sub> (J = 1 and 2) ground states of Eu<sup>3+</sup> as labeled in Fig. 5(a). Upon 395 and 465 nm excitation, the spectra showed the similar shape with the spectra under CTB excitation. The spectra showed weak magnetic dipole transition (<sup>5</sup>D<sub>0</sub> $\rightarrow$ <sup>7</sup>F<sub>1</sub>, 590 nm) and strong electric dipole transition (<sup>5</sup>D<sub>0</sub> $\rightarrow$ <sup>7</sup>F<sub>2</sub>, 615 nm), indicating that Eu<sup>3+</sup> ions occupied A-site with a low symmetry in CaLaMgSbO<sub>6</sub> lattice. As shown in Fig. 5(d), intensities of electric dipole transitions increased firstly for all the three excitations. The luminescence intensities of the <sup>5</sup>D<sub>0</sub> $\rightarrow$ <sup>7</sup>F<sub>2</sub> transition at x = 0.5 were about 2.48, 4.43 and 4.22 times comparing to x = 0.05 for the excitation of CTB, 395 nm and 465 nm, respectively. Continuing increasing x value, the intensities decreased fast owing to the concentration quenching.

According to Judd-Ofelt theory, the transition of  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  is dominant if the Eu<sup>3+</sup> ion occupies a site with high symmetry. Otherwise, the transition of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  is dominant. The ratio R = I (615 nm)/I (590 nm) was used to detect the symmetry of Eu<sup>3+</sup> ion's site [26]. The intensity rations of CaLa<sub>1-x</sub>Eu<sub>x</sub>MgSbO<sub>6</sub> are shown in Fig. 6. With increasing Eu<sup>3+</sup> concentration, the ratios increased firstly and then decreased for all the three excitations. Differently, under the excitation of 395 and 465 nm the ratios reached the maximum at x = 0.3while the ratios reached the maximum at x = 0.5 under the CTB excitation. The ratios were between 5.2 and 6.2, indicating that  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is the dominant transition. Therefore, the Eu<sup>3+</sup> ions occupied the site with a low symmetry in the lattice.

The optimized concentration 50.0 mol% indicates that this matrix has larger quenching concentration of  $Eu^{3+}$  than the reported [3,16,27,28]. As reported by Ozawa [29], initial quenching concentration could be obtained by 1/(1 + Z). Z is the number of the nearest cations around  $Eu^{3+}$ . Eq. (1) gives the relationship between the emission intensity *I* and concentration *x*.

$$I = Bx(1 - x)^Z \tag{1}$$

For a given matrix, B is invariable. Therefore, the equation could be simplified by natural logrithm:

$$\ln(I/x) = Z \ln(1-x) + C$$
(2)

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