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A novel double perovskite tellurate Eu^{3+}-doped Sr_2MgTeO_6 red-emitting phosphor with high thermal stability

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ABSTRACT

A series of novel double perovskite tellurate red-emitting phosphors $Sr_2MgTeO_6:xEu^{3+}$ (x = 0.05–0.40) were successfully synthesized by a high-temperature solid-state reaction method. The phase structure, photoluminescence properties and thermal stability of the phosphor were investigated in detail. The phosphor shows dominant emission peak at 614 nm belonging to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition under 465 nm excitation. The luminescence intensity keeps increasing with increasing the content of Eu^{3+} to 25 mol%, and the critical transfer distance of Eu^{3+} was calculated to be 12 Å. The quenching temperature for $Sr_2MgTeO_6:0.25Eu^{3+}$ was estimated to be above 500 K. This spectral feature reveals high color purity and excellent chromaticity coordinate characteristics. Therefore, Eu^{3+}-doped Sr_2MgTeO_6 phosphors are potential red phosphors for blue chip-based white light-emitting diode and display devices.

1. Introduction

Recent years, white light-emitting diodes (WLEDs) are replacing the traditional incandescent lamp and fluorescent lamp rapidly due to its high brightness, compactness, long lifetime, good material stability, better flexible design, fast switching and environmental protection [1,2]. Currently, the most popular way to achieve white light is combining a blue-emitting InGaN LED chip and a yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) phosphor. However, this combination leads to the low color rendering index (CRI < 70) due to the lack of red-light components, which is not suitable for indoor lighting. This difficulty can be completely overcome by adding a suitable blue-light-activated red phosphor in LEDs [3]. Many oxynitride and nitride phosphors have been extensively reported to be good potential red phosphors due to their stable physical and chemical properties based on their rigid crystal structure [4,5]. However, the mass production cost of nitride phosphor is still a key issue [6]. Recently, more and more attention has been paid to explore novel red phosphor for the NUV/UV or blue light activation [7–10].

The compounds with double perovskites of the general formula $A_2BB'O_6$ (with A typically being an alkaline earth, B a low oxidation state transition metal and B′ a small and highly charged ion) in which $B'O_6$ and $B''O_6$ octahedra are corner-shared alternately. This framework forms cube-octahedral cavities filled by *A*-site cations [11,12]. Eu^{3+}-doped double perovskite oxides have been given great attentions because of the possible applications as luminescence materials. For example, the emission intensity of Eu^{3+}-doped Sr_2CaMoO_6 is 1.5 times higher than that of commercial $Y_2O_2S:Eu^{3+}$ [13]; $Sr_{1.5}Eu_{0.05}Li_{0.05}Ba_{0.4}CaWO_6$ has 4.5 times stronger luminescence intensity than that of commercial red phosphor (Nichia) under 465 nm excitation [14].

Tellurate glasses have been shown to have excellent properties for applications such as planar waveguides, amplifiers, and lasers [15,16]. The low phonon energy of tellurate is about 800–900 cm^{-1}, which can avoid very competitive nonradiative decay for doped rare earth ions [17], so the tellurate will be considered as suitable host matrices for phosphors. In 2008, Dias et al. investigated the vibrational spectroscopic and microwave dielectric properties of A_2MgTeO_6 (A = Sr, Ba, Ca) ceramics [11]. In 2010, Rich Ubic et. al. investigated the dielectric properties of the $(Sr_{2-x}Ca_x)MgTeO_6$ ceramics were studied by the resonance method [18]. To the best of our knowledge, there are no detailed reports on the luminescent properties of Eu^{3+}-doped double perovskite Sr_2MgTeO_6 under blue excitation. In this work, red emitting phosphors $Sr_{2(1-x)}Eu_xNa_xMgTeO_6$ (x = 0.05–0.40) were synthesized by the conventional solid-state reaction. The structure, composition and photoluminescence properties of $Sr_2MgTeO_6:Eu^{3+}$ phosphors were investigated. In addition, the thermal quenching behavior

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and CIE chromaticity coordinate of the phosphors were also discussed.

2. Experimental procedure

The synthesis of Sr_2MgTeO_6 phosphors doped with Eu^{3+} ions was carried out via a high-temperature solid-state reaction method. $SrCO_3$ (99.99%), $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ (99.99%), TeO_2 (99.9%), and Eu_2O_3 (99.99%) as raw materials, they were purchased from Sigma–Aldrich company. Subsequently, the powder mixture was thoroughly mixed in an agate mortar by grinding and was transferred into crucibles. They were pre-heated at 600 °C for 8 h in air, then re-ground and sintered at 1100 °C for 24 h in air. Finally, white powers were obtained by grinding. The relevant reaction formulas are as follows:

$$2(1-x)SrCO_3 + (1/5)4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O + TeO_2 + x/2Eu_2O_3 + x/2Na_2CO_3 \rightarrow Sr_{2(1-x)}Eu_xNa_xMgTeO_6$$

X-ray powder diffraction (XRD) patterns of the products were recorded on a Philips X'Pert MPD (Philips, Netherlands) with Cu Kα radiation (λ = 1.5418 Å). The diffraction patterns were scanned within an angular range of 10–70° (2θ) with a scan rate of 0.05°/s. The morphology and size of the phosphors were measured using a scanning electron microscope (SEM, JEOL JSM-6490). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were analyzed using a Hitachi F-4600 spectrophotometer at room temperature. The temperature-dependent PL emission spectra and PL decay of the synthesized products were recorded by the Edinburgh FLS 920 spectrometer.

3. Results and discussion

It has been reported that the Sr_2MgTeO_6 crystallizes in pseudocubic tetragonal structure with space group $I4/m$ [18]. The crystal structure of Sr_2MgTeO_6 is shown in Fig. 1. Sr^{2+} (A-site) (teal sphere) ions are coordinated to 12 oxygen atoms and Mg^{2+}/Te^{6+} are coordinated to 6 oxygen atoms and the Mg^{2+} (gray sphere) and Te^{6+} (dark yellow sphere) ions are ordered in the B-site [19]. Ordering between the B and B′ ions is quite common for cubic perovskites of the type $A_2BB'O_6$, if the charge difference between B and B′ ions is ⩾4 [11]. The positions of the ordered ions are like those of cations and anions in the rock-salt structure. The appearance of superlattice lines (1 1 1), (3 1 1) and (5 1 1) evidences the rock-salt ordering of Mg^{2+} and Te^{6+} (Figs. 1 and 2).

The representative XRD structural refinements of Sr_2MgTeO_6:Eu^{3+} phosphors were carried out using GSAS (general structure analysis system) program. Fig. 1 displays the typical results from the refinements. The refined parameters and atom positions are listed in Table 1. All the peaks of the samples are found to be well matched with the standard data for the Sr_2MgTeO_6 phase according to PDF 16-0549. It indicated that a single-phase phosphor is obtained and that the doped Eu^{3+} ions have been successfully dissolved into the host crystal lattice. No impurity lines were observed. The calculated lattice parameters for phases with Eu^{3+}-substituted at Sr-sites along with those of parent phases are tabulated in Table 1. For the composition of Sr_2MgTeO_6:$0.25Eu^{3+}$, the unit cell lattice parameters and the volume of the matrix are a = 5.6037(25), b = 5.5895(19), c = 7.8953(31) Å, and V = 247.30(9) Å^3, respectively, which are consistent with previously reported results [18]. As the ionic radii for the Sr^{2+} and Eu^{3+} ions were around 1.053 Å and 1.079 Å (coordination number, CN = 12) [20], the Sr^{2+} ions could be easily taken place by Eu^{3+} ions without inducing any distinct changes to the structure of the Sr_2MgTeO_6 host lattice.

The surface morphology and particle sizes of the synthesized phosphor are important for their applications in commercial WLEDs. Fig. 3 shows the representative SEM images of two different concentrations of Sr_2MgTeO_6:xEu^{3+} (a, x = 0.05; b, x = 0.30). It seemed as if these small spherical particles combined together to form big crystallites. The size of particles is found to be in micrometer dimension. Meanwhile, doping content of Eu^{3+} ions in Sr_2MgTeO_6:xEu^{3+} from 0.05 to 0.30 mol did not alter the particle size and agglomeration. Meanwhile, most commercial phosphor particles currently available on the market are in a size range of 2–10 μm. The present particle sizes consist of a few microns, which made them suitable for use in typical screening processes used in the construction of display and illuminance.

Fig. 4 shows the excitation spectra of Sr_2MgTeO_6:$0.25Eu^{3+}$ monitored at 614 nm emission at room temperature. The broad band of 225–350 nm centered at around 302 nm is called as charge transfer (CT) band which is ascribed to the charge-transfer state (CTS) transition of $O^{2-} \rightarrow Eu^{3+}$ ions. It is similar to the CTS of $NaBaLaTeO_6$ [21]. A sequence of sharp excitation bands between 350 and

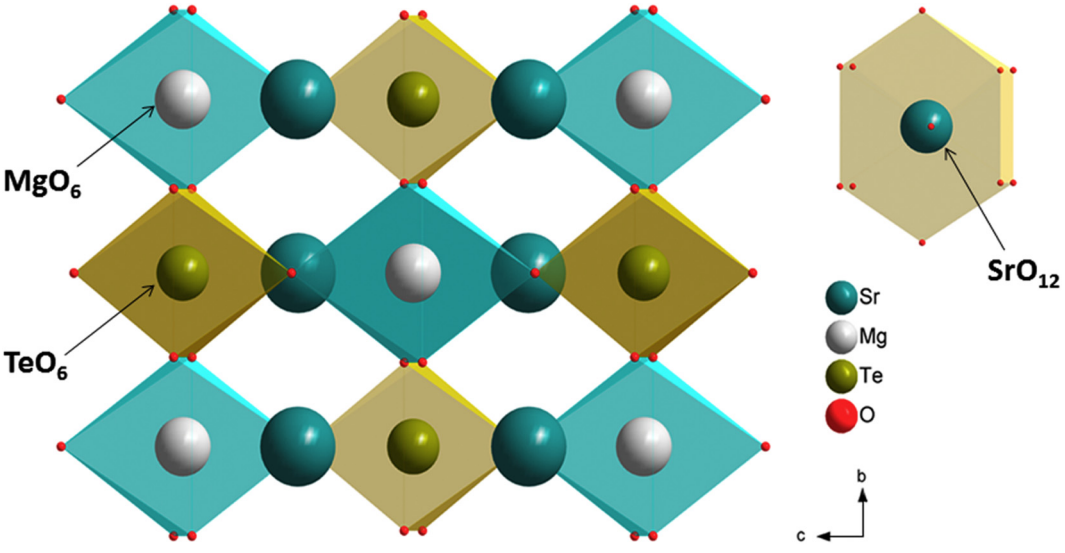

Fig. 1. Sr_2MgTeO_6 cell and the coordination environments therein (The teal balls are strontium atoms, the gray ones are magnesium atoms, the dark yellow ones are tellurium atoms, and the red ones are oxygen atoms). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)