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Full Length Article

Effects of Ta–O charge transfer band on the color-tunable emissions of Dy^{3+}-activated $SrLaMgTaO_6$ phosphors

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ABSTRACT

The color-tunable emissions of Dy^{3+}-activated $SrLaMgTaO_6$ phosphors were synthesized *via* a conventional high temperature solid-state reaction method. The phase and the luminescent properties were well characterized by X-ray diffraction patterns (XRD), diffuse reflectance spectra, luminescent spectra and lifetime. The XRD result revealed the as-prepared samples exhibited a monoclinic structure with the space group $P2_1/n$. Moreover, the obtained phosphors could be efficiently excited by the UV (250 nm), near-UV (354 and 390 nm) and blue (452 nm) lights. A gradual enhancement of PL emission intensity was observed with elevating the Dy^{3+} ion concentration and reached its maximum value when the doping concentration was 7 mol%. The critical distance was estimated to be 15.13 Å. In addition, the emission color of the as-synthesized samples were changed from blue to pure white and finally to yellow by properly adjusting the excitation wavelength and the doping concentration. All the results confirmed that Dy^{3+}-activated $SrLaMgTaO_6$ phosphors may have potential applications in white light-emitting diodes as white light-emitting phosphors.

1. Introduction

Nowadays, the phosphor-converted white light emitting diodes (w-LEDs) are regarded as new light sources for the next generation lighting industry and display systems owing to their advantages of long lifetime, high luminescent efficiency, low power consumption and eco-friendly [1–4]. As we know, to obtain the high quality white lights, it is necessary to develop some phosphors that can be efficiently excited by the ultraviolet (UV) or blue lights. Fortunately, these phosphors, which possess host absorptions in the UV region and can transfer the energy to the luminescent center, can satisfy the aforementioned requirements of the generation of the white lights. Generally, inorganic luminescent materials possess ligand-to-metal charge transfer (LMCT) transitions along with intense broad absorption band in the UV region. Therefore, excellent luminescent performances are expected to be obtained in these rare-earth ions activated inorganic luminescent materials.

Compared with other inorganic materials, the double-perovskite type compounds are widely used because of their superior physical and chemical properties, like pyro and piezo-electricity, dielectric susceptibility, linear, and nonlinear optic effects [5]. Especially, the rare-earth ions activated the ordered double-perovskite type with the formula of $AA'BB'O_6$ (A=Sr, Ca, Ba; A'=Gd, La, Pr; B=Mn, Fe, Mg, Zn; B'=W, Mo, Ta, Nb, Ti, Sb) have attracted much attention [6–9]. As for these double-perovskite type luminescent hosts, there are two kinds of sites, namely, the randomly assigned A (A') sites with twelve-oxygen coordinated and long-range rock-salt arrangement B (B') sites with six-oxygen coordinated, both can be occupied by the rare-earth ions. Among these two kinds of sites, the A (A') sites do not only possess high crystal field strength but also have the asymmetry center, implying the A (A') sites are the superior positions for some symmetry-sensitive ions, such as Eu^{3+} and Dy^{3+} ions. Nevertheless, the energy absorbed by the B (B') sites are strongly quenched by $B(B')\ O_6$ group, which can block the energy transfer path and leads little energy transfer to the luminescent center [10]. Therefore, to achieve the color-tunable emissions, the rare-earth ions are expected to be occupy the A (A') sites. Furthermore, in our previous work, we designed the Eu^{3+} ions to occupy the A(A)' sites in $SrLaMgTaO_6$ host and found that the as-prepared phosphors had promising application in w-LEDs as a red-emitting phosphor [11].

For $SrLaMgTaO_6$, the crystal structure obtained from CIF file is presented in Fig. 2, which contains each atom information, read by Diamond 3.2 software. The CIF file comes from NIMS without any refinement. The Sr^{2+} and La^{3+} ions were randomly distributed in A (A') sites surrounded by 12 oxygen ions, whereas the Mg^{2+} and Ta^{5+} ions were orderly located in the B (B') sites with the oxygen-

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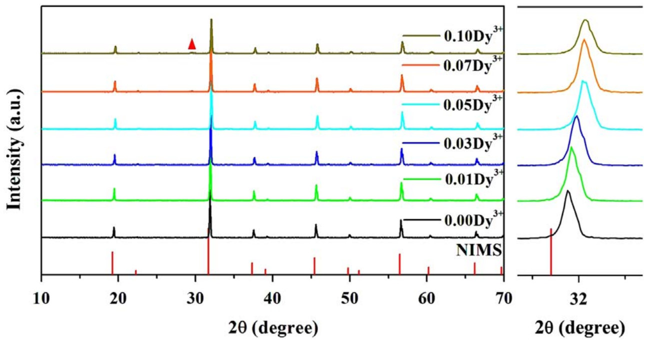

Fig. 1. XRD patterns of prepared $SL_{(1-x)}MTO{:}xDy^{3+}$ ($x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.10$) phosphors.

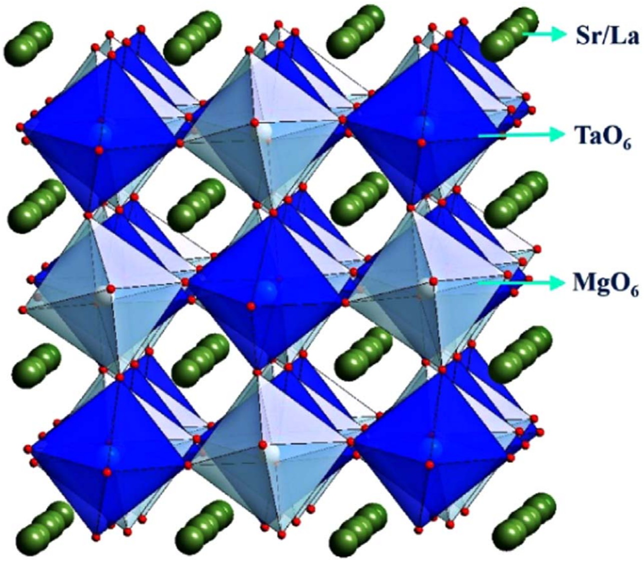

Fig. 2. Crystal structure of SLMTO.

octahedral surrounded by 6 oxygen ions [12,13]. Both the oxygen-octahedral MgO_6 and TaO_6 formed a three-dimensional network with octahedral tilting distortions. Octahedral tilting distortions are common in double-perovskite. The distortion from the ideal crystal could be explained by the mismatch between the ionic radius of Sr = 1.18 Å, La = 1.172 Å, Mg = 0.72 Å, Ta = 0.64 Å, and O = 0.09 Å. Besides that, both the MgO_6 and TaO_6 are forced to increase Mg–O band lengths and to reduce Ta–O band lengths due to the Ta^{5+}-cation is smaller than Mg^{2+}-cation [14]. Hence, the presence of octahedral is constrained to keep the double-perovskite structure, which supporting the octahedral tilting distortions. In order to find the mismatch between the inter-atomic bond lengths, we calculated the tolerance factor (t) of complex perovskite oxides as $t = (r_{Sr} + r_O)/\sqrt{2}(r_{(Mg,Ta)} + r_O)$, where, r is the composition weighted ions radius at the given site, and $r_{(Mg,\ Ta)}$ is the averaged ionic radii of Mg and Ta cations. The calculated t value of SLMTO is 0.952. Therefore, there is an octahedral tilting distortion that affects the symmetry of the crystal field in this structure.

Over the last decades, the trivalent rare-earth ions have attracted considerable attention due to their excellent luminescent properties in the visible and near-infrared regions [15]. Generally, the dysprosium (Dy^{3+}) ions have two characteristic emissions, one is the blue emission at about 480 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and another is the yellow emission at approximately 580 nm due to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. Moreover, by properly adjusting the yellow-to-blue (Y/B) intensity ratio, the white light can be obtained in Dy^{3+}-activated luminescent material. However, due to the low molar absorption coefficients aroused by spin-forbidden f–f transitions, the direct excitation of the rare-earth ions is not sufficient to generate the highly-efficient luminescent properties [16]. To overcome this problem, the alternative approach is choosing an appropriate host which can act as a sensitizer and can transfer the energy to activator (rare-earth) ions. Taking the Dy^{3+}-activated Y_6WO_{12} phosphors for example, the WO_6 group can absorb UV light efficiently and then transfer the energy to the Dy^{3+} ions, leading to the strong luminescent performances [17]. Similarly, as for the $SrLaMgTaO_6$ (SLMTO), it has a strong absorption in the UV region and can transfer the energy to dopant ions. Thus, highly-efficient luminescent properties can be achieved in rare-earth ions activated SLMTO phosphors. Moreover, the SLMTO can exhibit a broadband blue emission from 420–600 nm, which is helpful to generate the white light, under UV light excitation. Unfortunately, to the best of our knowledge, the reports on the luminescence properties of Dy^{3+}-activated SLMTO are sparse. Hence, in the present work, the Dy^{3+}-activated SLMTO phosphors were synthesized and their luminescent properties were systematically investigated under UV, near-UV and blue light excitation.

2. Materials and methods

2.1. Sample preparation

A series of Dy^{3+}-activated SLMTO phosphors ($SL_{(1-x)}MTO{:}xDy^{3+}$; $x = 0$, 0.01, 0.03, 0.05, 0.07 and 0.10) were prepared by a high temperature solid-state reaction method. All the ingredients are commercially available and used as received. $SrCO_3$ (Yakuri Pure Chemical, 99%), La_2O_3 (Aldrich, 99.9%), $(MgCO_3)_4Mg(OH)_2{\bullet}5H_2O$ (DaeJung Chemical Pure, 99%), Ta_2O_5 (Aladdin, 99.5%), and Dy_2O_3 (Aladdin, 99.99%) were weighed according to the stoichiometric ratio. The mixtures-based precursors were grinded thoroughly for 30 min in an agate mortar and pre-sintered at 650 °C for 2 h in a muffle furnace to decompose the carbonates. Then, the harvest mixtures were reground and re-sintered at 1400 °C for 12 h in air atmosphere. Finally, the samples were ground into powder for characterization. The Dy^{3+}-activated $SrLaMgTaO_6$ phosphor was supplied by the Display and Lighting Phosphor Bank at Pukyong National University.

2.2. Materials characterization

The phase purity and crystal structure were examined by D8 Advance X-ray diffractometer (Bruker, Cu K_α irradiation, $\lambda = 1.5406$ Å) operating at 40 kV and 30 mA. The diffraction patterns with a fixed scanning step of 10°/min were recorded over 2θ; ranges from 10°–70° and 0.5 s residence time. UV–vis diffuse reflectance spectra (DRS) were measured on a V-670 UV–vis spectrophotometer (JASCO Corp., Japan). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded by a Photon Technology International (PTI, USA) fluorimeter equipped with a 60 W xenon lamp as the excitation source. The fluorescence lifetime curves were measured with a phosphorimeter attached to the fluorescence spectrophotometer with a 25 W xenon flash lamp. All measurements were performed at room temperature.

3. Results and discussion

3.1. Phase characterization

The phase purity of the as-synthesized samples were identified by X-ray diffraction (XRD). Fig. 1 shows the XRD patterns of $SL_{(1-x)}MTO{:}xDy^{3+}$ double-perovskite phosphors, which were