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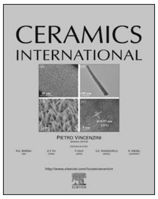

Deep-red emission of Mn^{4+} and Cr^{3+} in $(Li_{1-x}A_x)_2MgTiO_4$ (A=Na and K) phosphor: Potential application as W-LED and compact spectrometer

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ABSTRACT

Mn^{4+} doped and Mn^{4+}/Cr^{3+} co-doped alkali metal titanate phosphors have been prepared by solid state reaction method. A part of Li$^+$ ions in the Li_2MgTiO_4: Mn^{4+} are substituted with Na$^+$ and K$^+$ ions and consequently the intensity of Mn^{4+} emission at 678 nm is enhanced by 1.7 and 2.5 times, respectively. In the Mn^{4+}/Cr^{3+} co-doped $(Li_{0.95}K_{0.05})_2MgTi_{0.999}O_4$, both emission of Cr^{3+}at 726 nm and emission of Mn^{4+} at 678 nm of Mn^{4+} are observed. It is interesting to find that the intensity ratio of 726–678 nm emissions in the Mn^{4+}/Cr^{3+} phosphor continually increases with excitation wavelength increasing from 290 nm to 455 nm, which means that the intensity ratio in turn can be used to identify the excitation light wavelength. This refers a possible approach to design novel compact light-wavelength detector or spectrometer based on the phosphor. The mechanism of Na$^+$ or K$^+$ substitution induced luminescence enhancement in the Mn^{4+} phosphor and the competition between the Cr^{3+} and Mn^{4+} emissions in the Mn^{4+}/Cr^{3+} co-doped has been discussed.

1. Introduction

White light-emitting diodes (W-LED) have been extensively regarded as the new generation of solid-state lightings, attracted substantial attentions due to their many advantages such as high efficiency, life-durable, compactness, low energy consumption, high reliability, good stability and environmental friendliness properties [1–7]. Currently, the leading commercial W-LEDs are achieved by combination of InGaN blue-emitting LED chip with a yellow phosphor (YAG: Ce^{3+}) packed on the chip surface using epoxy resin or silicone [8–10]. However, in practical applications, w-LEDs fabricated by this method do not reach the optimal requirements for white light due to some deadly weaknesses, such as low color rendering index and high color correlated temperature caused by the innate deficiency in the red spectral region [7,11]. Thus, it is quite important to find a suitable red phosphor which can convert blue light into long wavelength region with high efficiency in order to improve the aforementioned weaknesses and attain the optimal quality requirements for W-LEDs.

Recently, rare-earth (RE) elements, in particular Eu^{2+} or Ce^{3+}, are widely used in the outstanding red emitting phosphors and meet the actual requirement of practical application, such as $Sr_2Si_5N_8$: Eu^{2+} [12], M[Mg_3SiN_4]: Eu^{2+}/Ce^{3+}(M = Ca, Sr, Eu) [13], $CaAlSiN_3$: Eu^{2+} [14], $BaCa_2Y_6O_{12}$: Eu^{3+}, Dy^{3+} [15] and (SrCa)$AlSiN_3$: Eu^{2+} [16]. However, besides the high-cost, rare-earth (RE) elements, especially europium, usually have strong photon re-absorption in green or yellow spectral region due to the 4f-5d transitions and synthesis of most nitride phosphors requires extremely high temperature, high pressure reaction condition and harsh synthesis procedures [17]. Therefore, it is necessary to develop new red phosphors without RE elements that can be produced by simple synthesis process for the future W-LED market.

As a non-rare-earth activator, Mn^{4+} or Cr^{3+} doped phosphors with broad band excitation and deep-red narrow band emission may be an alternative choice. $^4A_2$ - $^4T_1$ and $^4A_2$ - $^4T_2$ transitions in Cr^{3+} or Mn^{4+} in octahedral coordination environment exhibit respective near UV and visible light absorption, so that the luminescence of Cr^{3+} or Mn^{4+} doped phosphors is always dominated by the spin-forbidden transition ($^2E_g - {}^4A_{2\,g}$) under near UV or blue light excitation. Recently Cr^{3+} or Mn^{4+}-doped crystals have been drawing attention as candidate materials for the red phosphor used in W-LEDs.

According to Tanabe–Sugano diagram, the Cr^{3+} and Mn^{4+} emission is almost independent on the crystal field splitting but is significantly influenced by different host lattice [7]. For Cr^{3+} or Mn^{4+} activated oxide phosphors, aluminates are investigated as major hosts such as $MgAl_2O_4$: Cr^{3+} [18], $SrMgAl_{10}O_{17}$:Mn^{4+}, M (M=Li$^+$, Na$^+$, K$^+$, Cl$^-$) [19], $Sr_4Al_{14}O_{25}$: Mn^{4+} [20], $CaAl_4O_7$: Mn^{4+} [21] and $Y_3Al_{5-x}Ga_xO_{12}$: Cr^{3+} [22] so far. Whereas titanates can be treated as a potential host group for Mn^{4+} substitution because of suitable characteristics, that is, the similarity of ionic radius between Ti^{4+}(60.5 pm) and Mn^{4+}(53 pm) and non-necessity of substitution for charge compensation owing to the same oxidation number. Recently, some Mn^{4+}-activated titanates are

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reported as phosphors, for example, Mg_2TiO_4: Mn^{4+} [23], La_2MTiO_6: Mn^{4+}(M=Mg and Zn) [24], Li_2TiO_3: Mn^{4+} [25] and Gd_2ZnTiO_6: Mn^{4+} [26]. Thus, it is of great significance to incorporate Mn^{4+} ions into titanate hosts with abundant octahedral sits and to gain insight into what influences and determines the emission of Mn^{4+} [7].

Considering that Li_2MgTiO_4 with rock salt structure type contains three types of octahedral sites ([TiO6], [MgO6] and [LiO6]) and can be synthesized easily with cheap raw materials. In this work, Mn^{4+} doped and Mn^{4+}/Cr^{3+} co-doped Li_2MgTiO_4 was prepared by a conventional solid-state reaction method in air atmosphere. A part of the Li^+ ions were tried to be substituted with other alkaline metal ions (Na^+ or K^+), in order to enhance the luminescence efficiency and improve the excitation properties. Meanwhile, the luminescence properties the Mn^{4+}/Cr^{3+} co-doped phosphor have also been investigated.

2. Experimental

A series of $(Li_{1-x}A_x)_2MgTi_{0.999-y}O_4$:$0.001Mn^{4+}$, yCr^{3+}(A=Na, K and x=0–0.1, y=0–0.012) phosphors samples were synthesize by a traditional high temperature solid-state reaction method with Li_2CO_3, K_2CO_3, Na_2CO_3, MgO, TiO_2, Cr_2O_3 and $MnCO_3$ as starting materials. All the chemicals used in the experiments were of analytical reagent (AR) grade. Stoichiometric amounts of raw materials were weighed according to the chemical proportion of $(Li_{1-x}A_x)_2MgTi_{0.999-y}O_4$: $0.001Mn^{4+}$, yCr^{3+}(A=Na, K and x=0–0.1, y=0–0.012) with thoroughly mixed and ground to fine particle in an agate mortar. Subsequently, the mixtures were filled in corundum crucibles and preheated at 1000 °C for 4 h under air atmosphere, and then cooled down naturally to room temperature. After the reactants were milled again to improve the homogeneity, they were heated up to 1300 °C and held for 2 h in air atmosphere. Finally, the samples were cooled down to room temperature naturally for further characterization.

The crystalline phases of the phosphors were identified by a D/MAX 2500 X-ray diffract (XRD) meter using Cu tube with Kα radiation in the 2θ range of 20°~90°. The excitation and emission spectra were obtained by a monochromator (Zolix Instrument, Omni-λ320i) coupled with photomultiplier (PMTH-S1-CR131), which is equipped with a 150 W xenon lamp as the excitation source. The luminescence decay curves were measured by PTI QM 40 spectrofluorometer using a pulse xenon lamp as the excitation source. The temperature dependent photoluminescence spectra of the phosphors under 470 nm excitation were measured with an FLS920 (Edinburgh) spectrometer.

3. Results and discussion

Fig. 1(a) shows the representative XRD patterns of $(Li_{0.95}A_{0.05})_2MgTi_{0.999-y}O_4$: $0.001Mn^{4+}$, yCr^{3+}(A=Na and K, y=0, 0.003 and 0.008). Pure phase Li_2MgTiO_4 (JCPDS#89–7118) [27] has a cubic rock salt structure belonging to Fm-3 m (225) space group. All the diffraction peaks of as-prepared samples can be matched well with the data of pure Li_2MgTiO_4 and no obvious peaks of impurity phase have been observed, indicating that the doping of Mn^{4+}, Cr^{3+} and alkaline metal ions (Na^+ or K^+) into the host lattice does not cause significant influence on the host crystal structure. Fig. 1(b) further shows the enlarged XRD patterns of $(Li_{0.95}A_{0.05})_2MgTi_{0.999-y}O_4$: $0.001Mn^{4+}$, yCr^{3+}(A=Na and K, y=0, 0.003 and 0.008) at 2θ =43–44°. The peaks at 43.46° and 43.58° correspond to the Cu-Ka1 and Cu-Ka2 ray diffractions from the (200) plane of the Li_2MgTiO_4, respectively. Although 5 mol% of Li^+ sites are substituted with other alkaline metal ions (Na^+ or K^+) or 0.8 mol% of Cr^{3+} ions are incorporated in the Li_2MgTiO_4 powder, no shift of the diffraction peak is observed.

Fig. 2(a) shows the excitation spectra of $(Li_{0.95}A_{0.05})_2MgTi_{0.999}O_4$: $0.001Mn^{4+}$(A=Na and K). When monitored at 678 nm, the excitation spectra between 250 nm and 600 nm present two peaks at about 352 nm and 470 nm assigned to the ${}^4A_2 \rightarrow {}^4T_1$ and ${}^4A_2 \rightarrow {}^4T_2$ transitions of Mn^{4+} ions, respectively. The emission spectra exhibit a broad emission band covering from 600 to 800 nm with a maximum at 678 nm, as show in Fig. 2**(b)**. This emission is ascribed to transitions ${}^2E \rightarrow {}^4A_2$ of Mn^{4+} suited in an octahedral site. Usually the Mn^{4+} emission is composed of some distinguishable sharp R lines and Stokes/anti-Stokes side-peaks due to different vibration modes for the $3d^3$ electrons when Mn^{4+} is of octahedral structure [28–30]. However, the abnormal red emission in Mn^{4+}-doped Li_2MgTiO_4 phosphor shows an undistinguishable broad asymmetric band, which is rarely observed in Mn^{4+}-doped oxides. Though the Ti, Mg and Li occupy the octahedral sites in Li_2MgTiO_4 structure randomly, the occupancy probability of corners of a given octahedron is affected by the nearest neighbor sites. In the Li_2MgTiO_4 structure, the relaxation of one set of Ti-O (Mg-O or Li-O) tends to interfere with the relaxation of the other set of Ti-O (Mg-O or Li-O). The overlap of the corresponding ions is increased, leading to the enhancement of chemical bond strength and nephelauxetic effect, which may cause the seemingly broadened emission of Mn^{4+} [7]. Although there was no peak shift in the excitation spectra for these alkaline metal-doped samples, the excitation intensity is effectively enhanced at both 352 nm and 470 nm when part of Li^+ is substituted by other alkaline metal (Na^+ or K^+). The substitution of Li^+ by other alkaline metal (Na^+ or K^+) also increases the luminescence intensity. Fig. 2**(c)** further shows the dependence of luminescence intensity on the concentration of substituted alkaline metal ions. The luminescence intensities of $(Li_{0.97}A_{0.05})_2MgTi_{0.999}O_4$: $0.001Mn^{4+}$(A=Na and K) were 1.7(Na) and 2.5(K) times higher than that of $Li_2MgTi_{0.999}O_4$: $0.001Mn^{4+}$, respectively. This result suggests that the substituted Na^+ or K^+ ions might slightly change the local

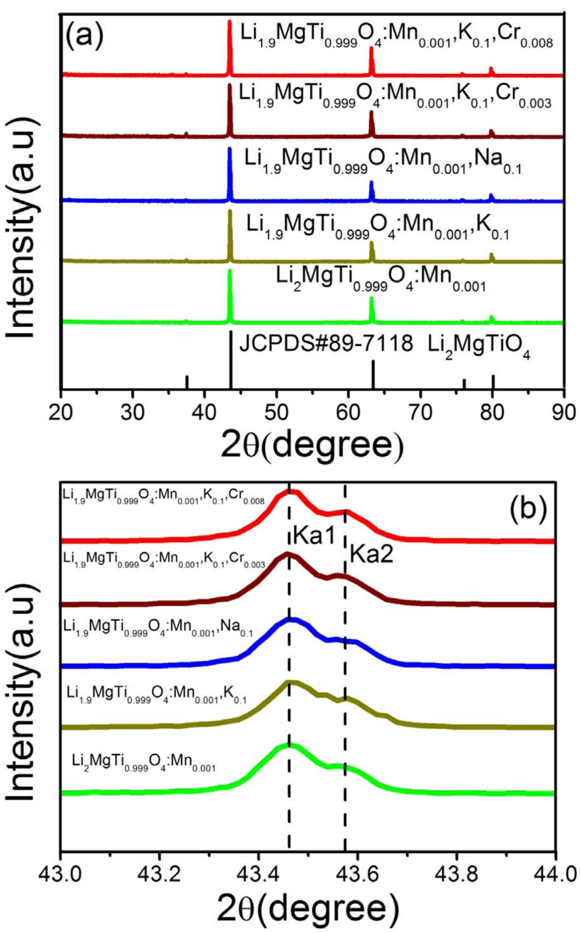

Fig. 1. (a) XRD patterns of $(Li_{0.95}A_{0.05})_2MgTi_{0.999-y}O_4$: $0.001Mn^{4+}$, yCr^{3+}(A= Na and K, y=0, 0.003 and 0.008) and the JCPDS card *#89–7118* for Li_2MgTiO_4. (b) Enlarged XRD patterns of $(Li_{0.95}A_{0.05})_2MgTi_{0.999-y}O_4$: $0.001Mn^{4+}$, yCr^{3+}(A= Na and K, y=0, 0.003 and 0.008) at 2θ=43 – 44.