

Enhancement of the luminescence efficiency of $\text{Li}_2\text{TiO}_3\text{:Mn}^{4+}$ red emitting phosphor for white LEDs

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A red-emitting $\text{Li}_2\text{TiO}_3\text{:Mn}^{4+}$ phosphor has excellent luminescence property. To enhance the optical absorption in the blue light region and to apply the phosphor to tri-color LEDs, we tried that a part of the Li^+ and Ti^{4+} sites in the $\text{Li}_2\text{TiO}_3\text{:Mn}^{4+}$ phosphor was substituted with alkaline metal ions ($A = \text{Na}$, K and Rb) and Ge^{4+} ions, respectively. The resulting phosphor exhibited efficient red emission and the luminescence intensity was about 3 times higher than that of $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$. The relative emission intensity of the phosphor was approximately 70%, compared with that of YAG:Ce^{3+} (P46) when the phosphors were excited at 460 nm. These results indicate that the red-emitting $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.70}\text{Ge}_{0.30})\text{O}_3\text{:Mn}^{4+}$ phosphor is a promising candidate for white LEDs.

Key words: Li_2TiO_3 , Mn^{4+} , White LED, Substitution.

Introduction

White LEDs combined with a blue LED and a yellow $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$ (YAG:Ce³⁺) phosphor [1] have been widely commercialized. This two-color white LED is one of the promising candidates for a new lighting system, instead of the fluorescent lamp. However, enough high color rendering cannot be obtained in the current two-color white LEDs due to a deficiency of red and green emissions. The alternative method to obtain white LEDs of high color rendering is to construct tri-color white LEDs in which a blue LED is combined with the red and green phosphors. Therefore, development of novel red and green phosphors, which can be excited by the blue light, is necessary to improve color rendering properties of white LEDs for the lighting system.

Recently, Eu^{2+} -doped nitride phosphors for white LEDs have been actively researched. The 4f-5d transition of Eu^{2+} ion is sensitive to the crystal field and covalency, and Eu^{2+} -doped nitride phosphors can be efficiently excited by the blue light and emit green to red luminescence. The nitride phosphors, such as $\text{CaSiN}_2\text{:Eu}^{2+}$ [2], $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ ($M = \text{Ca}$, Sr , and Ba) [3] and $\text{CaAlSiN}_3\text{:Eu}^{2+}$ (CASN) [4] have been reported as the red emission phosphors excitable by the blue LED. However, synthesis of most nitride phosphors requires high pressure nitrogen gas and a special type of furnace for extremely high temperatures.

In this study, we focused on rare-earth-free Mn^{4+} -doped oxide phosphors. The Mn^{4+} ion is known as luminescent centers of red emitting phosphors. The most well-known phosphors among them are $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ [5] and $\text{K}_2\text{GeF}_6\text{:Mn}^{4+}$ [6]. Furthermore, some Mn^{4+} -doped phosphors such as $3.5\text{MgO} \cdot 0.5\text{MgF}_2 \cdot \text{GeO}_2\text{:Mn}^{4+}$ [7], $\text{CaAl}_2\text{O}_{19}\text{:Mn}^{4+}$ [8] and $\text{La}_2\text{MgGeO}_6\text{:Mn}^{4+}$ [9] have been reported. These phosphors are excited by near-UV or blue light and exhibit red emission at 620 - 700 nm assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ and ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transitions of Mn^{4+} . Since the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition is spin-allowed, Mn^{4+} -doped phosphors could be promising candidates for the red-emitting phosphor in tri-color white LEDs.

In this study, we focused on a red-emitting $\text{Li}_2\text{TiO}_3\text{:Mn}^{4+}$ phosphor [10]. Li_2TiO_3 has a layered rock salt structure containing TiO_6 octahedral layers. This phosphor shows two excitation peaks at 350 and 495 nm assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions of Mn^{4+} and an emission peak at 680 nm assigned to the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of Mn^{4+} . However, the emission intensity is not enough. The shift of the excitation peaks to the shorter-wavelength side and the increase in the excitation intensity of $\text{Li}_2\text{TiO}_3\text{:Mn}^{4+}$ would improve the luminescence efficiency of this phosphor. Therefore, we tried to substitute a part of the Li^+ sites with alkaline metal ions ($A = \text{Na}$, K and Rb), and that of the Ti^{4+} sites with Ge^{4+} ions to improve the luminescence efficiency of the $\text{Li}_2\text{TiO}_3\text{:Mn}^{4+}$ phosphor.

Experimental

The phosphor powders were synthesized by a conventional solid-state reaction method. The starting

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materials were Li_2CO_3 (Kanto Chemical, Co., Inc, 3N5), Na_2CO_3 (Kanto Chemical, Co., Inc, 2N), K_2CO_3 (Kanto Chemical, Co., Inc, 2N), Rb_2CO_3 (Acros Organics, 2N), anatase-type TiO_2 (Wako Pure Chemical Industries, Ltd, 3N), GeO_2 (Kanto Chemical, Co., Inc, 4N) and MnO_2 (Kojundo Chemical Laboratory Co., Ltd, 4N) powders. Each reagent was weighed in the stoichiometric ratio of $(\text{Li}_{1-x}\text{A}_x)_2(\text{Ti}_{0.99-y}\text{Ge}_y\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}$ and $x = 0 - 0.1$, $y = 0 - 0.40$), and was mixed with acetone using an agate mortar and pestle. The mixtures were pressed into 15 mm-diameter disk pellets under a pressure of 30 MPa for several minutes. The pellets were heated in a platinum boat at 1273 K for 12 h in air. The crystal structure of the phosphors was characterized using X-ray powder diffraction analysis using a diffractometer (MX Labo with $\text{Cu K}\alpha$ radiation; Mac Science Ltd.). The photoluminescence excitation and emission (PLE) spectra were measured at room temperature using a fluorescence spectrophotometer (FP-6500 / 6600 with 150 W Xenon lamp; Jasco Inc.) in the ranges of 220 - 600 nm and 620 - 750 nm, respectively. The morphology of the samples was observed using scanning electron microscopy (JEOL JSM - 5310 scanning microscope) at an accelerating voltage of 5 kV.

Results and Discussion

Effect of alkaline metal carbonate addition to the $\text{Li}_2\text{TiO}_3\text{:Mn}^{4+}$ phosphor

Figure 1 shows the XRD patterns of $(\text{Li}_{0.97}\text{A}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb) and Li_2TiO_3 in ICSD (#162215). Kataoka et al. reported that Li_2TiO_3 has a monoclinic cell, $a = 0.50623(5)$, $b = 0.87876(9)$, $c = 0.97533(15)$ nm and $\beta = 100.212(11)^\circ$ with the space group C2/c [11]. Each diffraction pattern for all samples was identified to a single phase of Li_2TiO_3 and any impurity diffraction peaks were not observed.

Figure 2 shows the enlarged XRD patterns at $2\theta = 17 \sim 20^\circ$ of $(\text{Li}_{0.97}\text{A}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb). The diffraction peak at 18.4° corresponds to the diffraction from the (001) plane of Li_2TiO_3 . Although 3 mol% of the Li^+ sites were substituted with alkaline metal ions ($\text{A} = \text{Na}, \text{K}$ and Rb), no shift was observed in the diffraction peak.

Figure 3 shows SEM images of $(\text{Li}_{0.97}\text{A}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb). The average particle size of $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ was about 2 ~ 3 μm (a), while those of the other samples, in which a part of Li^+ ions was replaced by various alkaline metal ions, were 5 ~ 10 μm (b - d) and larger than that of $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$. As the results of the XRD and SEM measurements, the alkaline metal ions did not substitute for the Li^+ sites in $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$, but the alkaline metal carbonates probably worked as flux to affect the particle size of the phosphors.

Figure 4 shows PLE spectra of $(\text{Li}_{0.97}\text{A}_{0.03})_2$

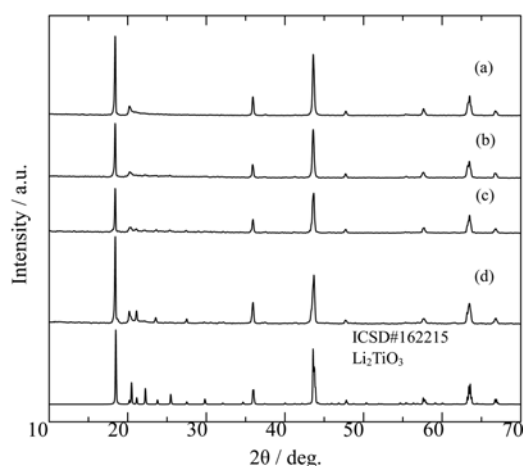


Fig. 1. XRD patterns of $(\text{Li}_{0.97}\text{A}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb): (a) Li, (b) Na, (c) K, and (d) Rb. The reference pattern corresponds to that of Li_2TiO_3 in ICSD (#162215).

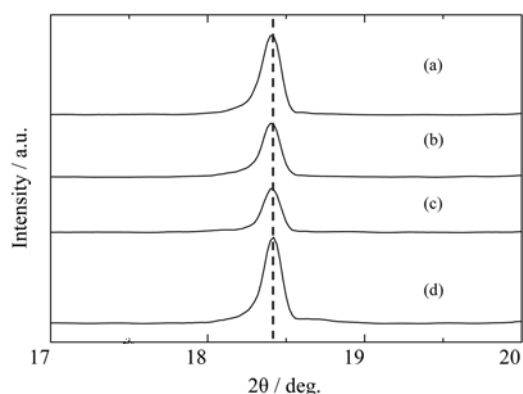


Fig. 2. Enlarged XRD patterns of $(\text{Li}_{0.97}\text{A}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb) at $2\theta = 17 - 20^\circ$: (a) Li, (b) Na, (c) K, (d) Rb.

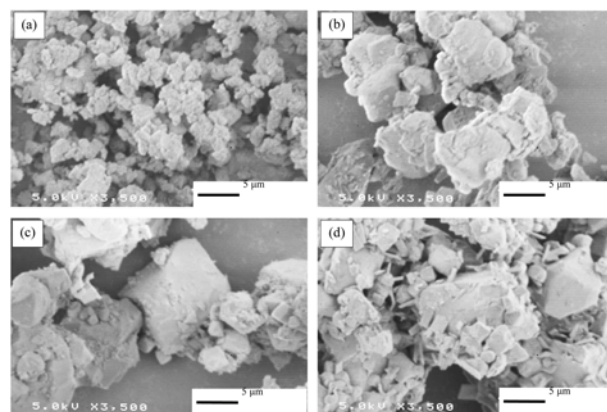


Fig. 3. SEM images of the samples: (a) $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$, (b) $(\text{Li}_{0.97}\text{Na}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$, (c) $(\text{Li}_{0.97}\text{K}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$, and (d) $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$.

$(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb). The emission spectra exhibited narrow and sharp peaks at 680 nm assigned to the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of Mn^{4+} . The excitation spectra between 250 and 600 nm showed two peaks at about 350 and 500 nm assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions of Mn^{4+} , respectively.

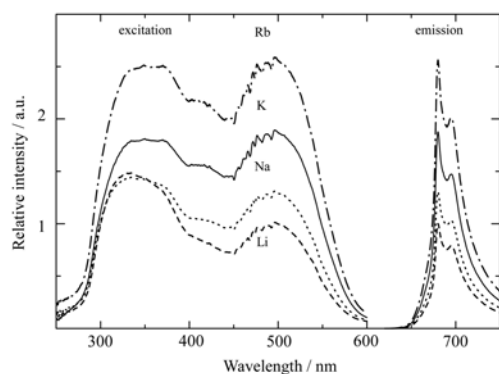


Fig. 4. PLE spectra of $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ (broken line) and $(\text{Li}_{1-x}\text{A}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb): Na (dotted line), K (solid line), and Rb (dash-dotted line).

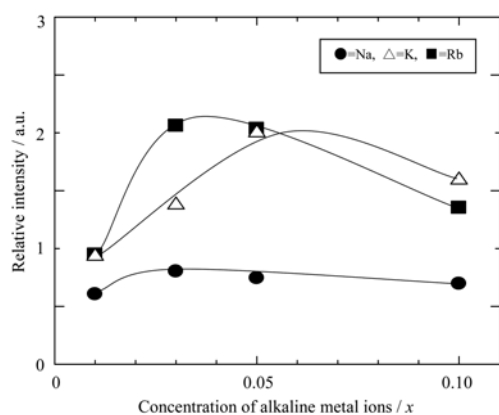


Fig. 5. Concentration dependence of the luminescence intensity of $(\text{Li}_{1-x}\text{A}_x)_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($x = 0 - 0.1$, $\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb): $\bullet = \text{Na}$, $\triangle = \text{K}$, and $\blacksquare = \text{Rb}$.

These are spin-allowed transitions. Although there was no peak shift in the excitation spectra of the alkaline metal-doped samples, the luminescence intensities increased. The luminescence intensities of $(\text{Li}_{0.97}\text{A}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Na}, \text{K}$ and Rb) were 1.3 (Na), 1.8 (K) and 2.6 (Rb) times higher than that of $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$, respectively. These results support that alkaline metal carbonates worked as flux. On the other hand, the emission intensity ratio of two peaks at 350 and 500 nm depended on the alkaline metal species. This suggests that a small amount of alkaline metal ions was slightly doped into the Ti^{4+} sites, and the local crystal field around Mn^{4+} ion was slightly changed. To elucidate this speculation, it is necessary to identify the local structure of these samples by Neutron Diffraction Analysis in the near future.

Figure 5 shows the concentration dependence of the alkaline metal ions on the luminescence intensity of $(\text{Li}_{1-x}\text{A}_x)_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Na}, \text{K}$ and Rb). The luminescence intensity of $(\text{Li}_{0.97}\text{Na}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ was 1.3 times that of $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$. Moreover, the luminescence intensities of $(\text{Li}_{0.95}\text{K}_{0.05})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ and $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ were 2.5 and 2.6 times higher than that of $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$, respectively.

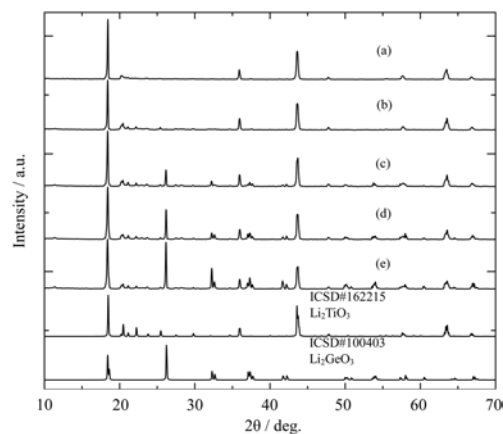


Fig. 6. XRD patterns of the $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99-y}\text{Ge}_y\text{Mn}_{0.01})\text{O}_3$ samples: (a) $y = 0$, (b) 0.10, (c) 0.20, (d) 0.30, (e) 0.40. The reference patterns indicate those of Li_2TiO_3 in ICSD (#162215) and Li_2GeO_3 in ICSD (#100403).

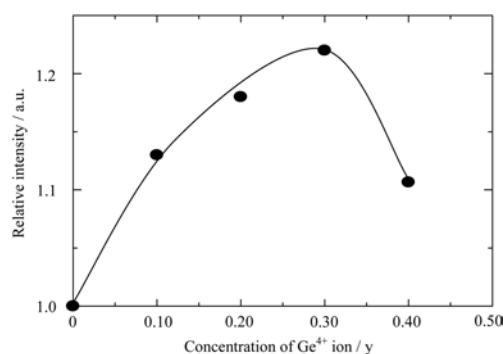


Fig. 7. The Ge^{4+} concentration dependence on the luminescence intensity of $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99-y}\text{Ge}_y\text{Mn}_{0.01})\text{O}_3$.

Effect of GeO_2 addition to the $(\text{Li}_{0.97}\text{Rb}_{0.03})_2\text{TiO}_3:\text{Mn}^{4+}$ phosphor

Figure 6 shows XRD patterns of $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99-y}\text{Ge}_y\text{Mn}_{0.01})\text{O}_3$ ($0 \leq y \leq 0.40$) samples. The XRD patterns were compared with those of Li_2TiO_3 (ICSD#162215) and Li_2GeO_3 (ICSD#100403). It was reported that Li_2GeO_3 has a orthorhombic cell, $a = 0.9634(2)$, $b = 0.5481(2)$ and $c = 4.843(1)$ nm with the space group $\text{Cmc}2_1$ [12]. The crystal structure of Li_2GeO_3 is different from that of Li_2TiO_3 . The diffraction corresponding to Li_2GeO_3 was increased with increasing the concentration of Ge^{4+} ions in the samples, but no peak shift was observed. This result shows that Ge^{4+} ions did not substitute for Ti^{4+} or a nominal amount of Ge^{4+} was doped into the Ti^{4+} sites. To clarify the details, determination of molecular structure by neutron diffraction analysis is also necessary in this case.

Figure 7 shows the Ge concentration dependence on the luminescence intensity of $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99-y}\text{Ge}_y\text{Mn}_{0.01})\text{O}_3$. The luminescence intensities of the $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99-y}\text{Ge}_y\text{Mn}_{0.01})\text{O}_3$ samples were slightly higher than that of $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ and the maximum luminescence intensity was obtained at $x = 0.30$. Similar results were observed in the samples

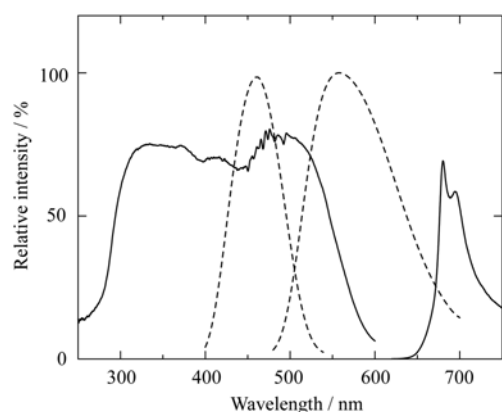


Fig. 8. PLE spectra of $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.69}\text{Ge}_{0.30}\text{Mn}_{0.01})\text{O}_3$ (solid line) and $\text{YAG}:\text{Ce}^{3+}$ (P46) (broken line) excited at 460 nm.

containing another alkaline metal ion. Unfortunately, the reasons for the increase in the luminescence intensity are not clear at this moment.

Figure 8 shows the PLE spectra of $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.69}\text{Ge}_{0.30}\text{Mn}_{0.01})\text{O}_3$ and $\text{YAG}:\text{Ce}^{3+}$ (P46) excited at 460 nm. The relative luminescence intensity of $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.69}\text{Ge}_{0.30}\text{Mn}_{0.01})\text{O}_3$ compared with that of $\text{YAG}:\text{Ce}^{3+}$ (P46) was approximately 70%. In addition, this $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.70}\text{Ge}_{0.30})\text{O}_3:\text{Mn}^{4+}$ phosphor is excited by blue light and exhibits red emission efficiently.

Conclusions

$\text{Li}_2\text{TiO}_3:\text{Mn}^{4+}$ phosphors treated with various alkaline metal carbonates exhibited efficient deep red emission. The luminescence intensities of $(\text{Li}_{0.97}\text{A}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Rb) were higher than that of $\text{Li}_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$. From the XRD and SEM results, two possible explanations can be proposed. One is that the alkaline metal carbonate worked as flux. The other is that a nominal amount of alkaline metal ions were doped into the Ti^{4+} sites, and the local crystal field around Mn^{4+} ion was slightly affected. Additionally, the

$(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.69}\text{Ge}_{0.30}\text{Mn}_{0.01})\text{O}_3$ phosphor showed higher emission intensity than that of $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$, and the relative luminescence intensity of this phosphor compared with that of $\text{YAG}:\text{Ce}^{3+}$ (P46) was approximately 70%. These results indicate that the red-emitting $(\text{Li}_{0.97}\text{Rb}_{0.03})_2(\text{Ti}_{0.70}\text{Ge}_{0.30})\text{O}_3:\text{Mn}^{4+}$ phosphor is a promising candidate for white LEDs.

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