FULL PAPER

Synthesis of Li–Ta–Ti–O new red phosphors with Mn^{4+} as activator and the relationship between photoluminescence intensity and crystal structure

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In the Li_2O – Ta_2O_5 – TiO_2 system, $\text{Li}_{1+x-y}\text{Ta}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ ($0.14 \leq x \leq 0.175$, $0.04 \leq y \leq 0.175$) forms a superstructure by periodical insertion of an intergrowth layer in a matrix having a trigonal structure. In this study, to apply this unique structure as a host material of phosphor, new phosphors with a red emission color were synthesized by doping Mn^{4+} ion. The phosphor emitted at around 685 nm excited by 493 nm. The photoluminescence (PL) intensity closely related to the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ion because the ratio changed by sintering temperature and/or Ti content in the matrix. The relationship between PL intensity and crystal structure was investigated using X-ray diffraction, a transmission electron microscope, and X-ray absorption fine structure.

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1. Introduction

In the Li_2O – Ta_2O_5 – TiO_2 system, $\text{Li}_{1+x-y}\text{Ta}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ ($0.14 \leq x \leq 0.175$, $0.04 \leq y \leq 0.175$) (LTT) forms a superstructure known as the M-phase, by periodical insertion of an intergrowth layer in a matrix having a trigonal structure.¹⁾ The unique structure is formed by a self-organized regular array and the period can be controlled by Ti concentration. It has been reported that the superstructure's area of LTT (Li_2O – Ta_2O_5 – TiO_2) is narrower than that of LNT (Li_2O – Nb_2O_5 – TiO_2).^{2),3)} It is necessary to synthesize repeatedly many times to obtain homogeneous materials, depending on the composition of LTT.⁴⁾ (Some materials require 10 days of sintering.) Therefore, we focused an air-pressure atmosphere control furnace (AAF) to synthesize in a shorter time. The AAF was developed jointly with a local company (FULL-TECH FURNACE CO., Ltd.), and succeeded in synthesizing the homogeneous materials in only 30 min.⁵⁾ Next, this unique material was applied to the host material of new phosphor doped rare-earths (RE^{3+} : Eu, Er, Tb, Tm, or Dy).⁶⁾ Among them, the red phosphor of Eu^{3+} doped LTT especially showed highly efficient red-light emission upon excitation at 399 nm, with an internal quantum efficiency of 98%.^{7),8)} The material, including Ti ion cannot be synthesized under

reduction atmosphere because it is darkened by the Ti^{3+} ion. Therefore, we did not use Eu^{2+} ion as an activator for the phosphor.

Therefore, we focused on phosphors with Mn^{4+} doped as an activator. The Mn^{4+} ion is well known as an activator of red phosphors. Among the most well-known phosphors are $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ ⁹⁾ and $\text{CaAl}_2\text{O}_9\text{:Mn}^{4+}$.¹⁰⁾ 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,¹¹⁾ Mn^{4+} doped phosphors could be promising candidates for the red emitting phosphor in tri-color white light emitting diodes. However, in general, fluoride phosphors are problematic, with low chemical stability, and are difficult to synthesize. On the other hand, oxide phosphors with Mn^{4+} ion have a high chemical stability and are easy to synthesize, but few papers have been reported.

Given the above, we focused on the new red phosphor of Mn-doped LTT. At first, we synthesized on Li_2TiO_3 : Mn^{4+} phosphor in Li–Ta–Ti–O system,¹¹⁾ and analyzed the photoluminescence (PL) property. Next, we investigated the LTT:Mn phosphors based on the data obtained from the Li_2TiO_3 :Mn phosphor. The new phosphors were analyzed in detail using PL spectrophotometer, X-ray diffraction (XRD), transmission electron microscope (TEM) and X-ray absorption fine structure (XAFS) by a synchrotron beam. In this paper, we discuss how to improve the

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PL intensity from the viewpoint of composition, Mn⁴⁺/Mn³⁺ ratio and crystal structure.

2. Experimental procedures

The starting materials used to prepare the phosphors were Li₂CO₃, Ta₂O₅, TiO₂ and MnO₂ (>99.9% grade). The compositions of Li₂TiO₃:Mn phosphor prepared in this work followed Li₂(Ti_{0.98}Mn_{0.02})O₃. The starting powders were well mixed by planetary ball milling (P-6, Fritsch Japan Co., Ltd.). The mixed and pressed powders were calcined at 1073 K for 5 h and continuously sintered at 1273 to 1473 K for 15 h in a conventional electric furnace (EF) in air. The compositions of the LTT solid solutions prepared in this work followed the general formula Li_{1+x-y}Ta_{1-x-3y}Ti_{x+4y}O₃ with 0.00 ≤ *x* ≤ 0.33, 0.00 ≤ *y* ≤ 0.11. MnO₂ was doped as an activator at 0.2 wt%. The starting powders were well mixed by planetary ball milling. The mixed and pressed powders were calcined at 1073 K for 5 h. After that, the bulk were sintered at 1273 to 1423 K for 24 h in EF, and sintered at 1273 to 1373 K for 30 min to 3 h in AAF. Excitation and emission spectra were obtained using a PL spectrophotometer (F-7000 Hitachi, Japan). Crystal structure analysis was carried out by XRD using a RINT 2500 (Rigaku Co., Ltd., Japan). The angles were corrected by an external standard method for calculation of the lattice parameters. Microstructure images were observed with a scanning electron microscope (JSM-IT100, JEOL, Ltd., Japan). High-resolution TEM images and selected area electron diffraction (SAED) patterns were also observed by a device (2100-F, JEOL Co., Ltd., Japan). XAFS and X-ray absorption near edge structure (XANES) were obtained using a synchrotron radiation (Aichi Synchrotron Radiation Center, Beam line 11S2). XAFS spectra were simulated using the Athena program. (Mn₂O₃ was used as standard sample for Mn³⁺, Li₂MnO₃ was used as standard sample for Mn⁴⁺.)

3. Results and discussion

The Li₂TiO₃:Mn phosphors were sintered at 1273 to 1473 K for 15 h. **Figure 1** shows the excitation and emission spectra of Li₂TiO₃:Mn phosphors at various sintering temperatures. These phosphors emitted a red colour around

Fig. 1. Excitation and emission spectra of Li₂TiO₃:Mn phosphors at various sintering temperatures.

685 nm excited by 498 nm. This phosphor shows the excitation peak around at 495 nm assigned to the ⁴A₂ → ⁴T₂ transition of Mn⁴⁺, and an emission peak around at 680 nm assigned to the ²E → ⁴A₂ transition.¹¹⁾ As a result, the sample sintered at 1273 K showed the highest PL intensity, but PL intensity decreased as the sintering temperature increased. In order to clarify the cause, we analysed the crystal structure by XRD measurement. **Figure 2** shows the XRD pattern of Li₂TiO₃:Mn phosphors at various sintering temperatures. As the result, all peaks of the XRD pattern were indexed based on the Li₂TiO₃ phase at 1473 K. However, it was difficult to observe the peaks around (020) because of broader peaks at 1273 K. Previous studies reported that PL intensity increases with an increase crystallinity.¹²⁾ However, the relationship between crystallinity and PL intensity could not be found, as shown in Fig. 2.

Therefore, we measured XANES spectra Mn *K*-edge. **Figure 3** shows the XANES spectra of Mn *K*-edge for Li₂TiO₃:Mn phosphors at 1273 and 1473 K. The difference in the oxygen concentration around manganese was calculated the ratio of Mn⁴⁺/Mn³⁺. Standard manganese oxides, Mn₂O₃ (Mn³⁺) and Li₂MnO₃ (Mn⁴⁺), were used. The Mn *K*-edge XANES peaks shifted to the higher energy side with an increase in the valence of the manganese ion. Specific peaks were observed at 6556 eV for Mn₂O₃ and 6560 eV for Li₂MnO₃. The Mn⁴⁺/Mn³⁺ ratio in the experimental phosphor was calculated by spectral fitting

Fig. 2. XRD patterns of Li₂TiO₃:Mn phosphors at various sintering temperatures.

Fig. 3. XANES spectra of Mn *K*-edge for Li₂TiO₃:Mn phosphors sintered at 1273 and 1473 K.

Fig. 4. Ternary phase diagram of Li_2O – TiO_2 – Ta_2O_5 .

Fig. 5. Excitation and emission spectra of LTT:Mn (No. 3 in Fig. 4).

using the Athena program.¹³⁾ As a result, the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio was 100 and 72% at 1273 and 1473 K, respectively. Increasing the sintering temperature, decreased the ratio of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ because the oxygen concentration was lower at the higher temperature. This is because the oxygen concentration decreased as the sintering temperature increased. This result clarified that the sintering condition was needed to increase the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio in order to improve the PL intensity.

Next, LTT:Mn phosphors were synthesized at 6 point, as shown in Fig. 4. In the oblique line area of Fig. 4, LTT forms with a superstructure.^{14),15)} Therefore, the crystal structures of compositions No. 1–4 were a LiTaO_3 type structure and the compositions of No. 5 and 6 possessed the superstructure. The compositions of the host materials were $\text{Li}_{1.11}\text{Ta}_{1.89}\text{Ti}_{0.11}\text{O}_3$, $\text{Li}_{1.25}\text{Ta}_{0.75}\text{Ti}_{0.25}\text{O}_3$, $\text{Li}_{1.33}\text{Ta}_{0.67}\text{Ti}_{0.33}\text{O}_3$, $\text{Li}_{1.08}\text{Ta}_{0.80}\text{Ti}_{0.23}\text{O}_3$, $\text{Li}_{1.06}\text{Ta}_{0.75}\text{Ti}_{0.30}\text{O}_3$, and $\text{Li}_{1.01}\text{Ta}_{0.58}\text{Ti}_{0.53}\text{O}_3$. Figure 5 shows the excitation and emission spectra of LTT:Mn phosphor (No. 3). The phosphor emitted a red color around 685 nm, excited by 493 nm like $\text{Li}_2\text{TiO}_3\text{:Mn}$ phosphor. The relationship between PL intensity and Ti content is shown in Fig. 6. In the LiTaO_3 structure, the PL intensity increased with an increase in the Ti content. On the other hand, if the superstructure formed at No. 5 and 6, the PL intensity clearly decreased.

In order to clarify the relationship between PL and composition, we focused on the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio. $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio was measured by Mn *K*-edge of XANES using

Fig. 6. PL intensity (at 685 nm) of LTT:Mn phosphors.

Fig. 7. XANES spectra of Mn *K*-edge for LTT:Mn phosphors.

Table 1. Mn^{4+} ratio of LTT:Mn phosphors

Phosphor	No. 1	No. 3	No. 5	No. 6
Ti (wt %)	10	25	25	40
Mn^{4+} ratio	42%	58%	43%	22%

a synchrotron beam, as shown in Fig. 7. Table 1 shows the calculation results of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio. The results showed that the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio was closely related to the PL intensity in LTT:Mn phosphor.

Here, the Ti content was the same, with 25 mol % at No. 3 and No. 5, but PL intensity and $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio was obviously different. We discussed the relationship between the superstructure and the PL intensity. Figure 8 shows the TEM and SAED patterns of compositions at No. 3 and No. 5. The crystal structure of No. 3 is an LiTaO_3 type structure. In No. 5, intergrowth layers were inserted into the superstructure along the *c*-axis. The authors have reported that the intergrowth layers were composed of Ti^{3+} ions, although in the LiTaO_3 matrix, Ti^{4+} ion was observed using TEM/EELS.¹⁶⁾ The crystal structure of the intergrowth layer was $[\text{Ti}_2\text{O}_3]^{2+}$ corundum-type and the single layers were inserted in the trigonal matrix of LiTaO_3 type. Therefore, the oxygen concentration was different after the superstructure was formed along the intergrowth layers. Figure 9 shows the XAFS spectra of Mn *K*-edge for No. 3

Fig. 8. TEM image and SAED patterns taken from the [100] axis of LTT:Mn phosphors with Ti 25 mol %, (a) No. 3 with LiTaO_3 type structure and (b) No. 5 with superstructure.

Fig. 9. XAFS spectra of Mn *K*-edge for LTT:Mn phosphors (No. 3 and No. 5 in Fig. 4).

and No. 5. The XAFS data also showed that the oxygen content of No. 5 was lower than that of No. 3. The second peak of No. 5 was also low, caused by the two types of structure: one was a matrix composed of LiTaO_3 and the second was intergrowth layer composed of corundum-type structures. From this result, we inferred that the PL intensity was different because Mn coordination environment changed due to superstructure formation. Further, it has been found that the particle's morphology changes, from spherical-like to plate-like, when the superstructure is formed, and the crystal anisotropy increases since the lattice constant decreases in the *c*-axis direction.¹⁷⁾ The *c*-axis of LTT with TiO_2 content of 1.379 nm for 20%, for 1.347 nm for 25% and 1.325 nm for 40%, and the *c*-axis decreased forming many intergrowth layers.¹⁷⁾ In the LTT: Eu^{3+} phosphor, in previous research we showed that the eccentricity of Eu at the crystal site increases as the PL intensity increases.^{8),16)} The Eu ion occupied in the Li site, and we calculated the eccentricity (centroid-to-cation distance) as a distortion parameter value of the $(\text{Li}, \text{Eu})\text{O}_{12}$ polyhedron from the refined structure using the Rietveld method. The LTT: Eu^{3+} phosphor with the highest PL intensity showed the largest centroid-to-cation distance value.⁸⁾ From the results, we considered two reasons for the lowering of the PL intensity, one was a low Mn^{4+} ratio, and second was a low eccentricity of Mn ion in the Ta site.

Fig. 10. Relationship between PL intensity (at 685 nm) and air pressure of AAF for Li_2TiO_3 :Mn phosphors.

Finally, we tried to use an AAF, and investigated the effect of oxygen partial pressure on PL intensity. The AAF can be controlled from 0.10 to 0.60 MPa; an oxygen concentration is corresponded to 0.21–1.13 atm.⁵⁾ We established a rapid sintering technique for $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5-\text{TiO}_2$ (LNT) solid solution using the AAF.⁵⁾ It was found that the optimal gas pressure was 0.35 MPa for LNT, and the superstructure with homogeneous periods was synthesized rapidly. We considered that interstitial oxygen could promote oxygen diffusion with a combination of vacancies along the intergrowth layer, and accordingly, grain growth surprisingly improved by controlling air pressure. In the Li_2TiO_3 :Mn phosphor, the highest PL intensity was obtained under 0.40 MPa, as shown in **Fig. 10**. We synthesized No.3 of the LTT:Mn phosphor using AAF under 0.40 MPa, which is the highest PL intensity in EF. We synthesized the No. 3 of LTT:Mn phosphor with the highest PL intensity in EF and compared the results to EF. **Figure 11** shows the excitation and emission spectra of the No. 3 of LTT:Mn phosphor that was synthesized by EF and AAF. The sintering was performed at 0.40 MPa for 2 h, which was optimal conditions for AAF. We succeeded in synthesizing a phosphor that showed about 1.6 times the PL intensity in a short sintering time of only 1/12 compared to EF. This short time sintering has been reported about LNT.⁵⁾ In order to understand the mechanism of the high PL intensity, XANES was used to measure the LTT:Mn phosphors synthesized by EF and AAF. **Figure 12** shows

Fig. 11. Excitation and Emission spectra of LTT:Mn phosphor (No. 3 in Fig. 4) synthesized by a conventional EF (black line) and an air-pressure control atmosphere furnace (red line).

Fig. 12. XANES spectra of Mn K-edge for LTT:Mn phosphors synthesized by a conventional EF (solid line) and an air-pressure control atmosphere furnace (dotted line).

the XANES spectra of Mn K-edge for LTT:Mn phosphors synthesized by EF and AAF. From the results, it was found that the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio was 58 and 66% in EF and AAF, respectively, and the 0.4 MPa of the pressure field was effective for increasing the PL intensity.

4. Conclusions

$\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-\text{TiO}_2$ system, $\text{Li}_{1+x-y}\text{Ta}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ ($0.14 \leq x \leq 0.175$, $0.04 \leq y \leq 0.175$) (LTT) forms a superstructure, known as smart material. In this work, we tried a new red phosphor using LTT solid solution as the host material and Mn^{4+} ions as an activator. We examined the results from the viewpoint of composition, Mn^{4+} ratio

and crystal structure and compared them to $\text{Li}_2\text{TiO}_3:\text{Mn}^{4+}$ phosphor.

1. The PL intensity of Mn^{4+} -based phosphor was closely related to the Mn^{4+} ratio.
2. The PL intensity increased with increasing Ti content in the LiTaO_3 structure.
3. The superstructure reduced the PL intensity. This was caused by oxygen deficiency and low eccentricity of the Mn ion in Ta site.
4. Using an AAF, it was possible to sinter in a shorter time than with a conventional EF, and a phosphor with high PL intensity was successfully synthesized.

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