Quantitative Determination of the Effective Mn\(^{4+}\) Concentration in a Li\(_2\)TiO\(_3\):Mn\(^{4+}\) Phosphor and Its Effect on the Photoluminescence Efficiency of Deep Red Emission

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ABSTRACT: Obtaining highly efficient photoluminescence with Mn\(^{4+}\)-activated phosphors, which have been extensively studied in diverse lighting devices, requires the precise control of the manganese valence states. However, this control is difficult to achieve because manganese ions can have various valence states ranging from divalent to heptavalent. Additionally, the concentrations of Mn ions in each valence state, especially the effective Mn\(^{4+}\) concentration, have never been quantitatively determined in a phosphor crystal lattice. The relationship between the effective Mn\(^{4+}\) concentration and the luminescence properties of Mn\(^{4+}\)-activated phosphors is of current interest for improving the phosphor properties. In the present study, the effective Mn\(^{4+}\) concentration in Li\(_2\)TiO\(_3\):Mn\(^{4+}\) (LTO:Mn) phosphors prepared by the sol–gel method with heating at various temperatures was quantitatively analyzed by X-ray absorption near-edge spectroscopy. Moreover, the effect of the existence of Mn\(^{2+}\), Mn\(^{3+}\), and Mn\(^{4+}\) ions on the photoluminescence efficiency was investigated. The effective Mn\(^{4+}\) concentration was found to be over 60% in all phosphor samples. The quantum efficiencies (QEs) of all LTO:Mn phosphors strongly depend on the effective Mn\(^{4+}\) concentration. In particular, the LTO:Mn phosphor prepared by heating at 800 °C (LTO:Mn@800) contained the highest effective Mn\(^{4+}\) concentration of 98.1% and exhibited the highest internal QE of 31.6%. The results of this work provide new and important insights for the development of Mn\(^{4+}\)-activated phosphors with high efficiency.

INTRODUCTION

A manganese (Mn) ion takes multiple valence states from divalent to septavalent. Since a tetravalent manganese ion, Mn\(^{4+}\), exhibits (deep) red emission under visible-light excitation, it has been widely applied to many fields, including lighting, holographic recording, and thermoluminescence dosimetry. In addition, it has a high potential to replace Eu\(^{3+}\)-doped phosphors from a cost-effective point of view because Mn\(^{4+}\) has photoluminescence properties similar to those of Eu\(^{3+}\) in inorganic phosphor materials with high quantum efficiency (QE) and high-purity red emission under visible-light irradiation. Mn\(^{4+}\)-doped oxide phosphors have been extensively investigated in many host materials. Although some Mn\(^{4+}\)-activated oxide phosphors exhibit deep red emission due to the \(\text{Eu}^{2+} \rightarrow \text{Eu}^{4+}\) transition under UV-light irradiation, the emission efficiency excited by visible-light irradiation is significantly lower than that excited by UV-light irradiation. Therefore, Mn\(^{4+}\)-activated oxide phosphors have not been commercialized for devices that enable visible-light excitation. To overcome such disadvantages, the enhancement of the emission intensity excited by visible-light irradiation has been investigated using various techniques as follows: Bi\(^{3+}\)–Mn\(^{4+}\) energy transfer generated by Bi\(^{3+}\) doping, the modification of chemical compositions, and the control of morphology. The improvement in the luminescence efficiency under visible-light excitation has also been investigated by suppressing lower oxidation state manganese ions, such as Mn\(^{2+}\) and Mn\(^{3+}\), which can act as quenching ions for the luminescence of Mn\(^{4+}\), i.e., an increase in the “effective Mn\(^{4+}\) concentration”. The following two types of techniques are known for their enhancement of the effective Mn\(^{4+}\) concentration: a charge compensation technique involving...
the doping of heterogeneous metal ions, $M^{2+}$ ($M^{2+}$:Mg$^{2+}$ and Zn$^{2+}$) ions and Mn$^{4+}$ in aluminate hosts,$^{11,12}$ and oxygen-pressure annealing processing.$^{13}$ A Mn$^{4+}$ ion involuntarily incorporates into Al$^{3+}$ due to charge compensation when Mn$^{4+}$ is doped into Al$^{3+}$ sites in a typical CaAl$\text{12}$$\text{O}_{19}$ host, and Mg$^{2+}$ is added simultaneously to the Al$^{3+}$ site to suppress the production of Mn$^{2+}$ by charge compensation in CaAl$_{12}$O$_{39}$:Mn$^{4+}$ phosphors.$^{11}$ The emission intensity of Mn$^{4+}$ ions involuntarily added simultaneously to the Al$^{3+}$ site to suppress the rock-salt structure.$^{17}$ Therefore, the LTO:Mn phosphor is the Mn$^{4+}$ activator into the TiO$_6$ octahedral site.$^{19,20}$ Lithium manganate(IV), Li$_2$MnO$_3$, which is completely substituted by Mn$^{4+}$-activated phosphors can enhance the photoluminescence intensity. In these investigations, Mn$^{4+}$ in phosphors has been analyzed by only qualitative analyses using some techniques, such as X-ray photoelectron spectroscopy, electron spin resonance, and X-ray absorption near-edge structure (XANES).$^{9,11,14−16}$ In addition, these reports provided no direct information regarding the relationship between the effective Mn$^{4+}$ concentration and the photoluminescence properties in a phosphor lattice. The direct and quantitative determination of the Mn$^{4+}$ ion, namely, the effective Mn$^{4+}$ concentration, in phosphor materials is highly important for understanding the Mn$^{4+}$-dependent enhancement of luminescence efficiency.

Recently, we focused on the Li$_2$TiO$_3$:Mn$^{4+}$ (LTO:Mn) phosphor as a good material to perform a quantitative analysis of the effective Mn$^{4+}$ concentration and investigate the relationship between the effective Mn$^{4+}$ concentration and photoluminescence properties. The Li$_2$TiO$_3$ host is composed of a layered rock-salt structure,$^{17}$ which is a sandwich of the two-dimensional layer of [(Li,Ti)O$_6$]octahedra and Li$^+$ ions.$^{18}$ The Mn$^{4+}$-doped Li$_2$TiO$_3$ phosphor shows a red emission with a maximum peak at approximately 680 nm by incorporating the Mn$^{4+}$ activator into the TiO$_6$ octahedral site.$^{19,20}$ Lithium manganate(IV), Li$_x$MnO$_3$, which is completely substituted by Mn instead of Ti in the Li$_2$TiO$_3$ host, also has the same layered rock-salt structure.$^{17}$ Therefore, the LTO:Mn phosphor is suitable for investigating the relationship between the effective Mn$^{4+}$ concentration and the photoluminescence properties without considering drastic changes in the main structure. LTO:Mn phosphors have potential as red-emitting phosphors for white light-emitting diodes and have been studied for the enhancement of the photoluminescence intensity by doping heterogeneous ion species, such as different alkali ions, Ge$^{4+}$ and Zn$^{2+}$.$^{15}$ However, the mechanism underlying the enhancement in the luminescence intensity is still unclear because the valence state of the manganese ions in the phosphors has not been determined. In the present study, the manganese ion valence state in high-quality LTO:Mn phosphors prepared by the sol−gel method was studied. In addition, we investigated the relationship between the photoluminescence properties and the manganese ion valence state determined by a quantitative analysis of X-ray absorption near-edge structure (XANES) spectra using the Athena program.$^{21}$

■ RESULTS AND DISCUSSION

Field-emission scattering electron microscopy (FE-SEM) images were employed to determine the morphological information and chemical composition of the typical LTO:Mn@800 phosphor (Figure S1a). The LTO:Mn phosphors have cubic or spherical particles, which are grown by an increase in the heating temperature (Figure S2). The particle of the LTO:Mn phosphor has a spherical morphology with a diameter of ∼500 nm. Generally, the spherical morphology enhances the luminescence efficiency generated from the improvement in the light-extraction efficiency. The signal of the lithium element cannot be observed in the energy-dispersive X-ray (EDX) because of its light atomic mass. According to the EDX spectrum of the LTO:Mn@800 phosphor, Ti and O can be clearly observed in the spectrum (Figure S1c). From the estimation of the chemical composition by the ZAF method by the energy-dispersive X-ray spectrometry (EDS) results, the elemental ratio of Mn/(Ti + Mn) was 8.9 × 10$^{-3}$ (0.89 mol %), indicating that approximately 1 mol % manganese was introduced into the Li$_2$TiO$_3$ host for the LTO:Mn phosphors. Additionally, it could be confirmed that Ti, O, and Mn were uniformly dispersed in the particles of a typical LTO:Mn@800 phosphor (Figure S1d–g). A refinement for the detailed crystallographic data of a typical LTO:Mn@800 phosphor was carried out using the Rietveld technique with a conventional XRD profile (Figure 1a). In the XRD pattern, the broad pattern consisting of

![Figure 1](image-url)
and this technique is generally used to analyze the Rietveld method for isostructural materials with Li2TiO3 and Li2MnO3. The refined results for the $R$ factors and $S$ values for all LTO:Mn phosphors prepared at different temperatures (600–1000 °C) are summarized in Table S1 and agree with the phase determination based on the powder XRD data. The results suggest that the crystal structure of all phosphor samples could be successfully refined to be similar (Figure S3). The crystal phases of all LTO:Mn phosphors were confirmed by the XRD patterns and Raman spectra. Figure 1b shows the XRD patterns for LTO:Mn phosphors prepared at various temperatures. All XRD peaks of all phosphors were characterized to be the well-known monoclinic Li2TiO3 phase as a single phase. Significant XRD peak shifts were not observed. Additionally, the XRD peak intensities for the LTO:Mn@600 and @700 samples were weaker than those for the samples calcined at higher temperatures because sufficient crystal growth did not occur in the low-temperature treatment. All peaks in the Raman spectra for the LTO:Mn@600–@900 samples were attributed to the Li2TiO3 phase (Figure 1c), whereas the weak Raman peak in the Raman spectrum for the LTO:Mn@1000 sample was observed at approximately 820 cm$^{-1}$, corresponding to the bending motion of Ti−O−Si in the Li$_2$TiSiO$_5$ phase,\textsuperscript{23} in which the Si element is a contaminant from the reaction boat.

To quantitatively determine an effective concentration for trace Mn$^{4+}$ ions in the crystal lattice of LTO:Mn phosphors, we measured the XANES spectra for these phosphor samples. Figure 2 shows the Mn $K$-edge XANES spectra in the energy range from 6520 to 6600 eV of the LTO:Mn phosphors as well as the standard compounds composed of various valence manganese ions with the octahedral MnO$_6$ unit (MnCO$_3$, Mn$_2$O$_3$, and Li$_2$MnO$_3$). The XANES spectrum of Li$_2$MnO$_3$ was similar to that of the MnO$_2$ standard sample (Figure S4). Here, Li$_2$MnO$_3$ was more suitable as the standard sample for Mn$^{4+}$ than MnO$_2$, although MnO$_2$ is often used as the Mn$^{4+}$ standard sample because the coordination environment surrounding Mn$^{4+}$ is close to that in LTO:Mn phosphors. Therefore, fitting the XANES spectra of LTO:Mn phosphors using Li$_2$MnO$_3$ could yield better results. In standard manganese oxide compounds, 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 6548 eV for MnCO$_3$ (Mn$^{2+}$), 6555 eV for Mn$_2$O$_3$ (Mn$^{3+}$), and 6557 eV for Li$_2$MnO$_3$ (Mn$^{4+}$), which are in good agreement with reported XANES spectra.\textsuperscript{24,25} Because the maximum peak in the XANES spectra for all LTO:Mn samples matches the peak at 6557 eV observed for Li$_2$MnO$_3$ due to the Mn$^{4+}$ ion, most of the manganese ions doped in the phosphor crystal lattice should exist as Mn$^{4+}$. However, the shoulder peak attributed to the Mn$^{3+}$ ion was also observed at 6548 eV. Although all LTO:Mn samples contain Mn$^{4+}$, the LTO:Mn@800 sample contains less Mn$^{2+}$ based on the shoulder peak intensities. Thus, it is suggested that the LTO:Mn@800 sample should have a relatively high concentration of Mn$^{4+}$. The discrete concentrations of the manganese ions in each oxidation state doped in the phosphor samples were estimated from spectral fitting using the Athena program\textsuperscript{21} based on the spectra of standard compounds with various oxidation states, as shown in Table 1. Although Mn$^{4+}$, Mn$^{3+}$, and Mn$^{2+}$ were contained in all phosphor samples, most manganese ions were present as Mn$^{4+}$. Particularly, the LTO:Mn@800 sample contained the highest effective concentration of Mn$^{4+}$ (98.1%) among all of the samples. The effective Mn$^{4+}$ concentration in the LTO:Mn@1000 sample drastically decreased because the manganese ion incorporates as a lower valence state into the impurity Li$_2$TiSiO$_5$ phase. Additionally, the average values of the bond valence sum (BVS) for Ti sites in the LTO:Mn phosphors are listed in Table 1. The LTO:Mn@600 sample had the lowest average BVS value, indicating that it contained more Mn$^{2+}$ and Mn$^{3+}$ than the other phosphors. The average BVS values of the Ti sites corresponded to the result of the XANES analysis. Therefore, the values of the effective Mn$^{4+}$ concentration obtained from XANES analysis were reasonable because they matched well with the trends of the BVS values of the Ti sites.

Figure 3a shows the diffuse reflectance (DR) spectra for the Li$_2$TiO$_3$ host and LTO:Mn phosphors. In the Li$_2$TiO$_3$ host, a strong optical absorption can be observed in the deep UV region from 200 to 300 nm due to a charge-transfer state (CTS) between the Ti$^{3+}$ and O$^{2−}$ ions, while the optical absorption of the LTO:Mn phosphors is close to zero but higher than the host because the CTS state is quenched by the manganese ions. The CTS peak in the LTO:Mn phosphors decreased with increasing temperature, and the relative decrease was greater in the LTO:Mn@800 sample.

### Table 1. Content of the Effective Concentrations of Manganese Ions Determined from Spectral Fitting Using the Spectra of Standard Compounds by the Athena Program and Bond Valence Sum (BVS) Values Estimated Using the Results of the Rietveld Refinement of the LTO:Mn Phosphors

| samples         | effective concentration (%) | BVS   |
|-----------------|-----------------------------|-------|
|                 | $\text{Mn}^{4+}$ | $\text{Mn}^{3+}$ | $\text{Mn}^{2+}$ | Ti site | Ti$^{3+}$ site | avg   |
| LTO:Mn@600     | 64.8         | 28.3         | 6.8           | 3.42   | 3.50           | 3.46  |
| LTO:Mn@700     | 95.0         | 5.0          | —             | 3.74   | 4.05           | 3.90  |
| LTO:Mn@800     | 98.1         | 1.9          | —             | 3.87   | 4.21           | 4.04  |
| LTO:Mn@900     | 96.5         | 3.5          | —             | 3.90   | 4.08           | 3.99  |
| LTO:Mn@1000    | 74.7         | 23.5         | 1.8           | 3.87   | 4.06           | 3.97  |
| LTO-SSR@1000   | 89.4         | 10.6         | —             | 3.63   | 3.77           | 3.70  |

![Figure 2. Mn $K$-edge XANES measurements for (a) LTO:Mn phosphors (inset: enlargement of XANES spectra in the range from 6545 to 6555 eV) and (b) standard samples containing various Mn valence states: MnCO$_3$, Mn$_2$O$_3$, and Li$_2$MnO$_3$.](image-url)
absorption edge was at 305.0 nm (4.07 eV) from the spectrum transferred by the Kubelka–Munk function, as shown in Figure S5. All LTO:Mn phosphors exhibited the three specific major optical absorption bands for Mn⁴⁺, such as the ⁴A₂ → ⁴T₁ and ⁴A₂ → ⁴T₂ transitions and R-lines, in addition to the CTS of the Li₂TiO₃ host. Furthermore, the Mn⁴⁺–O²⁻ CTS band is probably located in the deep UV range below 300 nm, with an overlap with the Ti⁴⁺–O²⁻ CTS in the Li₂TiO₃ host because the CTS between Mn⁴⁺ and O²⁻ is usually observed in the spectral region from 200 to 300 nm.²⁶ Photoluminescence (PL) and its excitation (PLE) spectra for the LTO:Mn phosphors are shown in Figure 3b. In all LTO:Mn phosphors, the PLE spectra monitored at the deep red emission at 680 nm consisted of two typical broad bands at 300–600 nm, which are ascribed to the ⁴A₂ → ⁴T₁ and ⁴A₂ → ⁴T₂ spin-allowed transitions of Mn⁴⁺ ions with peaks at approximately 321 and 470 nm, respectively.²⁷ These optical absorption bands of the phosphors due to Mn⁴⁺-derived absorptions correspond well to those from the DR spectrum. In the PL spectra of all LTO:Mn phosphors, two peaks were observed at 680 and 695 nm, corresponding to the ²E → ⁴A₂ transition of Mn⁴⁺. Dramičanin et al. reported an investigation of the detailed luminescence properties of Li₂TiO₃:Mn⁴⁺.²⁸ According to their report, the ²E → ⁴A₂ PL emission is located at 688 nm and the PLE bands due to the ⁴A₂ → ⁴T₁ and ⁴A₂ → ⁴T₂ transitions are located at approximately 28 000 (~350 nm) and 18 000–20 000 cm⁻¹ (500–550 nm), respectively. The PL and PLE positions in the LTO:Mn phosphors in this study were similar to those reported in LTO:Mn phosphors.²⁰,²⁹ In particular, the LTO:Mn@800 phosphor sample showed the highest PL and PLE intensities of all samples. The relative peak intensity from the visible-light region to that of the UV region for

LTO:Mn@900 and @1000 is weaker than that for LTO:Mn@800 (Figure S6). The PL intensities of the samples of LTO:Mn@900 and @1000 should decrease due to reabsorption of PL photons, and as a result, the baselines in the DR spectra for the LTO:Mn@900 and @1000 phosphors have a lower intensity than that for the LTO:Mn@800 phosphors. Absorbances and quantum efficiencies (QEs) under excitation at 477 nm for LTO:Mn phosphors are summarized in Table 2. Although no difference was clearly observed in the absorbance for all samples prepared at various temperatures, the internal QEs obviously changed depending on the calcination temperature. The internal QE of LTO:Mn@800 was the highest (31.6%) among all samples; in addition, the variation trend in the internal QE values was close to that in the PL intensities.

Furthermore, the PL intensity and internal QE under visible-light excitation were plotted against the calcination temperature, as shown in Figure 4a. The PL intensity and QE change in response to the effective Mn⁴⁺ concentration, and the relative PLE intensity changes from the visible-light region to the UV region due to the ⁴A₂ → ⁴T₂ transition in a trend similar to that of the PL intensity for all phosphors. We successfully demonstrated that the PL and PLE intensities are

Figure 3. (a) DR spectra of LTO host and LTO:Mn phosphors. (b) PL and PLE spectra of LTO:Mn phosphors (solid line).

Figure 4. (a) Heating temperature dependences of the effective Mn⁴⁺ concentration (red vertical bar), PL intensity (green plot), and internal QE (blue plot) of the peak of the ²E → ⁴A₂ transition under the excitation 470 nm transition of the LTO:Mn phosphors. (b) PL decay curves of the ²E → ⁴A₂ transition in the LTO:Mn phosphors.

Table 2. Absorbance and Internal/External QEs for the LTO:Mn Phosphors

| samples     | absorbance (%) | internal QE | external QE | PL decay lifetimes |
|-------------|----------------|-------------|-------------|-------------------|
| LTO:Mn@600  | 66.9           | 7.2 × 10⁻²   | 4.8 × 10⁻²   | 0.0456 0.196     |
| LTO:Mn@700  | 67.5           | 3.1         | 2.1         | 0.0493 0.176     |
| LTO:Mn@800  | 67.3           | 31.6        | 21.3        | 0.0853 0.183     |
| LTO:Mn@900  | 68.5           | 20.7        | 14.2        | 0.0386 0.119     |
| LTO:Mn@1000 | 74.2           | 1.9         | 1.4         | 0.0428 0.108     |
| LTO-SSR@1000| 66.9           | 9.6         | 6.4         | 0.0538 0.141     |

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strongly correlated to the effective Mn$^{4+}$ concentration. The room temperature decay curves of the emission of the $^2E \rightarrow ^4A_2$ transition in the LTO:Mn phosphors are shown in Figure S7. The decay curves were well fitted by the secondary exponential equations, as summarized in Table 2. The faster and slower components in the decay curves can be attributed to the nonradiative energy transfers of the Mn$^{4+} \rightarrow$ killer centers and Mn$^{3+} \rightarrow$ Mn$^{4+}$, respectively.\(^{30,31}\) The PL lifetime of the slower component tends to gradually decrease until LTO:Mn@800 and drastically decrease from LTO:Mn@800. The trend is commonly observed in the Mn$^{4+}$ concentration dependence on the PL lifetime in the conventional phosphors.\(^{32,33}\) However, that of the faster component tends to increase to LTO:Mn@800 and then drastically decrease. The PL decay behavior indicates that the energy transfer from Mn$^{4+}$ to the killer centers can be significantly reduced in the LTO:Mn@800 sample, i.e., the lower-valence manganese ions of Mn$^{2+}$ or Mn$^{3+}$ working as the killer center are incorporated into the LTO:Mn@800 lattice at the lowest concentration.

The LTO:Mn@800 phosphors prepared by the sol–gel method (LTO-SolGel), which have excellent photoluminescence properties, were compared to the LTO:Mn phosphors prepared at 1000 °C by the solid-state reaction method (LTO-SSR). The crystal structure of the LTO-SSR@1000 sample was refined using the XRD profile by a Rietveld analysis, as shown in Figure S7. The XRD profile of the LTO-SSR@1000 phosphor was well fitted to the Li$_2$TiO$_3$ phase. The DR, PL, and PLE spectra of the LTO-SolGel@800 phosphor were also compared to those of the LTO-SSR@1000 sample (Figure S5a). The LTO-SolGel exhibits approximately 2.4 times higher PL and PLE intensities under 480 nm excitation than those of the LTO-SSR, although the PL and PLE spectra of both samples have similar shapes. Furthermore, the internal QE value of the LTO-SSR phosphor was 9.6%, which is 3.3 times lower than that of the LTO-SolGel sample (Table 2). From the DR spectra of both phosphor samples, the LTO-SolGel sample shows a higher optical absorption for the $^4A_2 \rightarrow ^4T_2$ transition and lower baseline absorption than the LTO-SSR phosphor sample, indicating that the LTO-SolGel sample has a higher absorbance for visible light and more suppression of the reabsorption of Mn$^{4+}$ emission than the LTO-SSR phosphor sample. The differences in the optical properties of both samples can also be explained by the effective Mn$^{4+}$ concentration, as shown in Figure S5b. Additionally, the results of the effective Mn$^{4+}$ concentration and BVS values of the Ti sites of LTO-SSR@1000 are shown in Table 1. The BVS values of both Ti sites of the LTO-SSR@1000 sample were found to be around 3.70, which are relatively low than those of LTO-SolGel samples. Additionally, the effective Mn$^{4+}$ concentration in the LTO-SSR@1000 sample was correlated to the BVS values of all samples. The effective Mn$^{4+}$ concentration in the LTO-SSR phosphor sample was 89.4%, which is higher than that of LTO-SolGel@1000 because the impurity phase of Li$_2$TiSiO$_5$ was observed in the LTO-SolGel@1000 phosphor (74.7%); in contrast, the effective concentration was lower than that in the LTO-SolGel@800 sample (98.1%). Only a few percent difference in the effective Mn$^{4+}$ concentration causes a drastic change in the PL intensity. The PL intensity of LTO-SSR sample followed a trend of the effective concentration and BVS values. To evaluate the preparation behavior to form the LTO phosphors, thermogravimetric–differential thermal analysis (TG–DTA) curves for the precursors of both samples were recorded (Figure S8). The TG curve of the precursor for the LTO-SSR sample began to decrease at ∼500 °C, at which the reaction occurs, and an endothermic peak at ∼700 °C was observed. The reaction at higher temperatures will cause sintering of the precursor and form a nonuniform sample. The precursor for the LTO-SolGel sample began to decompose at 100 °C, which was due to the combustion of residual organic components, and the reaction was complete at approximately 550 °C without sintering, similar to the SSR method. Indeed, the high dispersibility of manganese was observed in the LTO-SolGel sample from the electron-probe microanalysis (EPMA) maps, while manganese was segregated in the LTO-SSR sample (Figure S9). Therefore, the uniformity of Mn atoms in phosphors at the atomic level leads to local disproportionation of the manganese valence states as well as a decrease in the PL intensity.

**CONCLUSIONS**

Deep red-emitting Li$_2$TiO$_3$:Mn$^{4+}$ phosphors were successfully prepared via a sol–gel route at various temperatures from 600 to 1000 °C. The morphology, elemental composition, and crystal structure of the phosphors were characterized in detail by FE-SEM, EDS, XRD, and Raman spectroscopy. By analyzing the chemical state for valence states from +2 to +4, even for a small amount of Mn in the lattice, we successfully used XANES to directly analyze and estimate the concentration ratio of discrete valence states of Mn ions. We found that the existence of a small amount of Mn$^{4+}$ or Mn$^{3+}$ leads to a drastic decrease in the quantum efficiency. This analysis technique can be applied to other Mn$^{4+}$-activated phosphors, such as oxides and fluorides. The effective Mn$^{4+}$ concentration in the phosphors is an important key to enhancing the luminescence efficiency. This work should provide a high impact, new concept to develop Mn$^{4+}$-doped oxide phosphors.

![Figure 5](https://example.com/figure5.png)

*Figure 5.* (a) PL and PLE spectra (solid lines) and DR spectra (broken line) for the LTO-SolGel@800 and LTO-SSR@1000 phosphors. (b) Mn$^{4+}$ concentration of the LTO-SolGel and LTO-SSR@1000 phosphors.
EXPERIMENTAL PROCEDURES

Materials. For the synthesis of the citric acid gelation route, lithium nitrate (>98.0%), titanium(IV) butoxide monomer (>95.0%), and manganese(II) acetate tetrahydrate (>99.0%) were purchased from FUJIFILM Wako Pure Chemistry Co.; citric acid anhydride (>98.0%) was purchased from Tokyo Chemical Industry Co., Ltd. For the conventional solid-state reaction (SSR) method, lithium carbonate (>99.0%) and rutile-type titanium (>99.0%) dioxide were purchased from Kojundo Chemical Laboratory Co., Ltd. For the standard samples containing Mn with each valence for the measurement of the XANES spectra, manganese(II) carbonate (99.9% up) and manganese(II) acetate tetrahydrate (>99.0%) were purchased from Kishida Chemical Co., Ltd. and manganese(III) oxide (98%) was purchased from FUCHT Co., Ltd. and manganese(III) oxide (98%) was purchased from Kishida Chemical Co., Ltd.

Synthetic Procedure. The Mn4+-activated \( \text{Li}_2\text{TiO}_3 \) phosphors (LTO:Mn), namely, \( \text{Li}_2\left(\text{Ti}_{0.99}\text{Mn}_{0.01}\right)\text{O}_3 \), were synthesized via a sol–gel method using citric acid as a complexing agent. First, 28.0 mmol citric acid anhydrate (CA) were stirred in 20 mL of deionized water at 80 °C until completely dissolved, and then, 9.25 mmol titanium(IV) butoxide monomer, \( \text{Ti}[	ext{C}_4\text{H}_9]_4 \), was dropwise added into the CA solution. Although a white precipitate was instantly generated by the addition of \( \text{Ti}[	ext{C}_4\text{H}_9]_4 \) the precipitate was dissolved by stirring at 80 °C for a few hours because of the formation of a titanium citrate complex. Then, 18.7 mmol lithium nitrate and 9.34 mmol titanium(IV) butoxide monomer were stirred in 20 mL of deionized water at 80 °C until a transparent gel formed, and then, the gel was heated at 500 °C for 6 h to decompose the organic components. A peach-colored precursor powder was obtained after heating and subsequently calcined in the reaction boat (63% SiO\(_2\)–37% Al\(_2\)O\(_3\)) at various temperatures ranging from 600 to 1000 °C for 6 h in the atmosphere. Here, in this paper, the LTO:Mn phosphors synthesized at several temperatures are described as LTO:Mn@600−1000. The obtained phosphor powder was reground to a fine powder using an agate mortar. Finally, the obtained phosphors were washed with deionized water, filtered, and dried at 60 °C. The LTO:Mn phosphor was also synthesized by the conventional solid-solid-state reaction (SSR) method according to previous reports in the literature. A fine raw material powder of \( \text{Li}_2\text{CO}_3 \), TiO\(_2\), and MnCO\(_3\) was weighed with stoichiometric amounts to create the chemical composition of \( \text{Li}_2\left(\text{Ti}_{0.99}\text{Mn}_{0.01}\right)\text{O}_3 \) and mixed in acetone using the agate mortar. The homogeneous mixture was calcined at 1000 °C for 6 h in air.

Characterization and Apparatus. The morphological information about the phosphors was obtained using field-emission scattering electron microscopy (FE-SEM; JEOL JSM-6500F) observations, and the elemental maps of the Ti, Mn, and O atoms on the particle surface of the phosphor samples were obtained by the energy-dispersive X-ray spectrometry (EDS) method using an FE-SEM electron beam; the measurement samples were coated with platinum by a sputtering treatment to enhance the electron conductivity. The crystal phases of the LTO:Mn phosphor samples were determined by X-ray diffraction (XRD) using an X-ray diffractometer (PANalytical, XPert PRO) with Cu K\( \alpha \) radiation (\( \lambda = 1.54059 \) Å) and Raman spectroscopy (HORIBA Jobin Yvon, T64000) using a continuous-wave Ar laser at a wavelength of 514.5 nm. Additionally, the detailed crystallographic parameters of all samples were refined by the Rietveld technique based on XRD with Cu K\( \alpha \) radiation using the RIETAN-FP program. The diffuse reflectance spectra were recorded using a UV−visible spectrometer (JASCO Corp., V-700) with an integrating sphere attachment. The photoluminescence emission and excitation spectra of the powder phosphor samples were measured by a spectrophotometer (JASCO Corp., FP-6500/6600) equipped with a 150 W Xe lamp as the excitation source at room temperature. The internal/external quantum efficiency (QE) of the phosphor samples was recorded by an instant multi Photomultiplier system (Otsuka Electronics Co. Ltd., MCPD-7000). The Mn K-edge XANES spectra of the phosphor samples and manganese reference samples (MnCO\(_3\), Mn\(_2\)O\(_3\), MnO\(_2\), and Li\(_2\)MnO\(_3\)), which were prepared and pelletized with a boron nitride powder, were recorded with beamline BL15A1 in the Photon Factory (PF) at the High Energy Accelerator Research Organization (KEK), Japan in fluorescence and transmittance modes. The photoluminescence decay curves of the phosphor samples were recorded by a spectrophotometer (Hamamatsu Photonics, Quantaurus-Tau C11367-12) at 365 nm using a Xe flush lamp as the excitation source. The thermal changes in the precursor samples were investigated by thermogravimetry and differential thermal analyses (TG=DTA; TG-2000, Bruker AXS K.K., Japan) in a temperature range from room temperature to 1000 °C under air conditions. The heating rate was 10 °C/min. The elemental mapping of the particle surface was observed by an electron-probe microanalyzer (EPMA: JEOL, JXA-8200).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02798.

EDS mapping; Rietveld refinement; structural parameters; band gap energy calculation; normalized PLE spectra; thermal analysis and EPMA maps of the LTO:Mn phosphors and host materials; Mn XANES measurements of the standard samples, MnO\(_2\) and Li\(_2\)MnO\(_3\) (PDF)

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Notes

The authors declare no competing financial interest.

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