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Rb₂SiF₆:Mn⁴⁺ and **Rb**₂TiF₆:Mn⁴⁺ Red-Emitting Phosphors

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Rb-based hexafluoride red-emitting phosphors, Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺, were synthesized by the coprecipitation method. Optical microscopy observation, X-ray diffraction (XRD) measurement, photoluminescence (PL) analysis, PL excitation (PLE) spectroscopy, and luminescence decay characteristics measurements were used to study the structural and optical properties of the phosphors. The photographs of the bulk samples showed clear crystallographic habits originating from the cubic and trigonal symmetries of the Rb₂SiF₆ and Rb₂TiF₆ hosts, respectively, in agreement with the XRD results. The phosphors exhibited an intense narrow-band Mn⁴⁺ (${}^{2}E_{g} \rightarrow {}^{4}A_{2g}$) red emission with internal quantum efficiencies higher than 90% upon blue light excitation. The Franck–Condon analysis of the PLE data yielded the Mn⁴⁺ intra-*d*-shell transitions to occur at ~2.47 eV (~2.34 eV) for the ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ transition in the Rb₂SiF₆:Mn⁴⁺ (Rb₂TiF₆:Mn⁴⁺) phosphor. Temperature dependence of the PL spectra from T = 20 to 500 K gave the quenching temperature values (T_q 's) at which the PL intensity has fallen to half its maximum value to be $T_q \sim 490$ and ~450 K for Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺, respectively, promising for use as high-temperature stable phosphors in solid-state lighting applications.

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Alkaline and alkali-earth hexafluorometallate red-emitting phosphors, such as $K_2SiF_6:Mn^{4+}$ and BaTiF₆:Mn⁴⁺, have been demonstrated to meet the efficacy and color-quality targets of future "warm-white" light-emitting diode (LED) devices.¹⁻⁴ Such Mn⁴⁺-activated phosphors exhibit efficient red emission under blue (~460 nm) or UV excitation (~360 nm). Of course, searching for new red-emitting phosphors or those containing a red emission component is still an important approach to the realization of warm-white LED applications.

Rubidium-based hexafluoride compounds Rb_2SiF_6 and Rb_2TiF_6 belong to the alkaline hexafluorometallate family. These materials can, therefore, be used as the hosts of efficient red-emitting phosphors doped with Mn^{4+} ions. In fact, several authors have previously synthesized $Rb_2SiF_6:Mn^{4+}$ red-emitting phosphors.^{5,6} Paulusz⁵ synthesized some alkaline hexafluorometallate phosphors, including $Rb_2SiF_6:Mn^{4+}$, and determined the quenching temperature values (T_q 's) at which the emission intensity has fallen to half its maximum value. The T_q values obtained by Paulusz⁵ were varied from ~410 K for $Cs_2ZrF_6:Mn^{4+}$ to ~490 K for $Rb_2SiF_6:Mn^{4+}$. Unfortunately, this author reported no detailed photoluminescence (PL) or PL excitation (PLE) spectral feature.⁵

Fang et al.⁶ synthesized powdered Rb₂SiF₆:Mn⁴⁺ phosphor and measured its structural and PL properties. The powdered Rb₂SiF₆:Mn⁴⁺ phosphor in 5–20 μ m size had a cubic $Fm\overline{3}m - O_h^5$ (225) symmetry with good thermal stability of $T_q > 600$ K. It should be noted that no such high T_q value has been reported on any Mn⁴⁺⁻ activated alkaline hexafluorometallate phosphors. Nobita et al.⁷ also performed a theoretical study on the luminescence properties of some alkaline hexafluorometallate red-emitting phosphors, including Rb₂MF₆:Mn⁴⁺ (M = Si, Ge, Mn).

The motivation of this study is stimulated by the results of Fang et al.⁶ Here, we synthesize not only Rb₂SiF₆:Mn⁴⁺ but also Rb₂TiF₆:Mn⁴⁺. To the best of our knowledge, only one paper has been published on Rb₂TiF₆ reporting that it crystallizes in the trigonal structure with a = 0.5892 nm and a = 0.4795 nm.⁸

Our synthesized phosphors were examined by the X-ray diffraction (XRD) measurement, PL, PLE, and PL decay curve measurements. Temperature dependence of the PL properties was also examined from T = 20 to 500 K in 10-K increments. Efficient sharp red emissions with internal quantum efficiencies larger than 90% were observed from our phosphors that may promise improving a color rendering index of the conventional white-LED lamps.

Experimental

The rubidium hexafluorometallate phosphors were grown by the coprecipitation method. First, XO_2 (X = Si, Ti) and Rb_2CO_3 in molar ratio of 1 : 1 were dissolved in an HF solution. Then, KMnO₄ powder was added in the HF solution at 300 K. This mixed solution was left in dark for a few days and resulted in a large single-crystalline phosphor growth (see Fig. 2 below). The resultant bulk single-crystalline phosphors were paper-filtered and dried in room ambient. They were grained in an agate mortar and then used for various measurements.

The crystal structures of the synthesized phosphors were examined by performing an XRD analysis using a SmartLab X-ray diffractometer (Rigaku) with Cu K α radiation at $\lambda = 0.1542$ nm. PL measurements were carried out using a single monochromator equipped with a charge-coupled device (Princeton Instruments PIXIS 100) in a CryoMini cryostat (Iwatani Industrial Gases) and a stainless cryostat (Technolo Kogyo) at T = 20 - 500 K in increments of 10 K. A He–Cd laser at $\lambda_{ex} = 325$ nm (Kimmon IK3302R-E) was used as the excitation light source.

PLE measurements were performed at 300 K using a monochromator (JASCO CT-25C), a Peltier-device cooled photomultiplier tube (Hamamatsu R375), and a 50 W Xe arc lamp (ILC Technology, Inc.) as the excitation light source. The internal quantum efficiencies were determined by using an absolute quantum yield measurement system (Hamamatsu Photonics Co. Ltd., C9920-02G), consisting of a Xe arc lamp, an integrated sphere, a monochromator, and a photomultiplier tube, and by measuring the emission and excitation intensities with and without the samples.

The PL decay measurements were performed by excitation at λ_{ex} = 355 nm (Nd:YAG laser) with a Peltier-element-cooled photomultiplier tube (Hamamatsu R375), a multichannel scaler (SR 430, Stanford Research Systems, Inc.), and a preamplifier (SR 445A, Stanford Research Systems, Inc.) at 300 K.

Results and Discussion

Structural properties.—Figure 1 shows the XRD patterns in the $\theta - 2\theta$ scan mode of the Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ redemitting phosphors. The XRD patterns obtained from the American Society for Testing and Materials (ASTM) cards are shown in the lower part of each figure. These ASTM cards remarked Rb₂SiF₆ to crystallize in the cubic structure (#00-007-0207) and Rb₂TiF₆ in the hexagonal structure (#00-051-0611). However, our experimental XRD data for the Rb₂TiF₆:Mn⁴⁺ phosphor in Fig. 1b seems to be a trigonal



Figure 1. XRD patterns in the $\theta - 2\theta$ scan mode of (a) Rb₂SiF₆:Mn⁴⁺ and (b) Rb₂TiF₆:Mn⁴⁺ red-emitting phosphors. The ASTM card images for Rb₂SiF₆ (#00-007-0207) and Rb₂TiF₆ (#00-051-0611) are shown in the lower part of each figure.

symmetry typically observed in K₂GeF₆,⁹ K₂TiF₆,¹⁰ Cs₂TiF₆,¹⁰ Cs₂TiF₆,¹⁰ Cs₂SnF₆,¹¹ and (NH₄)₂MF₆ (X = Ge, Sn, Ti)¹² rather than a hexagonal symmetry (cf. hexagonal diffraction pattern of K₂MnF₆ Ref. 13). All these trigonal-symmetry hexafluoride materials belong to the space group of $P\overline{3}m1 - D_{3d}^3$ (164).^{9–12} On the other hand, Rb₂SiF₆ belongs to the cubic space group of $Fm\overline{3}m - O_h^5$ (225), as also reported by Fang et al.⁶

Figure 2 shows the photomicrograph images for the Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ red-emitting phosphors. The photomicrographs were obtained under tungsten lamp and black light illuminations. The phosphors in this study were synthesized with the addition of KMnO₄ at quantities varied from 1 to 10 mol%. However, we observed no clear difference in the PL intensities among those samples. The X-ray photoelectron spectroscopy or electron-probe microanalysis enabled no accurate determination for the Mn⁴⁺ concentration doped in such red-emitting phosphors due to its low sensitivity but estimated to be about 1 mol% or less.⁹

The photomicrographs in Fig. 2 reveal that the phosphor crystals have cubic ($Rb_2SiF_6:Mn^{4+}$) and trigonal symmetries ($Rb_2TiF_6:Mn^{4+}$), in agreement with the XRD results in Fig. 1. Moreover, one can understand an efficient red emission from these phosphors taken by black light illumination. The diameter of the $Rb_2TiF_6:Mn^{4+}$ phosphor in Fig. 2b is ~0.5 mm. The largest single-crystallite size synthesized in this study was ~8 mm in diameter with ~2 mm thickness.

PL and PLE spectra.—We show in Fig. 3 the room-temperature PL and PLE spectra for the Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ redemitting phosphors. One can see no large difference in the PL and PLE spectral features for these phosphors. The sharp PL peak structures have been typically observed in some Mn⁴⁺-activated phosphors, such as CaAl₁₂O₁₉:Mn⁴⁺,¹⁴ α-LiAlO₂:Mn⁴⁺,¹⁵ Ca₁₄Zn₆Al₁₀O₃₅:Mn⁴⁺,¹⁶ La₂MgTiO₆:Mn⁴⁺,¹⁷ and K₂Ge₄O₉:Mn⁴⁺.¹⁸ A review paper of the luminescence properties of Mn⁴⁺ ions in a number of phosphors can be found in Brik and Srivastava.¹⁹ The red emission peaks at ~ 600–650 nm are attributed to the ²E_g \rightarrow ⁴A_{2g} transition of the 3d³ electrons in the MnF²⁻₆ octahedron of the Rb₂SiF₆ and Rb₂TiF₆ host crystals. To discuss the Mn⁴⁺ emission peaks in more detail, we present

To discuss the Mn^{4+} emission peaks in more detail, we present in Fig. 4 the PL spectra for the $Rb_2SiF_6:Mn^{4+}$ and $Rb_2TiF_6:Mn^{4+}$



Figure 2. Photomicrograph images for (a) $Rb_2SiF_6:Mn^{4+}$ and (b) $Rb_2TiF_6:Mn^{4+}$ red-emitting phosphors taken under tungsten lamp and black light illuminations.

red-emitting phosphors at (a) T = 20 and (b) 300 K, together with those for Cs₂SiF₆:Mn⁴⁺ and Cs₂TiF₆:Mn⁴⁺. The PL spectra for the Cs₂SiF₆:Mn⁴⁺ and Cs₂TiF₆:Mn⁴⁺ phosphors were taken from our previous studies.^{10,20} These spectra were plotted against $\Delta E = E - E_{ZPL}$, where *E* is the emitted photon energy and E_{ZPL} , is the zero-phonon line (ZPL) energy. Therefore, the region for E > 0 meV



Figure 3. Room-temperature PL and PLE spectra for the Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ red-emitting phosphors. These spectra were measured by excitation at $\lambda_{ex} = 355$ nm (PL) and by monitoring at $\lambda_{em} \sim 630$ nm (PLE). The vertical bars in the PLE spectrum of the Rb₂SiF₆:Mn⁴⁺ phosphor represent the fits using Eq. 2 with S = 4, $E_{ZPL} \sim 2.47$ eV (⁴ $A_{2g} \rightarrow {}^{4}T_{2g}$), S = 10, $E_{ZPL} \sim 2.86$ eV (⁴ $A_{2g} \rightarrow {}^{4}T_{1g}$), and $hv_{p,ex} \sim 65$ meV.



Figure 4. PL spectra for Rb₂SiF₆:Mn⁴⁺, Cs₂SiF₆:Mn⁴⁺, Ref. 20 Rb₂TiF₆:Mn⁴⁺, and Cs₂TiF₆:Mn⁴⁺ red-emitting phosphors Ref. 10 at (a) T =20 and (b) 300 K. The PL spectra were plotted against $\Delta E = E - E_{ZPL}$. The ZPL emission energies are observed at $E_{ZPL} \sim 1.993$ eV (~1.992 eV) for Rb₂SiF₆:Mn⁴⁺ at 20 K (300 K); at ~1.986 eV (~1.986 eV) for Cs₂SiF₆:Mn⁴⁺ at 20 K (300 K); at ~1.991 eV) for Rb₂TiF₆:Mn⁴⁺ at 20 K (300 K); and at ~1.995 eV (~1.994 eV) for Cs₂TiF₆:Mn⁴⁺ at 20 K (300 K).

(E < 0 meV) means that the light emission is due to the Stokes (anti-Stokes) emission process.¹

The PL spectra in Fig. 4 reveal the main peak features at $|\Delta E|$ ~ 30 meV (ν_6), ~40 meV (ν_4), and ~80 meV (ν_3). Such emission peaks are in principle forbidden but can be gained by the activation of local vibration modes (v_i) of the MnF₆²⁻ octahedron in the hexafluorometallate hosts.¹ It should be noted that Rb₂SiF₆ is isostructural with Cs_2SiF_6 (cubic; $Fm\overline{3}m - O_h^5$).²⁰ Similarly, Rb_2TiF_6 should be isostructural with Cs₂TiF₆ (trigonal; $P\overline{3}m1 - D_{3d}^3$).¹⁰ Therefore, the PL spectra for the cubic or trigonal structure are nearly the same among the isostructural pair. For example, the PL spectra for the cubic Rb₂SiF₆:Mn⁴⁺ and Cs₂SiF₆:Mn⁴⁺ phosphors show a series of the sharp red emission peaks with each peak almost symmetric against E. On the other hand, the v_6 and v_4 emission peaks of the trigonal Rb₂TiF₆:Mn⁴⁺ and Cs₂TiF₆:Mn⁴⁺ phosphors exhibit clear splittings, especially those observed at low temperatures (see also Fig. 6 below). The splitting energies are determined to be ~ 4 meV, which are caused by the effects of trigonally deformed lattice.¹⁰

The PLE spectra in Fig. 3 reveal the two broad excitation bands at ~470 and ~360 nm. The effects of the crystal field on the energy levels of the $3d^n$ electron system are interpreted by the standard energy-level diagram.²¹ The strong excitation band peaking at ~470 nm is assigned to the ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transition in the Mn⁴⁺ (3*d*³) ions. This band consists of a number of peak components with spacing of ~65 meV and is understood as a vibronic progression of the fundamental frequency combined with an unsymmetrical v_2 -mode vibration of the MnF₆²⁻ octahedron superimposed on the ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ transition.²²

The PLE band can be theoretically calculated with the configurational-coordinate model based on the Franck-Condon



Figure 5. Room-temperature PL decay curves for the red emission at ~630 nm in the Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ phosphors. The decay curves were measured by excitation at 355 nm. The solid lines represent the fitted results with single exponential decay times of $\tau \sim 8.5$ and ~5.2 ms for the Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ phosphors, respectively.

principle:22

$$I_{\rm PLE}(E) = \sum_{n} I_n^{\rm ex}(n) \, \exp\left[-\frac{\left(E - E_{\rm ZPL} - nhv_{\rm q,ex}\right)^2}{2\sigma_{\rm ex}^2}\right] \qquad [1]$$

where

$$I_n^{\text{ex}}(n) = I_0^{\text{ex}} \exp(-S) \frac{S^n}{n!}$$
[2]

Here, $hv_{q,ex}$ is the vibronic quantum for the excited state ($hv_{q,ex} \sim hv_2 \sim 65 \text{ meV}$), σ_{ex} is the broadening of each Gaussian component, I_0^{ex} is the ZPL absorption intensity, and *S* represents the average number of phonons involved in a vibronic transition (Poisson statistics). The PLE spectrum is finally given by an envelope of numerous Gaussian lines, each of which is due to a transition between one vibronic level of the excited electronic state and one vibronic level of the ground state.

The vertical bars in Fig. 3 show the results calculated using Eq. 2. The fit-determined parameters are: S = 4, $E_{ZPL} \sim 2.47$ eV (${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$), S = 10, and $E_{ZPL} \sim 2.86$ eV (${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$) for the Rb₂SiF₆:Mn⁴⁺ phosphor; S = 5, $E_{ZPL} \sim 2.34$ eV (${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$), S = 9, and $E_{ZPL} \sim 2.83$ eV (${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$) for the Rb₂SiF₆:Mn⁴⁺ phosphor. An oscillatory structure in the PLE spectrum of the Rb₂SiF₆:Mn⁴⁺ phosphor observed in Fig. 3 can be well explained by introducing $hv_{p,ex} \sim 65$ meV into Eq. 2 (Eq. 1). From the present E_{ZPL} energies, we obtain the crystal field parameters of $Dq \sim 1990$ and ~ 1890 cm⁻¹ for the Mn⁴⁺ ions in the Rb₂SiF₆ and Rb₂TiF₆ hosts, respectively.

Luminescence quantum efficiency and decay curve measurements.—PL quantum efficiencies (QEs) for the Rb₂SiF₆:Mn⁴⁺, Rb₂TiF₆:Mn⁴⁺, and K₂SiF₆:Mn⁴⁺ red-emitting phosphors were measured by excitation at $\lambda_{ex} = 475$ nm and at 300 K. The measured results were ~73%, ~76%, and ~67% for the Rb₂SiF₆:Mn⁴⁺, Rb₂TiF₆:Mn⁴⁺, and K₂SiF₆:Mn⁴⁺ phosphors, respectively.

The above-mentioned QE values were obtained with the samples after graining in an agate mortar. We also measured QE for the bulk single-crystalline Rb₂TiF₆:Mn⁴⁺ sample without graining and obtained to be ~92%, which is much larger than the powdered sample value of ~76%, indicating the generation of grain-induced nonradiative recombination pathway. The micronized K₂SiF₆:Mn⁴⁺ phosphor in a diameter of ~3.5 μ m, synthesized by nanosecond pulsed laser irradiation in liquid, also gave QE of ~22%.²³

Figure 5 shows the PL decay curves for the $Rb_2SiF_6:Mn^{4+}$ and $Rb_2TiF_6:Mn^{4+}$ phosphors at 300 K. The solid lines represent the fitted results by a single exponential formulation. The decay times determined here are ~8.5 and ~5.2 ms for the $Rb_2SiF_6:Mn^{4+}$ and



Figure 6. PL spectra for (a) $Rb_2SiF_6:Mn^{4+}$ and (b) $Rb_2TiF_6:Mn^{4+}$ redemitting phosphors measured from T = 20 to 500 K in steps of 50 K. The dashed lines represent the ZPL energy positions.

 $Rb_2TiF_6:Mn^{4+}$ phosphors, respectively. These values fall in the range of the ever-reported Mn^{4+} -activated hexafluorometallate values of ${\sim}3{-}9$ ms at 300 K.^{2,6,13,24-33}

Temperature dependence of PL spectra.—For practical application of the red-emitting phosphors in solid-state lighting system, temperature dependence of the luminescence intensity is very important. Therefore, we measured the PL spectra for the Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ phosphors at temperatures between T = 20 and 500 K. Figure 6 shows the results of these measurements. As expected,¹ the anti-Stokes component becomes more remarkable at higher temperatures. The ZPL peaks are clearly observed at ~622 nm but their intensities are very weak, regardless of *T*. An evidence of the v₆ and v₄ peak splittings is also understood at low temperatures in the PL spectra of the Rb₂TiF₆:Mn⁴⁺ phosphor. As mentioned before (Fig. 4), no such splittings in the emission peaks can be observed in the PL spectra of the highly symmetric (cubic) Rb₂SiF₆:Mn⁴⁺ phosphor.

Figure 7 shows the integrated PL intensity (I_{PL}) vs 1/T plots for the Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ phosphors. It should be noted that the I_{PL} values in the T = 100 - 400 K range gradually increased with increasing *T*. Fang et al.⁶ also observed an increase in the emission intensity from T = 20 to 200° C in the Rb₂SiF₆:Mn⁴⁺ phosphor. Such unusual phenomenon cannot be explained by the conventional thermal quenching model. It should be noted that the Mn⁴⁺ $3d^3$ (${}^2E_g \rightarrow {}^4A_{2g}$) emission is due to forbidden transition. Therefore, its luminescence intensity should be gained by the activation of vibronic quanta with energy of hv_q

$$I_{\rm PL}(T) = \frac{I_0}{1 + a \exp\left(-E_{\rm q}/k_{\rm B}T\right)} \left(n_{\rm p}^+ + n_{\rm p}^-\right)$$
[3]

where

$$n_{\rm p}^{\pm} = \frac{1}{2} \pm \frac{1}{2} + n_{\rm p}$$
 [4]

$$n_{\rm p} = \frac{1}{\exp\left(h\nu_{\rm q}/k_{\rm B}T\right) - 1}$$
[5]

 E_q is the thermal quenching energy and k_B is the Boltzmann constant. The first and second terms in the bracket of Eq. 3 correspond to the Stokes and anti-Stokes components, respectively. Equation 5 can be



Figure 7. Integrated PL intensity (I_{PL}) vs reciprocal temperature (1/T) for (a) Rb₂SiF₆:Mn⁴⁺ and (b) Rb₂TiF₆:Mn⁴⁺ red-emitting phosphors. The solid lines show the results calculated using Eq. 6.

simply written as

$$I_{\rm PL}(T) = \frac{I_0}{1 + a \exp\left(-E_{\rm q}/k_{\rm B}T\right)} \left(1 + \frac{2}{\exp(h\nu_{\rm q}/k_{\rm B}T) - 1}\right)$$
[6]

The solid lines in Fig. 7 show the results calculated using Eq. 6 with $I_0 = 0.83 (0.55)$, $a = 4.0 \times 10^{11} (3.0 \times 10^{11})$, $E_q = 1.10 \text{ eV} (1.03 \text{ eV})$, and $hv_q = 80 \text{ meV} (40 \text{ meV})$ for the Rb₂SiF₆:Mn⁴⁺ (Rb₂TiF₆:Mn⁴⁺) phosphor. Introducing the Stokes and anti-Stokes gained components in the thermal quenching model, the fit becomes excellent over the entire temperature range.

Because the light emission from Mn⁴⁺ ions occurs due to the intra-d-shell transitions, its nature is not strongly dependent on the surrounding lattice among the isostructural materials (in the present case, the hexafluorometallates). In fact, no large difference in the emission wavelengths and PLE spectral features was observed among the hexafluorometallate phosphors. Moreover, the quenching temperatures T_q 's at which the emission intensity has fallen to half its maximum value reported by Paulusz⁵ are almost the same ($T_{q} \sim 410$ - 490 K) among the different Mn⁴⁺-activated hexafluorometallate phosphors, e.g., 490 K (K₂SiF₆:Mn⁴⁺), 450 K (K₂TiF₆:Mn⁴⁺), 480 K $(Cs_2SiF_6:Mn^{4+})$, and 440 K $(Cs_2TiF_6:Mn^{4+})$. Our obtained T_s values in the inset of Fig. 7 are \sim 480 K (Rb₂SiF₆:Mn⁴⁺) and \sim 450 K $(Rb_2TiF_6:Mn^{4+})$. These results suggest that the "silicate" phosphors have a value of $T_q \sim 480$ K, but the "titanate" phosphors have a slightly smaller value ($T_q \sim 450$ K) than the silicate one. The Rb₂SiF₆:Mn⁴⁺ value reported by Fang et al. $(T_q > 600 \text{ K})^6$ is considerably larger than our and Paulusz's values $(T_q \sim 480 - 490 \text{ K})$. It is, therefore, interesting to further study T_s values in the Rb-based hexafluorometallate phosphors.

Conclusions

Rb₂SiF₆:Mn⁴⁺ and Rb₂TiF₆:Mn⁴⁺ red-emitting phosphors were synthesized using the coprecipitation method. The phosphors exhibited an intense narrow-band red luminescence at ~630 nm under blue and UV excitation with internal quantum efficiencies higher than 90%. The ZPL energies obtained from the PL and PLE spectra yielded the following Mn⁴⁺ 3*d*³ energy states and crystal field parameters in the Rb₂SiF₆ and Rb₂TiF₆ hosts: ~2.47 and ~2.34 eV (⁴A_{2g} → ⁴T_{2g}), ~2.86 and ~2.83 eV (⁴A_{2g} → ⁴T_{1g}), ~1990 and ~1890 cm⁻¹ (*Dq*), respectively. The PL spectra were measured at temperatures from T = 20 to 500 K in 10-K increments. The quenching temperature values determined in this study were $T_q ~ 490$ K (Rb₂SiF₆:Mn⁴⁺) and \sim 450 K (Rb₂TiF₆:Mn⁴⁺), promising for use as high-temperature stable phosphors in future warm-white LED applications.

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