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Mn-activated K$_2$ZrF$_6$ and Na$_2$ZrF$_6$ phosphors: Sharp red and oscillatory blue-green emissions

Ryota Kasa and Sadao Adachi$^{a)}$

Graduate School of Engineering, Gunma University, Kiryu-shi, Gunma 376-8515, Japan

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Mn-activated A$_2$ZrF$_6$ (A = K, Na) phosphors are synthesized by the chemical reaction method in HF-based solutions. The Mn-activated K$_2$ZrF$_6$ phosphor exhibits sharp red emission peaks at ~630 nm, which are typically observed in various Mn$^{4+}$-activated phosphors. The phosphor is, therefore, identified to be K$_2$ZrF$_6$:Mn$^{4+}$. The Mn-activated Na$_2$ZrF$_6$ phosphor, on the other hand, shows a broad blue-green emission band with a peak at ~520 nm while exhibiting an oscillatory feature. This emission band is considered to originate from the Mn$^{2+}$ ion in the Na$_{+}$—Na$_{+}$ site of Na$_2$ZrF$_6$. Such an oscillatory feature has not been previously reported for phosphors. Fourier transform analysis yields a main oscillatory period of ~0.10 eV together with a secondary oscillatory period of ~26 meV. Although the origin of the oscillatory feature in Na$_2$ZrF$_6$:Mn$^{2+}$ is unclear, it appears to be caused by an effect of the Mn$^{2+}$-induced strain in the Na$_2$ZrF$_6$ host. Such unique luminescence properties of Na$_2$ZrF$_6$:Mn$^{2+}$ are not only of technological importance but also of scientific interest. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4732139]

I. INTRODUCTION

Some Mn$^{4+}$-activated hexafluorometallate phosphors in the form of A$_3$XF$_6$:Mn$^{4+}$ (A = K, Na, and Cs; X = Si, Ge, and Ti) have been reported to exhibit efficient red emission under blue (~460 nm) or UV excitation (~360 nm). Setlur et al.$^2$ have used K$_2$SiF$_6$:Mn$^{4+}$ and K$_2$TiF$_6$:Mn$^{4+}$ as red phosphors in light-emitting diode (LED) lamps and demonstrated a significant reduction in the efficacy gap between warm-white and cool-white LED lamps employing down-conversion phosphors. However, no reports have been published on the optical properties of Mn$^{4+}$-activated A$_2$XF$_6$ phosphors with X = Zr as the host material. The main reason for this may be the difficulty of synthesizing such hexafluorozirconate host crystals. Moreover, the larger difference between the ionic radii of Mn$^{4+}$ and Zr$^{4+}$ (0.54 and 0.72 Å, respectively) makes it more difficult to introduce Mn activators into hexafluorozirconate host crystals.

The purpose of this study is twofold: (i) to demonstrate the synthesis of Mn-activated K$_2$ZrF$_6$ and Na$_2$ZrF$_6$ phosphors by the chemical reaction method and (ii) to report their photoluminescence (PL) properties in detail. It is shown that the present synthesis method enables the preparation of a red-emitting K$_2$ZrF$_6$:Mn$^{4+}$ phosphor and a blue-green-emitting Na$_2$ZrF$_6$:Mn$^{3+}$ phosphor but not a red-emitting Na$_2$ZrF$_6$:Mn$^{4+}$ phosphor. Surprisingly, the blue-green emission spectrum of Na$_2$ZrF$_6$:Mn$^{2+}$ shows an oscillatory feature, which has not been previously reported for phosphors.

II. EXPERIMENTAL

The Mn-activated K$_2$ZrF$_6$ and Na$_2$ZrF$_6$ phosphors were synthesized by the chemical reaction method. The raw materials used for the synthesis of K$_2$ZrF$_6$:Mn$^{4+}$ were HF, KMnO$_4$, and Zr. The overall chemical reaction can be given by

$$
6\text{HF} + 2\text{KMnO}_4 + (1 - x)\text{Zr} \rightarrow \text{K}_2(\text{Zr}_{1-x}\text{Mn}_x)\text{F}_6
$$

$$
+ (2 - x)\text{MnO}_2 + 3\text{H}_2\text{O} + \frac{1}{2}(2x + 1)\text{O}_2,
$$

(1)

where $\text{K}_2(\text{Zr}_{1-x}\text{Mn}_x)\text{F}_6$ represents the Mn$^{4+}$-activated phosphor, i.e., K$_2$ZrF$_6$:Mn$^{4+}$.

The Mn-activated Na$_2$ZrF$_6$ phosphor was synthesized from HF, NaF, KMnO$_4$, and Zr. First, pure Na$_2$ZrF$_6$ powder was synthesized by the following chemical reaction:

$$
4\text{HF} + 2\text{NaF} + \text{H}_2\text{O}_2 + \text{Zr} \rightarrow \text{Na}_2\text{ZrF}_6 + 2\text{H}_2\text{O} + \text{H}_2.
$$

(2)

Next, it was dipped in a mixture of aqueous HF, NaF, and KMnO$_4$ for 24 h. The Mn-activated Na$_2$ZrF$_6$ phosphor was then obtained by filtering the chemical solution with a filter paper, washing in methanol, and finally drying in air.

The structural properties of the synthesized phosphors were examined by scanning electron microscopy (SEM, JEOL JSM-6330F) and x-ray diffraction (XRD) analysis using an x-ray diffractometer (Rigaku RAD-IIIC) with Cu K$_\alpha$ radiation. Electron probe microanalysis (EPMA) measurements were performed with a Shimadzu EPMA-1610 microanalyser at a probe current of 100 nA and an accelerating voltage of 15 kV. PL and PL excitation (PLE) measurements were performed using a fluorescence spectrometer (Hitachi F-4500) at room temperature. The powdered phosphors were mounted on Si substrates using silver paint. Temperature-dependent PL measurements were performed using a single monochromator equipped with a charge-coupled device (Princeton Instruments PIXIS 100) in a CryoMini cryostat (Iwatani Industrial Gases) at $T = 300–3000$ K and also in a stainless-steel cryostat (Techno Kogyo) at $T = 300–470$ K. The 325 nm line of a He–Ca laser (Kimmon IK3302R-E) was used as an excitation light source.

$^a$Electronic mail: adachi@el.gunma-u.ac.jp.
III. RESULTS AND DISCUSSION

A. Structural properties

Figure 1 shows the XRD patterns of the Mn-activated K$_2$ZrF$_6$ and Na$_2$ZrF$_6$ phosphors measured in the $\theta$–2$\theta$ scan mode. The body colors of these phosphors are white in room light. The measured XRD traces reveal many diffraction peaks originating from the various crystallographic planes of the phosphor particles. The diffraction patterns of monoclinic (m–) K$_2$ZrF$_6$, cubic (c–) K$_3$ZrF$_7$, and m–Na$_2$ZrF$_6$ obtained from the American Society for Testing and Materials (ASTM) cards are shown in the lower parts of the experimental XRD data. The structures of these crystals belong to the space groups of C$_6$2$h$/C0C2 = c (m–K$_2$ZrF$_6$), O$_5$h/C0Fm3m (c–K$_3$ZrF$_7$), and C$_5$2$h$/C0P21 = c (m–Na$_2$ZrF$_6$). It is understood from Fig. 1(a) that the synthesized powder is a mixture of m–K$_2$ZrF$_6$ and c–K$_3$ZrF$_7$. The XRD trace in Fig. 1(b) indicates that the synthesized phosphor is m–Na$_2$ZrF$_6$.

SEM images of these phosphors are shown on the right-hand side of Fig. 1. The present synthesis method produced a mixture of m–K$_2$ZrF$_6$ and c–K$_3$ZrF$_7$ with a particle size of less than 10$\mu$m [Fig. 1(a)]. Similarly, many particles with a length of less than 100$\mu$m were found in the SEM image of m–Na$_2$ZrF$_6$ [Fig. 1(b)]. No clear crystal habit was observed in these SEM images. One reason for this may be the lower symmetry class of the monoclinic crystal structure. As shown in Fig. 1(b), good agreement was not observed in the relative strengths of the Bragg reflection peaks between the experimental and ASTM data. This may be due to the considerably large particle size ($\sim$100$\mu$m) of the Na$_2$ZrF$_6$ powder.

EPMA measurements were carried out to examine the chemical species in the synthesized phosphors, particularly the potassium (K) species in the Na$_2$ZrF$_6$ phosphor. Figure 2 shows our measured EPMA spectrum of Na$_2$ZrF$_6$. Only sodium (Na), zirconium (Zr), fluorine (F), and manganese (Mn) were detected. Although KMnO$_4$ was used as a source of the Mn dopant, no K signal was detected in our measured EPMA spectrum. Thus, the XRD and EPMA data, respectively, shown in Figs. 1 and 2 indicate that the Mn-activated phosphor synthesized from HF, NaF, H$_2$O$_2$, Zr, and KMnO$_4$ is m–Na$_2$ZrF$_6$, not potassium-based fluoride (e.g., K$_2$ZrF$_6$ or KNaZrF$_6$). Because of its small quantity, we could not exactly determine the concentration of Mn in our synthesized K$_2$ZrF$_6$ (K$_3$ZrF$_7$) and Na$_2$ZrF$_6$ phosphors. From x-ray photoelectron spectroscopy measurements of K$_2$SiF$_6$:Mn$^{4+}$, however, we estimated the quantities of the Mn$^{4+}$ and Mn$^{2+}$ ions in the present phosphors to be on the order of 0.1 mol% or less.

B. PL and PLE spectra

Figure 3(a) shows room-temperature PL and PLE spectra of the Mn-activated K$_2$ZrF$_6$ phosphor. The effective ionic radii of Mn$^{4+}$ and Zr$^{4+}$ are, respectively, 0.54 and 0.72$\AA$. Although there is a considerable difference between these radii, one can expect that the Mn$^{4+}$ ion will be substituted for the Zr$^{4+}$ ion in the ZrF$_6^{2–}$ octahedron, resulting in the formation of MnF$_6^{2–}$. Indeed, our synthesized K$_2$ZrF$_6$ (K$_3$ZrF$_7$) phosphor produces the sharp red emission typically observed in various Mn$^{4+}$-activated phosphors, such as dialkaline hexafluorometallates, CaAl$_{12}$O$_{19}$, Gd$_3$Ga$_5$O$_{12}$, SrTiO$_3$, YAlO$_3$, YAl$_3$(BO$_3$)$_4$, and 3.5MgO/1.5MgF$_2$/GeO$_2$. We can thus conclude that the K-based phosphor synthesized in this study is K$_2$ZrF$_6$:Mn$^{4+}$. The red emissions observed at ~2 eV can then be ascribed to the $^2E_g$–$^2A_{2g}$ transition of the Mn$^{4+}$ ion in the ZrF$_6^{2–}$ octahedron of K$_2$ZrF$_6$. The PLE
spectrum in Fig. 3(a) exhibits two broad absorption bands at ~2.7 and ~3.5 eV. These absorption bands are, respectively, assigned to the $^4A_{2g} \rightarrow ^4T_{2g}$ and $^4A_{2g} \rightarrow ^4T_{1g}$ transitions of the Mn$^{4+}$ ions in K$_2$ZrF$_6$.

The room-temperature PL and PLE spectra of the Mn-activated Na$_2$ZrF$_6$ are shown in Fig. 3(b). Unexpectedly, the PL spectrum of this phosphor shows a broad blue-green emission band with oscillatory peaks but no red emission peaks originating from Mn$^{4+}$. Moreover, no characteristic excitation bands of the Mn$^{4+}$ ions, typically observed at ~2.7 and ~3.5 eV [see, for example, Fig. 3(a)], are observed in our PLE spectrum in Fig. 3(b). Thus, the observed blue-green emission band is not due to Mn$^{4+}$.

The intra-$d$-shell transition in Mn$^{2+}$ is sensitive to the magnitude of the crystal field, and the luminescence wavelength can be tuned according to the coordination environment.

For example, tetrahedrally coordinated Mn$^{2+}$ usually exhibits a green emission, whereas octahedrally coordinated Mn$^{2+}$ exhibits an orange to red emission. Recently, we observed a yellow emission from K$_2$SiF$_6$:Mn$^{2+}$ and a yellowish-green emission from Na$_2$SiF$_6$:Mn$^{2+}$.

In Fig. 4, we show these emission spectra together with the excitation bands of the Mn$^{4+}$ ions, which are known as the Stokes and anti-Stokes lines. At $T = 20$ K, three sharp peaks dominate on the long-wavelength side of the zero-phonon line (ZPL). At $T = 300$ K, these sharp peaks appear not only on the long-wavelength side but also on the short-wavelength side. The long- and short-wavelength emission peaks are known as the Stokes and anti-Stokes lines, respectively. The three vibronic frequencies for the Mn$^{4+}$-activated A$_2$X$_6$ phosphors, a host material with lower crystal symmetry exhibits stronger ZPL emission intensity. This may be due to the dependence of the observability of the ZPL emission on the local symmetry of the environment of the Mn$^{4+}$ ion. Any piezoelectric or related effect, such as a longitudinal electric field induced by piezoelectrically active phonons and/or the $q$-dependent Frohlich interaction, will activate the dipole-forbidden ZPL emission in materials of low symmetry.

Note that our synthesized monoclinic K$_2$ZrF$_6$:Mn$^{4+}$ phosphor contains cubic phase K$_2$ZrF$_7$ as an inclusion. The Mn$^{4+}$ ions in K$_2$ZrF$_7$ may also emit light in the red spectral region. The symmetry class of monoclinic is much lower than that of cubic. Thus, the lack of strong ZPL emission in Fig. 5(a) indicates that the dominant red-emitting phosphor should be cubic K$_2$ZrF$_7$:Mn$^{4+}$ rather than monoclinic K$_2$ZrF$_6$:Mn$^{4+}$. This is a problem to be solved.

In Fig. 5(b), we show the temperature dependence of the PL spectra of the blue-green-emitting Na$_2$ZrF$_6$:Mn$^{2+}$ phosphor. The oscillatory peak structure can be clearly observed regardless of $T$ from 20 to 300 K. Moreover, no large peak

![FIG. 4. PL spectrum of Na$_2$ZrF$_6$:Mn$^{2+}$ at 20 K, together with those of K$_2$SiF$_6$:Mn$^{2+}$ (Ref. 15) and Na$_2$SiF$_6$:Mn$^{2+}$ (Ref. 16).](image)

![FIG. 5. PL spectra measured at temperatures between 20 and 300 K for (a) K$_2$ZrF$_6$:Mn$^{4+}$ (K$_2$ZrF$_7$:Mn$^{4+}$) and (b) Na$_2$ZrF$_6$:Mn$^{2+}$. The dashed line in (a) represents the position of the ZPL energy (~2.00 eV).](image)
shift with respect to $T$ is observed. These facts support the hypothesis that the blue-green emission is caused by the intra-$d$-shell transition in the metallic ions (Mn$^{2+}$).\textsuperscript{14}

### C. Temperature dependence of PL intensity

Figure 6 shows integrated PL intensity ($I_{PL}$) versus $T$ plots for $K_2ZrF_6$:Mn$^{4+}$ ($K_2ZrF_6$:Mn$^{4+}$) and $Na_2ZrF_6$:Mn$^{2+}$. The $I_{PL}$ value gradually increases with increasing $T$ from 20 to 350 K for $K_2ZrF_6$:Mn$^{4+}$ and from 20 to 200 K for $Na_2ZrF_6$:Mn$^{2+}$. A further increase in $T$ results in a decreased $I_{PL}$ value.

The interaction of the electrons with the lattice vibrations or, more rigorously, the electron–phonon coupling becomes stronger with increasing temperature. On the basis of this assumption, we analyze the $I_{PL}$ versus $T$ data using the expression:\textsuperscript{22}

$$I_{PL}(T) = I_{PL}^0 + I_{PL}^1 \left(1 + \frac{2}{\exp(h\nu/k_BT) - 1}\right), \quad (4)$$

where $\nu$ is the effective vibrionic frequency. The light solid lines in Fig. 6 show the fitted results calculated using Eq. (4) with $I_{PL}^0 = I_{PL}^1 = 0.612$ and $h\nu = 36$ meV for $K_2ZrF_6$:Mn$^{4+}$ and $I_{PL}^0 = 0.604$, $I_{PL}^1 = 0.067$, and $h\nu = 5.5$ meV for $Na_2ZrF_6$:Mn$^{2+}$. The effective vibrionic energy of $h\nu = 36$ meV for $K_2ZrF_6$:Mn$^{4+}$ is slightly smaller and larger than the internal vibration frequencies of $\nu_4$ (42 meV) or $\nu_6$ (28 meV) derived from Fig. 5(a). No experimental data have been reported on the internal vibration frequencies $\nu_4$ (i = 1–6) of the MnF$_2^-$ or ZrF$_6^-$ octahedron in $Na_2ZrF_6$. It is, however, evident that the value of $h\nu = 5.5$ meV for $Na_2ZrF_6$:Mn$^{2+}$ is much smaller that all internal vibration frequencies $\nu(i)$ of the MnF$_6^-$ or ZrF$_6^-$ octahedron in $A_2ZrF_6$ with $A = Li$, Na, K, Rb, Cs, or NH$_4$. This is because all the reported values of $\nu(i)$ for the MnF$_6^-$ or BF$_6^-$ octahedron (B = group IV metal) in various dialkaline hexafluorometallates are much larger than 5.5 meV.\textsuperscript{5,6,21,23} One candidate for such a small $h\nu$ value is the lattice acoustic phonons. Further study is needed to elucidate this problem.

The integrated PL intensities above $\sim 350$ K for $K_2ZrF_6$:Mn$^{4+}$ and above $\sim 200$ K for $Na_2ZrF_6$:Mn$^{2+}$ exhibit strong thermal quenching and can therefore be fitted with the following equation:

$$I_{PL}(T) = \frac{I_{PL}(0)}{1 + \exp(-E_0/k_BT)}. \quad (5)$$

The heavy solid lines in Fig. 6 show the results calculated using Eq. (5). The quenching energies determined here are $E_0 = 1.1$ and 0.22 eV for $K_2ZrF_6$:Mn$^{4+}$ and $Na_2ZrF_6$:Mn$^{2+}$, respectively.

### D. Oscillatory PL spectra

The oscillatory PL spectrum observed in our $Na_2ZrF_6$:Mn$^{2+}$ phosphor is reproduced in Fig. 7. The first efficient absorption band $^4A_{2g} \rightarrow ^2T_{2g}$ in the PLE spectra of dialkaline hexafluoride red phosphors ($K_2SiF_6$:Mn$^{4+}$, $Na_2SiF_6$:Mn$^{4+}$, etc.) is featureless at 300 K but has a sharp origin and some oscillatory peaks at low temperatures.\textsuperscript{2,5,24} The oscillatory peaks with a spacing of $\sim 55$–65 meV are understood to be a vibronic progression of the fundamental frequency combined with an unsymmetrical vibration $\nu_2$ of the MnF$_6^{2-}$ octahedron superimposed on the $^4A_{2g} \rightarrow ^2T_{2g}$ transition.

No oscillatory peaks have been observed in previously reported emission spectra of phosphors with the exception of PL spectra observed from thin-film samples. Light emitted in a thin film suffers from multiple reflections due to the large difference between the refractive indices of the thin film and underlying substrate. Thus, the multiple reflections lead to an oscillatory interference pattern, which is also known as Fabry–Perot interference. Such oscillatory PL spectra have been observed in epitaxial InGaN/GaN films\textsuperscript{25} and thin porous Si films.\textsuperscript{26–29} Since our measured samples are in powdered form, the possibility of interference fringes can be clearly ruled out.

The oscillatory structure in Fig. 7 reveals several large peaks with a period of $\sim 0.104$ eV superimposed on smaller secondary peaks at an interval of $\sim 26$ meV. We use the Fourier transform (FT) technique to analyze the oscillatory PL spectrum in more detail. The FT of a function $f(u)$ can be given by

$$W(\vec{q}) = \int_{-\infty}^{\infty} f(u) e^{-i\vec{q}\cdot\vec{u}} \, du,$$

where $\vec{q}$ is the wave vector.
where \( w(u) \) is a window function. The variable \( u \) in the present study is the photon energy. Because of the limited experimental range, it is necessary to limit the integral to a finite range of \( T_1 \leq u \leq T_2 \). The Hamming window function is useful in the analysis of Fourier components with small Fourier amplitudes. This function is given by

\[
    w_R(u) = w_R(t) \left\{ 0.54 - 0.46 \cos \left( \frac{2\pi u}{T_2 - T_1} \right) \right\},
\]

where \( w_R(u) \) is the rectangular function defined by

\[
    w_R(u) = \begin{cases} 1 & : T_1 \leq u \leq T_2 \\ 0 & : \text{otherwise} \end{cases}.
\]

Figure 8 shows the FT spectrum of the experimental PL data shown in Fig. 7. The integration in Eq. (6) is performed from \( T_1 = 2.0 \text{ eV} \) to \( T_2 = 2.6 \text{ eV} \). The FT spectrum is plotted against \( 1/t \), i.e., in units of energy. The frequency peak at \( 1/t = 0.1 \text{ eV} \) is in agreement with the pitch of the main oscillatory peaks in Fig. 7. The FT peaks at \( 1/t = 55 \text{ and } 35 \text{ meV} \) in Fig. 8 may be the second and third harmonics of the main FT frequency at \( \sim 0.1 \text{ eV} \), respectively. The FT peak at \( 1/t = 26 \text{ meV} \) is also in good agreement with the secondary oscillatory peak separation in Fig. 7. Furthermore, this energy is nearly the same as the internal vibration energy of \( \nu_i \) in various dialkaline hexafluorides.

The configurational-coordinate (CC) model has often been used to explain the optical properties of solids. The optical absorption and emission spectra in the CC model are obtained from an envelope of numerous lines, each of which is due to a transition between one vibrational level of the excited electronic state and one vibrational level of the ground state. The resulting optical spectra can be expressed by the statistical Poisson distribution function

\[
    S(u) = \exp(-S) \frac{(S)^u}{n!},
\]

where \( S \) represents the average number of phonons involved in a vibronic transition. The emission peaks observed in Fig. 7 have an equal interval of \( \sim 0.104 \text{ eV} \). The vertical bars show the PL spectral shape modeled using Eq. (9) with \( S = 1 \). This shape reproduces the experimental PL spectrum very well. However, the interval of \( 1/t \sim 0.104 \text{ eV} \) is much larger than the internal vibration energies of \( \nu_i \) (\( i = 1 \text{– } 6 \)). Thus, it appears that the oscillatory blue-green emission spectrum is not caused by vibronic quanta.

In Refs. 15 and 16, the Mn\textsuperscript{2+} ions in K\textsubscript{2}SiF\textsubscript{6} and Na\textsubscript{2}SiF\textsubscript{6} were assumed to be substituted for their K\textsuperscript{+}–K\textsuperscript{+} or Na\textsuperscript{+}–Na\textsuperscript{+} site, respectively. Such divalent ions of Mn\textsuperscript{2+} can emit yellow light in K\textsubscript{2}SiF\textsubscript{6}:Mn\textsuperscript{2+} (Ref. 15) and yellowish-green light in Na\textsubscript{2}SiF\textsubscript{6}:Mn\textsuperscript{2+}. Here, the blue-green emission observed in this study is also assumed to be due to the Mn\textsuperscript{2+} ions substituted for the Na\textsuperscript{+}–Na\textsuperscript{+} site in the Na\textsubscript{2}ZrF\textsubscript{6} host.

Recently, we investigated the luminescence properties of NaCl:Sn\textsuperscript{2+} at \( T = 20–300 \text{ K} \) with excitation at \( \lambda_{ex} = 250–330 \text{ nm} \) and observed oscillatory PL spectra only at low temperatures (\( T \sim 20 \text{ K} \)) with a limited range of excitation wavelengths \( \lambda_{ex} \sim 285–300 \text{ nm} \). It is known that divalent activators, such as Sn\textsuperscript{2+} and Pb\textsuperscript{2+}, in alkali halides generate charge-compensating cation vacancies near these divalent ions. The charge-compensating cation vacancies can induce lattice strain near the divalent ions in the host crystals. The resultant optical spectra are known to be very complex.

The oscillating spectra observed in NaCl:Sn\textsuperscript{2+} may be due to the effect of strain induced by the charge-compensating cation vacancies. Considering charge conservation, the Mn\textsuperscript{2+} ion substituted for the Na\textsuperscript{+}–Na\textsuperscript{+} site should be written as Mn\textsuperscript{2+} – \( V^0_{Na} \), where \( V^0_{Na} \) is a charge-compensating cation vacancy. The oscillatory period in Na\textsubscript{2}ZrF\textsubscript{6}:Mn\textsuperscript{2+} is \( \sim 0.104 \text{ eV} \) (Fig. 7), which is about half of that observed in NaCl:Sn\textsuperscript{2+} (\( \sim 0.22 \text{ eV} \)). The elucidation of oscillatory PL phenomena in Na\textsubscript{2}ZrF\textsubscript{6}:Mn\textsuperscript{2+} and also in NaCl:Sn\textsuperscript{2+} is expected to be interesting and challenging work and is now in progress.

**IV. CONCLUSIONS**

We synthesized Mn-activated K\textsubscript{2}ZrF\textsubscript{6} and Na\textsubscript{2}ZrF\textsubscript{6} phosphors using the chemical reaction method. The Mn\textsuperscript{2+} ion was substituted for the Zr site in the K\textsubscript{2}ZrF\textsubscript{6} host, resulting in sharp red emission peaks at \( \sim 630 \text{ nm} \) (m-K\textsubscript{2}ZrF\textsubscript{6}:Mn\textsuperscript{2+}). The XRD data, however, indicated that the synthesized potassium zirconate was a mixture of monoclinic K\textsubscript{2}ZrF\textsubscript{6} and cubic K\textsubscript{2}ZrF\textsubscript{7}. On the other hand, the Mn-activated Na\textsubscript{2}ZrF\textsubscript{6} phosphor exhibited only a broad blue-green emission band with several oscillatory peaks. Therefore, the activator was considered to be Mn\textsuperscript{2+} substituted for the Na\textsuperscript{+}–Na\textsuperscript{+} site in the Na\textsubscript{2}ZrF\textsubscript{6} host. The oscillatory PL spectra showed an energy separation of \( \sim 0.10 \text{ eV} \) for the main oscillatory peaks and \( \sim 26 \text{ meV} \) for the secondary oscillatory peaks. No such oscillatory phenomena have been previously reported for phosphors. The oscillatory feature is considered to be due to the effect of strain induced by the Mn\textsuperscript{2+} ions substituted for the Na\textsuperscript{+}–Na\textsuperscript{+} site in the Na\textsubscript{2}ZrF\textsubscript{6} host. These unique PL properties are not only of technological importance but also of scientific interest.

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