Narrow Red Emission Band Fluoride Phosphor KNaSiF₆:Mn⁴⁺ for Warm White Light-Emitting Diodes

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Supporting Information

ABSTRACT: Red phosphors AMF₆:Mn⁴⁺ (A = Na, K, Cs, Ba, Rb; M = Si, Ti, Ge) have been widely studied due to the narrow red emission bands around 630 nm. The different emission of the zero-phonon line (ZPL) may affect the color rendering index of white light-emitting diodes (WLED). The primary reason behind the emergence and intensity of ZPL, taking KNaSiF₆:Mn⁴⁺ as an example, was investigated here. The effects of pressure on crystal structure and luminescence were determined experimentally and theoretically. The increase of band gap, red shift of emission spectrum and blue shift of excitation spectrum were observed with higher applied pressure. The angles of ZFmF and ZFMF(M = Si, Ti, Ge) were found clearly distorted from 180° in MF₆⁻ octahedron with strong ZPL intensity. The larger distorted SiF₆⁻ octahedron, the stronger ZPL intensity. This research provides a new perspective to address the ZPL intensity problem of the hexafluorosilicate phosphors caused by crystal distortion and pressure-dependence of the luminescence. The efficacy of the device featuring from Y₃Al₅O₁₂:Ce³⁺ (YAG) and KNaSiF₆:Mn⁴⁺ phosphor was 118 lm/W with the color temperature of 3455 K. These results reveal that KNaSiF₆:Mn⁴⁺ presents good luminescent properties and could be a potential candidate material for application in back-lighting systems.

KEYWORDS: KNaSiF₆:Mn⁴⁺, red phosphor, ZPL, high pressure, warm white LED

White light-emitting diodes (WLEDs) are used extensively in backlights, flashlights, and automobile headlamps as replacements for conventional incandescent and fluorescent lamps because of their high energy efficiency, durability, reliability, and capacity for use in products with various sizes and more eco-friendly components.¹,² Phosphors have been widely investigated for use in phosphor-converted WLEDs. The most widely used WLED combines the yellow phosphor Y₃Al₅O₁₂:Ce³⁺ (YAG) with a blue InGaN LED chip. However, this LED presents a low color rendering index (CRI) (Ra < 80) and high correlated color temperature (CCT > 6000 K) because of the absence of red emission in its spectrum.³ Therefore, red phosphors, such as Sr₂Si₅N₈:Eu³⁺ and (Sr,Ca)₂Al₅O₁₂:Eu³⁻ or Mn⁴⁺-doped red phosphors, have been added to the devices in order to improve their color-rendering properties.⁴⁻¹⁵ The broad emission band of nitride phosphors is often longer than 650 nm, and serious reabsorption renders them unsuitable for improving the efficiency of a device.

Therefore, Mn⁴⁺-doped red phosphors, especially AMF₆:Mn⁴⁺ (A = Na, K, Cs, Ba, Rb; M = Si, Ti, and Ge) with narrow band emissions at around 630 nm, have recently attracted increased research attention.⁵⁻¹⁵ Team of Adachi et al.⁷⁻¹⁳ synthesized a series of fluorides, including KNaSiF₆ using wet chemical etching. The authors demonstrated the luminescence properties of the phosphor at normal pressure and showed that the KNaSiF₆:Mn⁴⁺ system is an intermediate of homodialkaline K₂SiF₆:Mn⁴⁺ and Na₂SiF₆:Mn⁴⁺ narrow emission band red phosphors,¹¹ whereas Zhu et al.¹³ successfully synthesized K₂TiF₆:Mn⁴⁺ through a simple cation exchange reaction.

The emission wavelength of the d→d transition of Mn⁴⁺ ions is easily influenced by various environmental factors, contrary to the parity-forbidden f→f transitions of rare-earth ions. The
AMF$_{2}$Mn$_{4}^{4+}$ (A = Na, K, Cs, Ba, Rb; M = Si, Ti, and Ge) have different zero-phonon lines (ZPLs) because of their MF$_{2}^-$ octahedral structures. In this study, for example, whereas K$_2$SiF$_6$Mn$_{4}^{4+}$ shows no ZPL intensity, an intense ZPL is observed for Na$_3$SiF$_6$Mn$_{4}^{4+}$. K$_2$GeF$_6$Mn$_{4}^{4+}$ exhibits two phases, one with an intense ZPL and another without ZPL.

In this work, KNaSiF$_6$Mn$_{4}^{4+}$ was synthesized via a simple coprecipitation method. The intermediate phase of KNaSiF$_6$Mn$_{4}^{4+}$ showed different structures and luminescent properties, especially in terms of ZPL intensity, from K$_2$SiF$_6$Mn$_{4}^{4+}$ and Na$_3$SiF$_6$Mn$_{4}^{4+}$. The mechanism of the ZPL emergence, as well as its intensity and position, has not been previously reported yet. This study aims to elucidate the mechanism of the ZPL intensity in AMF$_{2}$Mn$_{4}^{4+}$ (A = Na, K, Cs, Ba, Rb; M = Si, Ti, and Ge). We clearly found variations in the angles $\angle FMnF = \angle FMnF(M = Si, Ti, Ge)$ of the phosphors AMF$_{2}$Mn$_{4}^{4+}$ (A = Na, K, Cs, Ba, Rb; M = Si, Ti, and Ge). Distortion of the MnF$_6^{2-}$ octahedron is the key factor influencing ZPL intensity. The properties of the resultant phosphors were examined by photoluminescence (PL) under both ambient pressure and high pressure and are verified by the calculation method. Moreover, the LED obtained from mixing of the narrow-band red emission phosphor KNaSiF$_6$:Mn$_{4}^{4+}$ with conventional YAG:Ce$_3^{3+}$ yellow phosphor can be excited by blue LED chip. This LED shows an enhanced CRI for lighting and backlighting applications.

The fluoride phosphor compounds, namely, KNaSiF$_6$:0.06 Mn$_{4}^{4+}$, K$_2$SiF$_6$:0.06 Mn$_{4}^{4+}$, and Na$_3$SiF$_6$:0.06 Mn$_{4}^{4+}$, were prepared from high-purity NaF, KF, SiO$_2$, HF, KMnO$_4$, and H$_2$O$_2$ via two-step coprecipitation. K$_2$MnF$_6$ was prepared first as a mixture consisting of 6.7 g of KF and 0.45 g of KMnO$_4$ and 1.2 g of SiO$_2$ in 35 mL of 48% HF. Then, 0.3 mL of H$_2$O$_2$ was added to the solution drop by drop. The solution gradually precipitated from deep purple to yellow, and a yellow precipitate was obtained. The powder was washed several times using alcohol and acetone and then dried at 70 °C. The prepared K$_2$MnF$_6$ powder (0.30 g) was dissolved in silicon fluoride solution (1.2 g of SiO$_2$ in 35 mL of 48% HF) with stirring. Meanwhile, 1.26 g of NaF and 1.75 g of KF were dissolved in 15 mL of 48% HF. Then, the NaF and KF solution was added to the K$_2$MnF$_6$ solution with stirring for 5 min. Some yellow powder was obtained and then the powder was washed with ethanol (99.9%) and dried at 70 °C. The samples were subsequently prepared for measurement. K$_2$SiF$_6$:0.06 Mn$_{4}^{4+}$ and Na$_3$SiF$_6$:Mn$_{6}^{4+}$ were prepared using the same method. To prevent any injury from hydrogen fluoride, all the experimental processes are conducted under good protective cloth, gloves, and goggles.

The samples were analyzed by X-ray diffraction (XRD) using a D2 Phaser (Bruker) diffractometer operating with Cu Ka radiation ($\lambda = 1.5418$ Å) to identify their phase purity. The synchrotron XRD pattern of KNaSiF$_6$Mn$_{4}^{4+}$ was also examined for refinement at the BL01C2 beamline of the National Synchrotron Radiation Research Center (Taiwan) at a wavelength of 0.688808 Å. Total Pattern Analysis Solution (TOPAS) software was used to perform XRD Rietveld refinement. PL spectra were measured using a FluoroMax-3 spectrophotometer. Temperature-dependent luminescence (25–300 °C) was determined using a THMS-600 apparatus combined with PL equipment. All solid-state nuclear magnetic resonance (NMR) spectra were acquired on a 14.1 T wide-bore Bruker Avance III spectrometer equipped with a 4 mm magic-angle-spinning (MAS) probe head. The Larmor frequency for $^{29}$Si was 119.2 MHz, the spinning rate for the $^{29}$Si MAS NMR spectra was 10 kHz, and the recycle delay was 60 s. PL excitation (PLE) spectra were recorded using a system consisting of a 150 W Xe lamp, two monochromators SPM2, and two Hamamatsu R928 photomultipliers (the first for luminescence and the second for reference signal detection). Steady-state luminescence measurements were performed with an Andor SR-750-D1 spectrometer equipped with a CCD camera (DU420A-OE). The excitation source was a He–Cd laser at 442 nm. We used the system consisting of a PL 2143 A/SS laser and a PG 401/SH parametric optical generator to obtain luminescence decays. Emission signals were analyzed using a Bruker Optics 2501S spectrophotograph and a Hamamatsu Streak camera (model C4334–01). High hydrostatic pressure was applied to a Merrill Bassett-type diamond anvil cell. Polydimethylsiloxane oil was used as the pressure-transmitting medium, and pressure was measured in terms of shifts in the R$_1$ luminescence line of ruby.

The composition, crystal structure, and phase purity of the as-synthesized samples were investigated by powder XRD. The synchrotron XRD with synchrotron light source and TOPAS fitting software were also used to obtain more detailed structural information on KNaSiF$_6$:Mn$_{4}^{4+}$ phosphor. Figure 1a displays the Rietveld structure refinement results of KNaSiF$_6$:0.06Mn$_{4}^{4+}$. The crystallographic data of KNaSiF$_6$ are used as the initial structure model during refinement, and the actual structure of KNaSiF$_6$:0.06Mn$_{4}^{4+}$ is constructed. The diffraction peaks of KNaSiF$_6$:Mn$_{6}^{4+}$ could be indexed to an orthorhombic Pnma structure (ICSD No. 07–1334). The lattice parameters, including $a = 9.33208(21)$ Å, $b = 5.50742(11)$ Å, $c = 9.80288(22)$ Å, $\alpha = \beta = \gamma = 90^\circ$, and cell volume = 503.825(19) Å$^3$, are also accurately determined. The $\chi^2$ and R-Bragg values are 1.44 and 6.01, respectively, which indicates the validity of the refinement process.

The bond angle of the central atom was examined to study the relationship between the phosphor structure and its PL spectrum. The refinement data show that there are two different bond angles. The angle of the axial bond pair is approximately 179.29°, whereas the angle of two other bond pairs in the equatorial part is 174.11°. When Mn$^{4+}$ ions are introduced to the host, these ions substitute Si$^{4+}$ sites to form the MnF$_{2}^-$ group, comparing with the Si$^{4+}$ ion, the valence state ($r_{\text{Si}} = 0.040$ nm and $r_{\text{Mn}} = 0.053$ nm), and the unit cell crystal structure and coordination environment of KNaSiF$_6$ are shown in Figure 1b. A KNaSiF$_6$ unit cell clearly contains four formula units. Only one type of SiF$_{6}^{2-}$ octahedral group is observed. The Si$^{4+}$ ions are surrounded by six F$^{-}$ ions, with two different angles: $\angle F_{2}SiF_{2} = 174.11^\circ$ and $\angle F_{2}SiF_{4} = 179.29^\circ$ (Figure 1c). The $^{29}$Si NMR spectrum of KNaSiF$_6$:0.06Mn$_{4}^{4+}$ is shown in Figure 1d. The spectrum of KNaSiF$_6$ contains only one resonance at $-188$ ppm because this phosphor presents only one Si six-coordinate site.

To investigate the structure well, we performed two sets of density functional theory (DFT)-based calculations. These calculations are based on generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional and local density approximation (LDA) with the Ceperley–Alder–Perdew–Zunger (CA-PZ) functional. The calculations are performed with the CASTEP module of the Materials Studio package, and a summary of the experimental and calculated structural data for KNaSiF$_6$ is presented in Table 1. The electron configurations are considered as follows: Na, $2s^22p^63s^1$; K, $3s^23p^64s^1$; Si, $3s^23p^6$; and F, $2s^22p^5$. The cutoff
energy is chosen as 370 eV. The k-point mesh is set to $5 \times 8 \times 5$, corresponding to a separation between k-points of 0.02 Å. The convergence criteria are as follows: energy, $1 \times 10^{-5}$ eV/atom; maximal force, 0.03 eV/Å; maximal stress, 0.05 GPa; and maximal displacement, 0.001 Å.

Comparative results from Table 1 show that the experimental and theoretical structural data (including the lattice constants and fractional atomic positions) present good agreement among all data sets. The largest differences between experimental and optimized lattice constants were +4% for constant $c$ (LDA calculations) and −3% for a constant (GGA calculations). An overall agreement with the experimental data is beneficial for the GGA calculations.

After optimization of the KNaSiF$_6$ structure, the electronic and optical properties of the phosphor were calculated at ambient and elevated hydrostatic pressure. Figure 2 shows the calculated band structure at ambient pressure. The band gap is direct, and the band gap values are 7.417 eV (LDA) and 6.98 eV (GGA). The real band gap is approximately 8–9 eV because DFT-calculated band gaps are always underestimated.

The valence band of KNaSiF$_6$ is remarkably flat, which reveals the very low mobility of the holes. By contrast, the dispersion of electronic states forming the conduction band is highly pronounced. Well-resolved sub-bands separated by narrow gaps are found in the valence band. The nature of these gaps, as well as the origin and composition of all calculated bands, can be understood with the help of the density of states (DOS) diagrams (Figure 3).

![Figure 1](image1.png)

**Figure 1.** (a) Rietveld refinement results of the powder X-ray diffraction profile of KNaSiF$_6$:0.06Mn$^{4+}$ phosphor ($R_{wp} = 10.48\%$, $R_p = 8.18\%$ and $\chi^2 = 1.44$); (b) crystal structure of KNaSiF$_6$:Mn$^{4+}$; (c) crystal structure of the SiF$_6^{2-}$ octahedron; (d) $^{29}$Si NMR spectrum of KNaSiF$_6$:0.06Mn$^{4+}$.

![Figure 2](image2.png)

**Figure 2.** Calculated band structure (GGA-calculated, solid line; LDA-calculated, dashed line) of KNaSiF$_6$.

![Figure 3](image3.png)

**Table 1.** Experimental and Calculated Structural Data of KNaSiF$_6$

<table>
<thead>
<tr>
<th>exp.</th>
<th>LDA</th>
<th>GGA</th>
</tr>
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<tr>
<td></td>
<td>lattice constants (Å)</td>
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<tr>
<td>$a$</td>
<td>9.3246</td>
<td>9.102647 (+2.4%)</td>
</tr>
<tr>
<td>$b$</td>
<td>5.4992</td>
<td>5.293121 (+3.7%)</td>
</tr>
<tr>
<td>$c$</td>
<td>9.7892</td>
<td>9.388901 (+4.1%)</td>
</tr>
<tr>
<td></td>
<td>fractional atomic positions</td>
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</tr>
<tr>
<td>$x$</td>
<td>0.156</td>
<td>0.2500</td>
</tr>
<tr>
<td>$y$</td>
<td>0.2500</td>
<td>0.5154</td>
</tr>
<tr>
<td>$z$</td>
<td>0.2500</td>
<td>0.5117</td>
</tr>
<tr>
<td>$x$</td>
<td>0.5117</td>
<td>0.1753</td>
</tr>
<tr>
<td>$y$</td>
<td>0.2500</td>
<td>0.1753</td>
</tr>
<tr>
<td>$z$</td>
<td>0.1753</td>
<td>0.2500</td>
</tr>
<tr>
<td>K</td>
<td>0.3718</td>
<td>0.2500</td>
</tr>
<tr>
<td>Na</td>
<td>0.9206</td>
<td>0.2500</td>
</tr>
<tr>
<td>Si</td>
<td>0.2290</td>
<td>0.2500</td>
</tr>
<tr>
<td>F1</td>
<td>0.3274</td>
<td>0.2500</td>
</tr>
<tr>
<td>F2</td>
<td>0.1254</td>
<td>0.2500</td>
</tr>
<tr>
<td>F3</td>
<td>0.1244</td>
<td>0.2500</td>
</tr>
<tr>
<td>F4</td>
<td>0.3313</td>
<td>0.2500</td>
</tr>
</tbody>
</table>
The conduction band is formed by the 3s and 4s states of Na and K, respectively. The valence band is formed by the 2p states of F and 3p states of Si. The 2p states of F ions at nonequivalent crystallographic sites are separated from each other and form the unusual structure of the valence band. The 3p states of Si sharply peak at the bottom of the valence band at approximately \(-4\) eV, whereas the F 2p states are spread over the whole valence band. The 3p states of K produce a sharp peak at approximately \(-9\) eV, whereas the 2p states of Na, 2s states of F are spread from around \(-18\) to \(-22.5\) eV.

The calculated effective Mulliken charges are as follows (LDA/GGA data are given): K + 1.04/+1.02, Na + 0.74/+0.76, Si + 2.10/+2.16, and F \(-0.65/-0.65\). Nearly all of the ions (except for K) show charges that are very different from those expected from their chemical formula. These findings indicate a considerable degree of covalency between the Si–F and Na–F bonds; K ions are bound to their neighbors in the crystal lattice predominantly by ionic bonds.

The effects of pressure on the physical properties of a solid can be modeled by optimizing the structure of a considered material at elevated pressures. The pressure range was set from 0 GPa (ambient pressure) to 10 GPa, with a step size of 2 GPa. Decreases in the volume of a crystal with pressure can be modeled by optimizing the structure of a considered material at elevated pressures.

Figure 3. Calculated density of states diagrams of KNaSiF6.

The equation (solid line) yields the following values: for LDA, \(B = 0.58\) and for GGA, \(B = 0.65\). The lattice constants \(a\), \(b\), and \(c\) also decrease with pressure according to the linear (for \(a\) and \(c\)) and quadratic (for \(b\)) fits shown in Figure 4b. Furthermore, the band gap changes with pressure (Figure 4c). Figure 4d shows the cross-section of the electron density difference. In this figure, the loss of electrons is described by a blue coloration, and electron enrichment is indicated by a red coloration. The white regions correspond to a very small difference in electron density compared with that of a free atom. These characteristics confirm our conclusion obtained from the analysis of effective Mulliken charges that the chemical bonds between Si and F ions are strongly covalent because of the overlap of red and blue colors, whereas Na and K ions are bound to the crystal lattice by ionic bonds because of the scarce overlap of colors.

PL and PLE spectra of the phosphors measured at room temperature are shown in Figure 5a. The excitation spectrum contains two broad bands around 355 and 460 nm (matching with the LED chips), corresponding with the spin-allow transitions \(4A_{2g} \rightarrow 4T_{1g}\) and \(4A_{2g} \rightarrow 4T_{2g}\) of Mn4+, respectively. The phosphor emits red emissions originating from the spin-forbidden \(d-d\) transition \(4E_g \rightarrow 4A_{2g}\) with several narrow bands at 610–650 nm under 460 nm excitation. The strongest emission is found at 629 nm. According to group theory, there are six fundamental internal vibronic modes, namely, \(\nu_T\), \(\nu_\sigma\), \(\nu_o\), \(\nu_{\sigma}\), \(\nu_{\pi}\), and \(\nu_{\pi}\), of the octahedral group with \(O_h\) symmetry. Three peaks (longer than 620 nm) belong to Stokes \(\nu_T\), \(\nu_\sigma\), and \(\nu_{\pi}\) peaks, and two other peaks (shorter than 620 nm) are anti-Stokes \(\nu_\sigma\) and \(\nu_{\pi}\) peaks. The peak at approximately 620 nm is the ZPL (Figure 5b), which is the electronic dipole forbidden in the octahedral MnF62−. The MnF62− octahedron is distorted because of \(\angle F_2MnF_2 = 179.29^\circ\) and \(\angle F_4MnF_4 = 173.7^\circ\). Intense ZPL could be observed at 620 nm. The higher distortion of MnF62− octahedron gives rise to the stronger the ZPL intensity. The distortion of a coordination octahedron around Mn4+ ion removes the center of inversion and then the parity selection rule is lifted (there are no odd/even states). The following examples and the PL spectra of KNaSiF6:Mn4+ under high pressure are in good agreement with that fact or conclusion. ZPL intensities are different among K2SiF6:Mn4+, KNaSiF6:Mn4+, and Na2SiF6:Mn4+(at 616 nm) (shown in Figure S1) because of their distinct distortions. The crystal structures of K2SiF6 and
Na$_2$SiF$_6$ are shown in Figures S2 and S3. Only one type of MnF$_6^{2−}$ octahedron without distortion ($∠F_1MnF_1 = ∠F_1SiF_1 = 180°$) is found in K$_2$SiF$_6$. Thus, no ZPL or very weak is found in the PL spectrum of this phosphor. By contrast two types of MnF$_6^{2−}$ octahedrons are found for Na$_2$SiF$_6$. One octahedron is without distortion ($∠F_1MnF_1 = ∠F_1SiF_1 = 180°$), but the other is seriously distorted ($∠F_2MnF_3 = ∠F_2SiF_3 = 171.48°$). Thus, a strong ZPL is observed in KNaSiF$_6$:Mn$^{4+}$ phosphor. The position of the ZPL depends on the perturbation of the cation ion. The full-width at half-maximum of the PLE provides more evidence of distortion. The orbital overlaps or hybridizes because of the distortion. Moreover, the PLE spectrum is broadened. As the angles of K$_2$SiF$_6$, KNaSiF$_6$ and Na$_2$SiF$_6$ are 180, 174.11, and 171.48°, respectively (just considering only larger distortions), the full width at half-maximum of the PLE should follow the order: K$_2$SiF$_6 < $ KNaSiF$_6 < Na$_2$SiF$_6$. These characteristics are consistent with the following experimental results: 54, 69, and 75 nm for K$_2$SiF$_6$, KNaSiF$_6$ and Na$_2$SiF$_6$, respectively (Figure S1). The room temperature PLE spectra of KNaSiF$_6$:Mn$^{4+}$ measured under different pressures are shown in Figure 6b. The excitation spectra contain two broad bands at 355 and 460 nm, corresponding to the spin-allowed transitions $^4A_2g \rightarrow ^4T_1g$ and $^4A_2g \rightarrow ^4T_2g$, respectively. Both excitation bands have blue shift as the pressure increases. The energy of the maxima shifts nearly linearly with increasing pressure at a rate of approximately 90 cm$^{-1}$/GPa (Figure 7). As will be shown in the next paragraph the PLE blue shift is related to increase of the crystal field strength and the PL red shift could be ascribed to hybridization of the orbital or an energy level split due to the decrease in lattice parameters $a$, $b$, and $c$ with increasing pressure, as shown by the calculation results in Figure 4. Also, although the emission transition from $^2E_g$ to $^4A_{2g}$ in the T-S diagram does not change with the pressure, the ZPL intensity also increases with pressure. All experimental results, including the high-pressure PL, and calculation results, support our supposition of the ZPL intensity of Mn$^{4+}$ in fluoride, which has not been previously reported.
energetic structure of the 3d^3 system is described quantitatively
by the Racach integrals B and C and by the crystal field strength
10Dq.23,24 The Tanabe-Sugano diagram presents the dependence
of the energies of localized states on the quantity of Dq/B. The
configurational coordinate diagram in Figure 8b presents the
ground and the first excited states of Mn^{4+}. The configuration
coordinate Q in this diagram represents the
positions of F^- with respect to Mn^{4+}. Because the ground 4A_{2g}
state and the doublet state 2E_g (as well as the 2T_{1g} and 2T_{2g}
states, which are not presented in Figure 8b) belong to the
ground electronic configuration t_2, the transitions between
these states do not change the electrons special distribution.
Therefore, the interactions between 3d^3 electrons and fluorite
ions are the same in these states. The related parabolas have
minima at the same value of Q. The excited quartet states
4T_{2g} and 4T_{1g} belong to the excited electronic configuration
t_2^e. Thus, transitions from the ground state to these states
change the spatial electrons distributions, which causes
expansion of the lattice around Mn^{4+} and the minima of the
respective parabolas are shifted to position Q. The lattice
relaxation energy can be calculated as follows

\[ Sho = \frac{k(Q - Q_0)^2}{2} \]

(2)

where S and k are the Huang-Rhys factor and elastic constant,
respectively, and \( \omega \) is the energy of local vibration mode.

Given that the PL spectrum consists of narrow bands related
to \( ^4E_g \rightarrow ^4A_{2g} \) transition and their phonon repetitions, Mn^{4+}
in KNaSiF_6 is the high-field system where the energy of the
4T_{2g} state is larger than that of the \( ^2E_g \) state. According to the
crystal field model, the energy of \( ^4T_{2g} \) with respect to the ground state
is equal to 10Dq,23−25 where D = \( \frac{3\Sigma Z^2}{4R^5} \) and

\[ Dq = \frac{Ze^2}{6R^5} \int |R_{3s}(r)|^2 r^4 dr \]

(3)

where R in eq 3 is the average distance between Mn^{4+} and F^- ions,
and \( R_{3s} \) is the radial part of the 3d wave function. According to eq 3, the value of 10Dq should increase when
pressure increases.

The value of 10Dq and Dq from the excitation spectrum
can be determined by the following relation

\[ 10Dq = E(4A_{2g} \rightarrow 4T_{2g}) - Sho \]

(4)

where E(4A_{2g} \rightarrow 4T_{2g}) is the energy of the lower excitation band
maximum and Sho is the energy of electron lattice coupling.
Analysis of the excitation spectra reveals Sho = 2500 cm^-1,
which is independent of pressure. Under this assumption, eq 4
allows calculation of the pressure dependence of Dq. The
following relations allow calculation of B and C for different
pressures.

\[ B = \frac{Dq(\Delta E/Dq)^2 - 10(\Delta E/Dq)}{10(\Delta E/Dq) - 8} \]

(5)

\[ C = \frac{\Delta E^2 - 9B + 9B^2/Dq}{3} \]

(6)

where \( \Delta E \) is the difference between the energy of the \( ^4T_{1g} \) and
\( ^4T_{2g} \) states and \( \Delta E' \) is the energy of the \( ^2E_g \) state. All quantities
depend nearly linearly on pressure. The obtained values for
ambient pressure and pressure rates are listed in Table 2.

Quantity of bulk modulus and their first derivative with
respect pressure obtained from ab initio calculations facilitate
verificiation of eq 3 which is fundamental relation for crystal
field model.

Figure 7. Energies of the specific transitions of KNaSiF_6: Mn^{4+} as a
function of pressure; solid lines represent the linear fittings (Table 2).

Figure 8. (a) Tanabe-Sugano diagram for Mn^{4+}; (b) configurational
diagram including the ground and first excited states; excitation and emission transitions are represented by arrows, respectively.
Table 2. Parameters of the Crystal Field Model and Their Dependence on Pressure

<table>
<thead>
<tr>
<th>Value</th>
<th>Pressure shift (cm⁻¹/GPa)</th>
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<tbody>
<tr>
<td>$D_q$</td>
<td>1925 ± 3</td>
</tr>
<tr>
<td>$B$</td>
<td>646 ± 20</td>
</tr>
<tr>
<td>$C$</td>
<td>4065 ± 20</td>
</tr>
<tr>
<td>$E(2E)$ for pressure &lt;7 GPa</td>
<td>16103 ± 3</td>
</tr>
<tr>
<td>$E(2E)$ for pressure &gt;8 GPa</td>
<td>16000 ± 3</td>
</tr>
<tr>
<td>$\Delta = E(2T_1g) - E(2E)$ for pressure &lt;7 GPa</td>
<td>3250 ± 6</td>
</tr>
<tr>
<td>$\Delta = E(2T_1g) - E(2E)$ for pressure &gt;8 GPa</td>
<td>4092 ± 6</td>
</tr>
</tbody>
</table>

Considering that pressure is isotropic and effects in the similarly in the microscopic and macroscopic scale, the following relation should be valid

$$\frac{dD_q}{dp} = \frac{dD_q}{dR} \frac{dR}{dp} = \frac{5D_q}{3B} \tag{7}$$

Our spectroscopic data yield the pressure rate for crystal field strength as $dD_q/dp = 9.4$ cm⁻¹/GPa; the calculated value of bulk modulus $B = 24$ GPa provides $SD_q/3B = 26$ cm⁻¹/GPa. The calculated result is over twice the experimental $dD_q/dp$. Such a difference has been previously reported for materials doped with C$^+$ and is believed to be related to increases in local microscopic compressibility with respect to the bulk material.  

The $^2E_g \rightarrow ^4A_{2g}$ luminescence decay curves were measured at different pressures under excitation at 442 nm to elucidate the luminescence behavior of KNaSiF$_6$. The results are shown in Figure 9a. The decay of the emission intensity can be well-fitted by a single exponential equation for all considered pressures. The decay constant for Mn$^{3+}$ emission is equal to 6.099 ms at ambient pressure before compression and 6.416 ms at 1.3 kbar after pressure-decompression. Figure 9b shows that the decay time of the Mn$^{4+}$ emission increases as pressure increases. Such behavior has been observed for C$_2$H$_4$ and for Mn$^{4+}$ in other materials.  

The $^2E_g \rightarrow ^4A_{2g}$ transition is spin-forbidden, and luminescence can appear because of the admixture of the lowest quartet state $^4T_2g$ to the first excited state labeled $^2E_g$ in Figure 8, through spin–orbital interaction. The complete model allowing the calculation of the probability of $^2E_g \rightarrow ^4A_{2g}$ transition in high field materials considering the spin–orbital interaction and electron phonon coupling in the excited $^2E_g$, $^2T_{1g}$, and $^4T_{2g}$ electronic states with their vibronic structures, is discussed in detail in the literature. In a high-field system where the $^2E_g$ and $^4T_{2g}$ states are separated by a large energy distance, the quartet contribution to the $^2E_g$ electronic manifold can be expressed using the perturbation approach. The lowest emitting state in this framework is the zero-phonon state of the first excited electronic manifold $^2E_g$. This state is represented by superposition of the spin doublet and spin quartet wave function, as follows

$$\Phi_Q(q, Q) = \psi^Q_E(q, \frac{1}{2})^2 \chi^Q_2(Q) + \psi^Q_E\left(q, \frac{3}{2}\right)^2 V_{r-o}$$

$$\sum_n \chi^Q_2(Q) S_{on} \approx (\Delta + n\omega) \tag{8}$$

In eq 8, $\psi^Q_E(q, \frac{1}{2})$ and $\psi^Q_E\left(q, \frac{3}{2}\right)$ are the electronic wave functions describing the $^2E_g$ and $^4T_{2g}$ states, $r$ is the electronic coordinate, and $\chi^Q_2(Q), \chi^Q_1(Q)$ are the respective vibronic wave functions of the $^2E_g$ and $^4T_{2g}$ electronic manifolds. $V_{r-o}$ is the spin orbit coupling constant, which can be determined as follows:

$$V_{r-o} = \int \phi^Q_E(q, \frac{1}{2}) H_s \psi^Q_E\left(q, \frac{3}{2}\right) dq \tag{9}$$

where $H_s$ is the spin–orbit coupling Hamiltonian and $S_{on}$ is the vibronic overlap integral, calculated as follows

$$S_{on} = \int \chi^Q_2(Q) \chi^Q_1(Q) \int dq = e^{-S/2} S^{n/2} \sqrt{n!} \tag{10}$$

$^2E_g \rightarrow ^4A_{2g}$ luminescence lifetime can be calculated from following relation:

$$\frac{1}{r} = \frac{1}{\tau_T} \frac{W_{r-o}^2}{\sum_{n} S_{on}^2 (\Delta + n\omega)^2} \tag{11}$$

where $1/\tau_T$ is the probability of $^4T_{2g} \rightarrow ^4A_{2g}$ radiative transition. When both $Sh\omega$ and $\hbar\omega$ are smaller than the separation energy $\Delta$, the following relation can be obtained:

$$\frac{1}{r} \approx \frac{W_{r-o}^2}{\tau_T (\Delta + Sh\omega)^2} \tag{12}$$

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The $^2E_g \rightarrow ^4A_{2g}$ luminescence lifetime can be calculated using eq 12, and the results are presented by the solid curve in Figure 9b. Fitting was achieved by assuming that $\tau = (5.3 \pm 0.5) \times 10^9$ cm$^{-2}$ s$^{-1}$ and is independent of pressure. For pressures greater than 15 GPa the lifetime $\tau$ increase slower, then it is predicted by eq 12. This result can be explained by the nonhydroelasticity of pressure, which generates shear-strength in the pressure transmitting medium and sample. The $^4T_{2g} \rightarrow ^4A_{2g}$ transition is parity forbidden and can be allowed due to interactions with optical phonons and odd parity lattice distortions. The effects of shear-strength at high pressure generate odd parity distortion that diminishes the value of $\tau_T$ and this effect is responsible for additional diminishing of the Mn$^{4+}$ luminescence decay time at high pressure, not considered in relation 12. It is consistent with the effect of the increase of the intensity of the ZPL with respect to phonon repetitions with increasing pressure. Considering possible distortions one can related this effect to odd parity static distortion of the MnF$_6$ system induced by pressure above 15 GPa.

Figure 10 shows the temperature-dependent luminescent spectrum of KNaSiF$_6$Mn$^{4+}$ under 460 nm excitation. No peak shifts while the intensity decreases as the temperature increasing. The integrated area, rather than the intensity, is considered in this study because of the narrow-band emissions of Mn$^{4+}$. Figure 10b shows the integrated area of KNaSiF$_6$Mn$^{4+}$ in the temperature range of 298–573 K. At 350 K, the relative intensity remains over 100% compared with that at 298 K and then decrease to 79% at 400 K. This result indicates excellent thermal stability for LEDs because the chip temperature of LED is approximately 400 K. The KNaSiF$_6$Mn$^{4+}$ red-emitting phosphor is a prospective candidate material for LEDs.

Quantum efficiency (QE), another important parameter for practical applications, can be calculated using the following expression:

$$\eta_{QE} = \frac{\int L_s \eta}{\int E_s - \int E_r}$$ (14)

where $L_s$ is the emission spectrum of the studied sample, $E_s$ is the spectrum of the light used to excite the sample, and $E_r$ is the spectrum of the excitation light without the sample in the integrating sphere. The internal efficiency QE of KNaSiF$_6$0.06Mn$^{4+}$ at 460 nm excitation is 0.90, and its external QE is 0.41. All of the results indicate that KNaSiF$_6$Mn$^{4+}$ phosphor may be a candidate material for LED applications.

Package experiments were performed to evaluate the potential application ability for KNaSiF$_6$Mn$^{4+}$ (Figure 11). Table 3 compares two different LED devices. The $R_a$ and $R_9$ of
the device combining a blue LED chip with YAG phosphor are only 69 and 0, respectively, because of the absence of red phosphor. Moreover, the CCT is 3518 K; thus, the device emits cool white light. The CCT should be lower than 4000 K and Rd should be higher than 80 to obtain warm white light. For comparison, the device consistent with the blue chip, YAG, and KNaSiF₆:Mn⁴⁺ shows warm white light with Rd = 90 and Rg = 93. The CCT of this device is much lower than that of the previous one. Normally, adding red phosphor into LED devices will decrease their luminescent efficacy because of Stokes shifting. However, the efficacy of the device we fabricated from YAG and KNaSiF₆:Mn⁴⁺ phosphor was 118 lm/W as the color temperature is 3455 K. These results reveal that KNaSiF₆:Mn⁴⁺ presents good luminescent properties and could be a potential candidate material for use in for back-lighting systems.

In summary, a simple two-step coprecipitation method was used to synthesize the hexafluorosilicate phosphor compounds, namely, Na₂SiF₆:Mn⁴⁺, K₂SiF₆:Mn⁴⁺, and KNaSiF₆:Mn⁴⁺. We clearly demonstrated the luminescence properties and ZPL intensity of the phosphors based on their PL spectra under ambient pressure and high pressures. Distortion of the MnF₆²⁻ octahedron was demonstrated based on the crystal structure of the phosphors. Analytical results from the PL spectra under ambient pressure and high pressure, XRD measurements, and corresponding calculations of lattice parameters showed that the ZPL intensity of the phosphors behaves as follows: the ZPL intensity appears when the MnF₆²⁻ octahedron is distorted and the more distorted the angle ∠FMnF = ∠FMF (M = Si, Ti, Ge) is from 180°, the more intense the ZPL intensity. This study provides a new perspective of the ZPL intensity of AMF₆:Mn⁴⁺ phosphors. The LED device was fabricated from YAG and KNaSiF₆:Mn⁴⁺ phosphor and its efficacy was 118 lm/W with the color temperature of 3455 K. These results reveal that KNaSiF₆:Mn⁴⁺ presents good luminescent properties and could be a candidate material for use in back-lighting systems.

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