High Color Rendering Index of Rb$_2$GeF$_6$:Mn$^{4+}$ for Light-Emitting Diodes

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Supporting Information

White light-emitting diodes (WLEDs) have been employed in different illumination systems worldwide, because of their high luminosity, low energy consumption, high durability, and eco-friendliness.1,2 To enhance the color rendering index of the device, red light phosphors are necessary to enrich the red region of the spectra. Nitride phosphors such as M$_2$Si$_5$N$_8$:Eu$^{2+}$ (M = Ca, Sr, and Ba) and MAliSiN$_3$:Eu$^{2+}$ (M = Ca and Sr) are commonly used red phosphors applied in a WLED device.3,4 However, the human eye is least sensitive to red light; therefore, we hardly detect red light emission above 650 nm wavelength. As a result, the broadened band emission peak at approximately 650 nm may cause high energy loss in WLED usage. Fluoride phosphor with high intensity and line spectra, with peak at 630 nm, can be detected by human eyes.5 Moreover, fluoride phosphors have two broad excitation bands located at 360 and 460 nm where the blue light and ultraviolet regions are located. Fluoride phosphors do not show excitation in 550 nm, i.e., green-yellow light region, which can help WLED devices avoid reabsorption, thus making fluoride phosphor a suitable candidate for use in WLED devices. Nowadays, fluoride phosphors have been synthesized in different chemical composition. To make the changing in fluoride phosphors spectra, the distortion of the crystal is necessary to cause the formation of the zero-phonon line (ZPL), which gains another line peak at around 620 nm. In this study, we synthesized a new fluoride phosphor, namely, Rb$_2$GeF$_6$:Mn$^{4+}$ (RbGF), with the formation of zero-phonon line, which can further improve the color rendering index of WLED devices.6–8

The X-ray diffraction (XRD) pattern of the RbGF (Figure S1a), in which all the diffraction peak can be indexed to the hexagonal RbGF, indicates that pure single-phase RbGF can be obtained in a hexagonal system with the particle size around 30 to 50 μm (Figure S1b). Moreover, we conducted Rietveld refinement to obtain further information on RbGF (Figure 1a). The Rietveld refinement indicates that the $R_p$ = 2.55% and $R$-wp = 4.80% adequately represent real data, with the crystal parameter $a$ = 5.958 715(8) Å and $c$ = 9.670 58(2) Å belonging to hexagonal system with space group of P6$_3$mc (Table S1). Moreover, the geometry of GeF$_6^{2-}$ site has been simulated (Figure 1b). Results from the fitting show that the F−Ge−F bond angle is slightly distorted by the crystal structure, with an angle equal to 175.734(7)$^\circ$. The angle is different compared to that of a commercial fluoride phosphor such as K$_2$SiF$_6$:Mn$^{4+}$ (KSF), which has an F−Si−F angle equal to 180$^\circ$ with the point group of SiF$_6^{2-}$ site being O$_h$. Consequently, once the MnF$_6^{2-}$ activator was doped into RbGF in GeF$_6^{2-}$ site, MnF$_6^{2-}$ geometry may also be distorted, and the MnF$_6^{2-}$ point group will be decreased to C$_3$, which may directly affect RbGF spectra.

Room temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra (Figure 1c) have been measured. Emission spectra illustrate that RbGF differs from the commercial KSF by an extra peak at approximately 620 nm resulting from the zero-phonon line transition. Normally, fluoride phosphor, which has structural symmetry in the Mn$^{4+}$-doped site, undergoes a Laporte forbidden emission process. Without the coupling with odd (ungerade) vibration mode, Mn$^{4+}$ doped fluoride phosphor will not be able to conduct any electric dipole transition. To enable ZPL transition, the activator site symmetry must be distorted. Based on the Rietveld results, in the RbGF system, the activator site has been distorted, causing the point group to descend from O$_h$ to C$_3$. The electronic state is no longer described an even (gerade) function and Laporte rule is broken through because of the descent of the point group, and the ZPL transition process has been altered to an allowing transition. Moreover, unlike other fluoride phosphors where ZPLs always had extremely low quantum efficiency and external quantum efficiency (EQE) was

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only approximately 35%, RbGF has higher EQE at 57% (Table S2), which makes RbGF suited for application in commercial devices.\(^6\)

In the PLE spectra, four broad excited bands were clearly observed. To verify the origin of these peaks, energy levels of the Mn\(^{4+}\) ions in RbGF crystal were calculated using exchange charge model, which only uses a small number of fitting parameters of crystal field.\(^9\) The crystal field parameters (CFPs) and energy levels of crystal impurities could also be calculated without making any assumptions related to the impurity center symmetry.\(^10\) According to the results from XRD refinement, the cluster consisting of 87,384 ions, which considers the site of the impurity ion at the crystal lattice ions located at a distance of up to 119 Å, was built up. The Mn\(^{4+}\)–F\(^−\) overlap integrals were calculated numerically using the radial wave functions.\(^11,12\) Table S3 shows the obtained values of the CFPs and the comparison of the CFPs for Mn\(^{4+}\) ions in some other crystals. As seen from the table, the trigonal symmetry of the Mn\(^{4+}\) site (which upon doping occupies the Ge\(^{4+}\) position) is confirmed by the structure of the crystal field Hamiltonian: only three CFPs \((B_{2g}^{0}, B_{4u}^{0} \text{ and } B_{1u}^{0})\) are not zero. All data are consistent and indicate the presence of a large component of the low-symmetry crystal field (represented by the \(B_{2g}^{0}\) parameter). The values of the Racah parameters \(B\) and \(C\) for the Mn\(^{4+}\) ions at the Ge sites in Rb\(_2\)GeF\(_6\) crystal are reduced with respect to those for the Mn\(^{4+}\) ions in the free state and are very close to those for Mn\(^{4+}\) in the isostructural compound K\(_2\)GeF\(_6\).\(^13,14\)

Table S4 shows the calculated energy levels of Mn\(^{4+}\) ions in Rb\(_2\)GeF\(_6\). Figure 1c,d illustrates the relation between the calculated Mn\(^{4+}\) energy levels and experimental excitation/emission spectra. Assigning the most prominent spectral features in the RbGF spectra can be done as follows: two maxima at approximately 460 and 360 nm, which are attributed to the two transitions, namely, \(^4\)A\(_2\)→\(^4\)T\(_2\) and \(^4\)A\(_2\)→\(^4\)T\(_1\) (\(^4\)F). The maximum at approximately 215 nm is produced by the \(^4\)A\(_2\)→\(^4\)T\(_1\) (\(^4\)P) transition. Finally, the maximum at 163 nm is assigned to the band-to-band host absorption based on the first-principles calculations. The calculations were completed using the CASTEP module\(^{15}\) of the Materials Studio package. Both the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional\(^16\) and the local density approximation (LDA) with the Ceperley–Alder–Perdew–Zunger (CA–PZ) functional used (Table S5).\(^17,18\) The band gap (Figure S2) is direct, with the calculated band gap values at 6.583 eV for LDA and 5.773 eV for GGA. Because the DFT calculation of the band gaps always resulted in values lower than the actual value, the real band gap is estimated to be approximately 8–9 eV. The valence band of Rb\(_2\)GeF\(_6\) is remarkably flat, which indicates very low mobility of the holes. Oppositely, the dispersion of the electronic states forming the conduction band is well pronounced (Figure 1e). The origin of the calculated bands can be understood by using the density of states diagrams. The conduction band results from the 4s and 5s states of Ge and Rb ions. The 4p states of Ge and Rb ions contribute to the lower part of the valence band.

For detailed analysis of the relations between the ZPL and phonon sideband, the RbGF spectra and luminescence decay curve have been measured at high hydrostatic pressure from ambient to 300 kbar and at different temperatures ranging from 10 to 600 K. PL spectra were obtained at different pressures at room temperature. Both the ZPL and the phonon sideband shifted to lower energy when pressure increased (Figure 2a). The shift is almost linear, and the rate is equal to \(-2.6 \text{ cm}^{-1}/\text{kbar}^{-1}\) (Figure S2). The excitation bands related to the
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Figure 2. (a) Pressure dependent excitation spectra ($\lambda_{ex} = 442$ nm) and emission ($\lambda_{em} = \nu_0$ emission peak) of Rb$_2$GeF$_6$:Mn$^{4+}$. (b) Comparison of ambient pressure emission spectra before and after compression–decompression cycle. (c) Temperature dependent spectra from 10 to 600 K.

$^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_1$ transition exhibited linear pressure-induced spectral shift toward higher energies at a rate equal to 6.0 and $5.7$ cm$^{-1}$/kbar (Figure S2) as a result of increasing the crystal field strength (10 $D_q$) with pressure (see Figure 1d). Pressure dependence of the ZPL intensity (relative to the phonon lines) was observed. Starting from ambient pressure, the relative intensity of ZPL gradually increases with increasing pressure, reaching a maximum at 70 kbar. Above this value, the relative intensity of ZPL decreases. The comparison of initial emission spectrum with a spectrum after compression to 290 kbar and decompression back to ambient pressure (Figure 2b) shows that the decrease of relative intensity of ZPL is a permanent effect. In temperature dependent spectra, ZPL and Stokes sideband are observed at all temperatures, ranging from low 10 to 600 K, whereas the anti-Stokes sideband appears when the temperature rises above 100 K. At low temperature, the systems are more likely to distribute in the vibration ground state where only relaxation back to ground with ZPL and Stokes emission primarily occurs. When temperatures rises, electrons have enough energy to populate the upper vibration state and relax back to ground state with anti-Stokes emission. Moreover, the relative intensity of the ZPL gradually decreases as the temperature increases. That is, the ZPL and vibronic process may compete with each other during the radiative relaxation process. The decrease of the ZPL with respect to anti-Stokes sideband with increasing temperature (Figure 2c) is because at higher temperatures the system prefers transitions from the higher vibration states, which reduce the intensity of ZPL. Moreover, the RbGF shows a good thermal stability which remain 83% PL quantum efficiency at 500 K related to the room temperature intensity (Figure S3).

Figure S4 presents the ambient pressure- and temperature-dependent decay curves of RbGF $^2E \rightarrow ^4A_2$ ZPL whereas Figure 3 contains decay times calculated from single exponential fitting. The decay time (Figure 3a) at the lowest temperature is the longest (12 ms at 8 K) and swiftly decreases with increasing temperature in an approximately linear manner, reaching 1 ms at 480 K. Figure S3b shows pressure dependence of the $^2E \rightarrow ^4A_2$ ZPL decay time that gradually increases with increasing pressure (see calculated decay times in Figure 3b). Pressure and temperature dependence of PL decay time was analyzed using the model developed by Grinberg$^{19}$ for Cr$^{3+}$, which has the same electronic configuration as the Mn$^{4+}$. Because Mn$^{4+}$ is the typical high-field system where the energy of the $^2T_2$ state is much larger than the energy of the emitting $^2E$ state, the simplified model based on the perturbation approach was used. According to this model, the spin-forbidden $^2E \rightarrow ^4A_2$ transition occurs because of the spin–orbit coupling of the $^2E$ and $^4T_2$ states. Thus, the perturbation approach results in the following relation between the low temperature lifetime of the $^2E \rightarrow ^4A_2$ luminescence $\tau_E$ and probability of radiative transition $1/\tau_T$ that would characterize the $^4T_2 \rightarrow ^4A_2$ luminescence:

$$\frac{1}{\tau_E} \approx \frac{V^2}{\tau_T} \frac{1}{(\Delta')^2}$$  

(1)

where $V$ is the quantity of the spin–orbit coupling and $\Delta$ is the difference between energies $^2E$ and $^4T_2$ states obtained from excitation spectrum (in our case, $\Delta' = 5500$ cm$^{-1}$). Considering these data, we used eq 1 to obtain value of the ratio $V^2/\tau_T = 2630$ cm$^{-2}$/µs.

The decrease of the $^2E \rightarrow ^4A_2$ lifetime with increasing temperature results from the opening of additional relaxation pathways with increasing temperature. The shape of the temperature dependence of the PL decay shows that we deal with at least two different pathways that open approximately at temperatures 100 and 300 K. We have considered two effects that open the additional de-excitation possibilities. The first one, with threshold near 300 K, results from thermal occupation of the $^4T_2$ state, which is located at energy $\Delta$ above the $^2E_g$ state. This energy is smaller than $\Delta'$ through lattice relaxation energy of the system in the $^4T_2$ state. The second pathway is related to anti-Stokes sharp line sideband
which opens at a temperature of 100 K and is characterized by the radiative lifetime $\tau'$. We have considered both effects. The quantity of $\Delta'$ was obtained from analysis of excitation spectrum. In our case, $\Delta' = 2900 \text{ cm}^{-1}$. The effective energy of phonons $\hbar\omega$ and relative (with respect to the transition probability from the ZPL and Stokes sideband) probability of radiative transition from anti-Stokes line $p'$ were considered as free parameters. We have related these quantities using the following equation:

$$\frac{1}{\tau} = \left(\frac{\hbar}{\tau} + \frac{\Delta}{\Delta'}\right)^2 p'. $$

The dependence of the PL lifetime on temperature was then fitted to the following equation:

$$\tau_R = \frac{1 + \exp\left(-\frac{\hbar\omega}{kT}\right) + 3\exp\left(-\frac{\Delta}{kT}\right)}{\frac{1}{\tau_1}\left(\left(\frac{\Delta}{\Delta'}\right)^2 \left[1 + p'\exp\left(-\frac{\hbar\omega}{kT}\right)\right] + 3\exp\left(-\frac{\Delta}{kT}\right)\right)} \tag{2}$$

The fitted dependence is presented in Figure 3a by a solid curve. The obtained values are listed in Figure 3a. The same values were used to fit dependence of PL lifetime on pressure. The best fitting was obtained when we used eq 2 with values $\hbar\omega = 437 \text{ cm}^{-1}$, $\tau_1 = 1.15 \mu$s, $V = 55 \text{ cm}^{-1}$, $p'/\tau_1 = 10.2 \mu$s$^{-1}$, and $\tau' = 1.13$ ms, and $p' = 11.7$; such a large quantity of $p'$ shows that appearance of the anti-Stokes sideband causes increase of the $3E\rightarrow^4A_2$ radiative transition probability by a factor about 10. The pressure effect was included considering that values $\Delta'$ and $\Delta$ increase linearly with pressure (see Figure 2a and Figure 3b), with the rate $d\Delta/dp = d\Delta'/dp = 8.6 \text{ cm}^{-1}/\text{kbar}$. The pressure dependence of the lifetime was fitted using eq 2, and the result is presented in Figure 3b by solid curve. Our analysis of temperature and pressure dependence of the $3E\rightarrow^4A_2$ PL lifetime shows that luminescence is mainly possible because of the spin–orbit interaction of $^2E$ and $^2T_2$ states. We found that effective spin–orbit coupling energy is equal to 55 cm$^{-1}$, which is much smaller than the spin–orbit coupling of free ion. This effect is the result of the reducing of the quantity of the spin–orbit interaction Hamiltonian by vibronic overlap integrals between the involved states expressed in Born–Oppenheimer approximation as a products of the electronic and vibronic wave functions. The estimated value of $^4T_2$ radiative lifetime is equal to 1.15 $\mu$s. Fitted value of effective phonon is a little bit larger than the lowest energies observed in phonons involved in phonon sideband.

Nowadays, we usually use fluoride phosphor without ZPL to conduct the packages; however, we can see that in Figure S5 the line spectra of fluoride phosphor are beneficial to avoid the visible-light-sensitive region (650 nm) of the human eyes. Although, human eyes only detected limited red light in 630 nm. In terms of ZPL formation, RbGF with ZPL showed a similar spectra position as KSF (Figure S6). However, the RbGF spectra get one more peak in the 620 nm region where human eyes are more light-sensitive. Therefore, if the RbGF would be fabricated into WLED device, ZPL formation can allow the efficient use of the spectra in WLED.

To verify whether ZPL formation can enhance the color rendering index in WLED, RbGF and KSF performance in the LED device has been compared (Figure 4a). We have chosen the KSF and RbGF with similar quantum efficiency (Table S2). The WLED devices were fabricated from the two fluoride phosphor (KSF and RbGF) with the same YAG and blue LED chip. To compare their performance (R9 and Ra), their CIE was controlled to the same position (Figure 4b,c) ($x = 0.4220$, $y = 0.4145$, with the color temperature at approximately 3400 K). Results show that the RbGF had a higher Ra at 91 and R9 at 79, which may be because the ZPL contributed to the 620 nm spectra, overwhelming KSF results, with Ra = 85 and R9 = 46 (Table S6). Therefore, with the similar quantum efficiency, we can get a better Ra in the fluoride with ZPL. Nevertheless, RbGF, as with other fluoride phosphors, did not show a good stability in the humidity/temperature condition (Figure S7), which needs to be improved in the future.

In summary, RbGF fluoride phosphor spectra have been studied theoretically and experimentally in detail. The ZPL formation mechanism and variation in spectra under different conditions have been studied. Pressure-dependent spectra exhibit a shift in PL and PLE band location and show an interesting alteration in the ZPL. Moreover, alteration of the spectra has been explained in dynamics through lifetime measurement and calculation, which can be a basis for successful application of RbGF fluoride phosphor in different temperatures and pressure conditions. The package results have shown that with the formation of ZPL, Ra can be increased from Ra = 85 (fabrication through KSF) to Ra = 91 (fabrication through RbGF). Consequently, the fluoride phosphor that formed ZPL and exhibited high quantum efficiency may be the critical material in revolutionizing WLED.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b05244.

Experimental methods, refinement tables, calculation tables of ECM, LDA and GGA, package tables, band structure, lifetime measurement, and fluorides phosphors comparison spectra (PDF)

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Notes

The authors declare no competing financial interest.

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