Synthesis, structure and optical performance of red-emitting phosphor $\text{Ba}_5\text{AlF}_{13}:\text{Mn}^{4+}$

Lin Qin, Peiqing Cai, Cuili Chen, Jing Wang and Hyo Jin Seo

Mn$^{4+}$-activated cubic phase $\text{Ba}_5\text{AlF}_{13}$ red phosphors were prepared by the two-step coprecipitation method. The structural and optical features were characterized on the basis of X-ray diffraction (XRD), transmission electron microscopy (TEM), emission and excitation spectra, and luminescence decay curves. The $\text{Ba}_5\text{AlF}_{13}:\text{Mn}^{4+}$ phosphors can be efficiently excited by near-UV to blue light and exhibit bright red emission at around 627 nm, which is assigned to the $2\text{E}_g$/$4\text{A}_{2g}$ transition of the 3d$^3$ electrons in $[\text{MnF}_6]$ octahedra. Temperature dependent emission spectra and decay curves from 10 to 550 K were measured to deeply understand the luminescence mechanism of Mn$^{4+}$ in the $\text{Ba}_5\text{AlF}_{13}$ lattice. Notably, this novel red phosphor shows excellent anti-thermal quenching behaviour (~700% of emission intensity at 300 K relative to 10 K).

1. Introduction

Compared with traditional oxide lattices, fluoride lattices have rich advantages; for example, lower phonon energy, high refractive index, high quantum efficiency, and high thermal stability. From the viewpoint of the low quenching probability of the excited states of the dopant ions, many fluoride lattices have been chosen as phosphors with various activators. Mn$^{4+}$, as a transition metal ion with an unfilled 3d$^3$ electron shell, plays an important role in lighting and display fields. Contrary to the rare-earth-ions with the parity-forbidden f–f transition, the luminescence properties of Mn$^{4+}$ with the d–d transition are easily influenced by various factors of the coordination environment. In fluoride lattices, Mn$^{4+}$ prefers to occupy sites with octahedral coordination, on which a strong crystal field acts. Therefore, the Mn$^{4+}$ ions exhibit an intense broad absorption band in the wavelength region near UV (550 nm) and a series of sharp emission lines peaking at around 630 nm. Due to these characteristics, considerable attention has been focused on this field.

A series of Mn$^{4+}$ activated red phosphors with high luminous efficacy have been reported as candidates for red-emitting phosphors, especially, Mn$^{4+}$-doped fluoride hosts. Mn$^{4+}$-activated microcrystals of K$_2$TiF$_6$ were successfully synthesized by Zhu et al. in 2014. The K$_2$TiF$_6$ microcrystals presented strong line emission with high luminescence quantum yield as high as 98%, high thermal stability, and extremely high emission intensity. Mn$^{4+}$-doped alkaline hexa-fluorides, $\text{B}_2\text{XF}_6:\text{Mn}^{4+}$ (B = K, Cs, Rb; X = Ti, Si and Ge), are well known as excellent red-emitting phosphors for warm w-LEDs. However, further exploration of novel Mn$^{4+}$-doped fluorides for red phosphors is deserved, and their properties should be investigated more deeply.

Here, in this work, we choose the Mn$^{4+}$-doped fluoride $\text{Ba}_5\text{AlF}_{13}$ as a red-emitting phosphor, which has not yet been reported in the literature to our best knowledge. The $\text{Ba}_5\text{AlF}_{13}:\text{Mn}^{4+}$ nanoparticles were synthesized via the two-step coprecipitation method. The phase formation, morphological features, excitation and emission spectra and thermal quenching behaviours were further investigated. The obtained product possesses a red line-emission spectrum with high thermal stability, which has the potential to enhance the color rendering index of an LED device.

2. Experimental

2.1 Synthesis process

The $\text{Ba}_5\text{AlF}_{13}:\text{Mn}^{4+}$ nanoparticles were prepared via the two-step coprecipitation method as shown in Fig. 1. The chemical reaction between K$_2$AlF$_6$ and $\text{Mn(NO}_3\text{)}_2$ in aqueous solution was first carried out, followed by the addition of NaOH solution to precipitate the Mn$^{4+}$ activated $\text{Ba}_5\text{AlF}_{13}$ nanoparticles. The precipitate was filtered, washed, and dried under UV light.

![Fig. 1 Two-step synthesis of the $\text{Ba}_5\text{AlF}_{13}:\text{Mn}^{4+}$ nanoparticles.](image-url)
reagents in the synthesis process were KMnO₄, KF, HF, Ba(NO₃)₂, Al(NO₃)₃, NaF, H₂O₂, and NaOH. Firstly, the tetravalent manganese source K₂MnF₆ was synthesized according to Bode’s method. The starting materials KF and KMnO₄ were both dissolved in HF solution. The mixed solution was stirred for at least 30 min and then doped with H₂O₂ aqueous solution drop by drop until the yellow precipitate K₂MnF₆ was obtained. In the process of preparing the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles, K₂MnF₆ was added to the HF solution, and then a double molar amount of NaF was added to yield the solution A.

In a separate vessel, Ba(NO₃)₂ and Al(NO₃)₃ were both dissolved in water to yield solution B. Then, the A and B solutions were mixed together, and an appropriate amount of NaOH was added drop-wise while stirring the solution to adjust the pH value to about 9. Finally, the resulting white slurry was filtered, washed several times using distilled water and then dried at 180 °C for 5 h.

2.2 Characterization

The structure of the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles was examined by XRD on a Rigaku D/Max 2000 diffractometer with operating parameters set to 40 kV and 30 mA. Transmission electron microscopy (TEM) was conducted to investigate the surface morphology of the samples. The samples were excited by using a 488 nm argon-ion laser and 355 nm pulsed Nd-YAG laser. The luminescence signal was detected using a photomultiplier tube (PMT, Hamamatsu, R928, Shizuoka, Japan) mounted on a 75 cm luminescence signal was detected using a photomultiplier tube (PMT, Hamamatsu, R928, Shizuoka, Japan). A 450 W Xe lamp dispersed by a 25 cm monochromator (Acton Research Corp. Pro-750). A 450 W Xe lamp dispersed by a 25 cm monochromator (Acton Research Corp. Pro-250) was used as a light source for the excitation and lamp dispersed by a 25 cm monochromator (Acton Research Corp. Pro-750). A 450 W Xe lamp dispersed by a 25 cm monochromator (Acton Research Corp. Pro-250).

3. Results and discussion

3.1 Structural characterization

Fig. 2 shows the XRD patterns of the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles as functions of Mn⁴⁺ concentration. The standard PDF card (PDF#44-1368) is displayed for comparison. All the diffraction peaks match well with the standard PDF card, indicating that the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles with different Mn⁴⁺ concentrations have been prepared as desired through the two-step coprecipitation method. The Ba₅AlF₁₃:Mn⁴⁺ nanoparticles crystallize in a cubic space group, Fd3m. The unit cell parameters are a = b = c = 17.378 Å, α = β = γ = 90°, V = 4427.83 Å³ and Z = 3. Although Ba₅AlF₁₃ and K₂MnF₆ have different crystal structures and there is a mismatch in the valence states between Al³⁺ and Mn⁶⁺, the Mn⁴⁺ ions can also be incorporated into the host lattice of Ba₅AlF₁₃ due to the similar ionic radii of Mn⁴⁺ (coordination number (CN) = 6, 0.53 Å) in [MnF₆] and Al³⁺ (CN = 6, 0.53 Å) in [AlF₆]³⁻.

Fig. 3 shows the structural map of Ba₅AlF₁₃ and an illustration of an [AlF₆] octahedron according to the atomic coordinate data from ref. 10. The Ba₅AlF₁₃ lattice contains only one unique crystallographic site of Al³⁺. All the Al³⁺ ions are located at the center of the regular octahedron [AlF₆] while Ba²⁺ forms [Ba(2)F₈] and [Ba(1)F₁₀] polyhedra connected together with the [AlF₆] octahedra. Since the ionic radius (0.530 Å) of Mn⁴⁺ is a little smaller than that (0.535 Å) of Al³⁺, the Mn⁴⁺-F⁻ distance is probably smaller than the Al³⁺-F⁻ distance. This means that a distorted system of [MnF₆] octahedra is preserved.

The actual size and morphology of the particles were analysed by TEM. Fig. 4a is a typical TEM image of the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles. The size of the nanoparticles is estimated to be about 120 × 120 nm². Fig. 4b shows the high-resolution TEM (HRTEM) image confirming the single-crystalline nature of the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles. In addition, the selected area electron diffraction (SAED) pattern (the inset of Fig. 4b) exhibits the cubic symmetry ascribed to the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles. The spacing of 3.33 Å corresponds to the (333) reflections of the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles.

3.2 Spectroscopic properties of Mn⁴⁺ ions in Ba₅AlF₁₃ lattice

The energy level scheme of Mn⁴⁺ in the lattice can be described by using the Tanabe–Sugano diagram and configuration coordinate model as shown in Fig. 5a and b, respectively. The
luminescence characteristics of the Mn⁴⁺ ions depend highly on the crystal field strength except for the ⁵T₂g and ⁵Eg states. The excitation spectrum of Mn⁴⁺ corresponds to the spin allowed ⁴A₂g / ⁴T₂g and ⁴A₂g / ⁴T₁g transitions, while the emission spectrum belongs to the spin-forbidden d–d transition from the ⁴Eg state to the ⁴A₂g state as in Fig. 5b. The lateral displacement between the parabolas of ground state ⁴A₂g and excited state ⁴T₁g (or ⁴T₂g) is large, while there is a small displacement between the parabolas of ⁴A₂g and ⁴Eg. A larger displacement implies a stronger electron–phonon interaction giving rise to a larger spectral bandwidth of the transition.¹² Thus, intense excitation bands with relatively large bandwidths are expected for the transitions between these states, as well as sharp emission lines due to the ⁴Eg → ⁴A₂g transition of Mn⁴⁺.

The room temperature excitation spectrum of Ba₅AlF₁₃:Mn⁴⁺ (0.5 mol%) is shown in Fig. 5c. The excitation spectrum is composed of two broad bands with the maxima at 360 and 460 nm corresponding to the spin allowed ⁴A₂g → ⁴T₁g and ⁴A₂g → ⁴T₂g transitions of Mn⁴⁺, respectively. A slight splitting phenomenon can be observed in the excitation band corresponding to the ⁴A₂ → ⁴T₂ transition but is not observed for the ⁴A₂ → ⁴T₁ transition, probably due to a strong overlap with the re-absorption band of the ⁴A₂ → ⁴T₁ and ⁴A₂ → ⁴E transitions.¹³ The excitation spectrum indicates that the red phosphor doped with Mn⁴⁺ can be effectively excited by near UV/blue light, which is especially ideal for blue light excitation LED chips.

Contrary to the excitation spectrum, the emission spectrum belongs to the spin-forbidden d–d transition from the ⁴Eg state to the ⁴A₂g state of Mn⁴⁺, as shown in Fig. 5d. The emission spectrum consists of several sharp lines with the main peak at 627 nm. In general, the zero-phonon line (ZPL) of Mn⁴⁺ in fluoride lattices is located at around 620 nm.⁴ The three peaks at wavelengths longer than 620 nm belong to Stokes ν₆ (t₃u bending), ν₅ (t₁u bending), and ν₃ (t₁u stretching) modes, whereas the two peaks at wavelengths shorter than 620 nm belong to anti-Stokes ν₆ (t₃u bending) and ν₅ (t₁u bending) modes. The ZPL is not observable for highly symmetrical lattice environments, for example, Rb₂SiF₆:Mn⁴⁺ and BaTiF₆:Mn⁴⁺ red phosphors.⁴,¹⁴ More distorted coordination environments cause a stronger intensity of the ZPL line.⁶ The intense ZPL observed in the emission spectrum of the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles indicates that the Mn⁴⁺ ions experience a lower crystal field symmetry which is mainly due to the distorted [MnF₆] octahedron in the Ba₅AlF₁₃:Mn⁴⁺ lattice. According to ref. 6, the existence of ZPL emission in a Mn⁴⁺ doped phosphor can further improve the color rendering index. The CIE chromaticity coordinates of Ba₅AlF₁₃:Mn⁴⁺ are calculated to be (x = 0.691, y = 0.31), which are close to the National Television System Committee (NTSC) standard values for red color (x = 0.67, y = 0.33).¹⁵

The local crystal field strength D₀ and two Racah parameters B and C can be introduced to describe the unique energy levels
of the Mn⁴⁺ ions in the Ba₅AlF₁₃ lattice. The local crystal field strength D₀ is given by the mean peak energy of the 4A₂g → 4T₂g transition as obtained by the following equation:

\[ D₀ = \frac{E(4A₂g - 4T₂g)}{10} \]  

(1)

In this work, 10D₀ is estimated to be 21 500 cm⁻¹ from the excitation spectrum. On the basis of the peak energy difference (11 900 cm⁻¹) between the 4A₂g → 4T₂g and 4A₂g → 4T₁g transitions, the Racah parameters B and C can be evaluated by the expressions:

\[ \frac{D₀}{B} = \frac{15(x - 8)}{(x² - 10x)} \]  

(2)

\[ \frac{E(3F_g - 4A₂g)}{B} = \frac{3.05C}{B} + 7.9 - \frac{1.8B}{D₀} \]  

(3)

where the constant x is defined as

\[ x = \frac{E(4A₂g - 4T₁g)}{D₀} - \frac{E(4A₂g - 4T₂g)}{D₀} \]  

(4)

From eqn (2)–(4), the crystal field parameters B and C are calculated to be 587 and 3800 cm⁻¹, respectively, which are comparable to those of K₂SiF₆:Mn⁴⁺ (10D₀ = 23 900 cm⁻¹, B = 605 cm⁻¹, C = 3806 cm⁻¹) 16

The well-known K₂SiF₆:1% Mn⁴⁺ red phosphor was prepared for comparison with the Ba₅AlF₁₃:Mn⁴⁺ phosphor. The excitation spectrum of Ba₅AlF₁₃:Mn⁴⁺ shifts to lower energy, by about 2400 cm⁻¹, than that of K₂SiF₆:Mn⁴⁺ as shown in Fig. 5c. This means that the crystal field strength of Mn⁴⁺ is weaker in the Ba₅AlF₁₃ lattice. As reported in ref. 3, the 10D₀ value depends on the metal–ligand distance according to the relationship 10D₀ = KRⁿ, where K represents a constant and the value of n is approximately 5. As calculated in this work and with reference to ref. 3, the Al–F bond distance in the [AlF₆] group is 1.781 Å in Ba₅AlF₁₃, while the Si–F bond distance in the [SiF₆] group is 1.682 Å. Hence, the crystal field strength of Mn⁴⁺ is weaker in the Ba₅AlF₁₃ lattice, which is consistent with the calculated 10D₀ values above. As a consequence, the excitation spectrum of Ba₅AlF₁₃:Mn⁴⁺ shifts to lower energy. In addition, the luminescence intensity of the K₂SiF₆:1% Mn⁴⁺ red phosphor is about three times higher than the phosphor prepared in this work.

Fig. 6 shows the emission spectra and decay curves of the Ba₅AlF₁₃:Mn⁴⁺ nanoparticles as functions of Mn⁴⁺ concentration. No difference in spectral features between different Mn⁴⁺ concentrations is observed in the emission spectra except for the relative intensities of the phonon lines. The emission intensity increases with increasing Mn⁴⁺ concentration from 0.1 mol% and then reaches the maximum intensity at 0.5 mol%. With a further increase in Mn⁴⁺ concentration, the emission intensity starts to decrease gradually because of concentration quenching. However, the emission intensity ratio (R) of the integrated ZPL intensity to the integrated νₗ line intensity depends on the Mn⁴⁺ concentration as shown in the inset of Fig. 6a. As mentioned above, the intensity of the ZPL depends highly on the local symmetry of the environment surrounding Mn⁴⁺. The substitution of the larger Mn⁴⁺ ion for the smaller Al³⁺ ion gives rise to lattice distortion. Therefore, higher Mn⁴⁺ concentrations cause more distortion of the [MnF₆] octahedron, thus lowering the crystal field symmetry with larger values of R.

Fig. 6b shows the luminescence decay curves of Ba₅AlF₁₃:Mn⁴⁺ (0.1–1.5 mol%) nanoparticles obtained by monitoring the 627 nm emission under excitation at 355 nm. The average decay time τ can be calculated by using the following equation:

\[ \tau = \frac{\int_0^\infty I(t)dt}{\int_0^\infty I(t)dt} \]  

(5)

The decay time decreases with increasing Mn⁴⁺ concentration and the decay curves gradually deviate from the single exponential. The decay times are estimated to be 8.03, 7.34, 6.07 and 5.13 ms for the Mn⁴⁺ concentrations of 0.1, 0.5, 1.0 and 1.5 mol%, respectively. Samples with low Mn⁴⁺ concentrations feature reduced interactions between the Mn⁴⁺ ions, leading to nearly single exponential decay curves. However, with increasing Mn⁴⁺ concentration, the distance between the ions shortens; subsequently, energy transfer between the Mn⁴⁺ ions can occur, which provides an additional decay channel, leading to non-exponential decay curves. A possible explanation for this luminescence quenching is due to the higher nonradiative
energy migration through direct transfer among the Mn$^{4+}$ ions.$^{18,19}$

3.3 Unusual temperature-dependent emission spectra

Fig. 7a shows the emission spectra of Ba$_5$AlF$_{13}$:Mn$^{4+}$ (0.5 mol%) as functions of temperature in the temperature region 10–500 K under excitation at 488 nm. As mentioned above, the emission lines are assigned to the spin-forbidden $^2E_g \rightarrow ^4A_{2g}$ transition of Mn$^{4+}$, but can gain intensity by the activation of vibronic modes.$^{20}$ Some features are worth noting:

1. The emission spectra show different spectral features at different temperatures. At 10 K, the dominant peaks are those on the low-energy side of the ZPL at 620 nm, while at $T > 100$ K the emission lines become broader and appear not only on the low-energy side but also on the high-energy side, and are known as the Stokes and anti-Stokes emission lines, respectively. At low temperature, the systems are more likely to occupy the vibrational ground state and Stokes emission primarily occurs. However, when the temperature rises, the electrons have enough energy to populate the upper vibration states and relax back to the ground state of $^4A_{2g}$ with anti-Stokes emission.$^{21}$

2. Based on the temperature dependent emission spectra in Fig. 7a, the total emission intensity as a function of temperature is shown in Fig. 8. The emission intensity increases firstly and then decreases with further increase in temperature. The emission intensity of some previously studied luminescent phosphors consistently decreases with the increase of temperature which is mainly due to the increase of the non-radiative transition probability.$^{22}$ However, differently from most oxide lattices, Mn$^{4+}$-doped fluoride lattices exhibit anti-thermal quenching behavior.$^{21,23,24}$ As shown in Fig. 8, the total integrated emission intensity of the $^2E_g \rightarrow ^4A_{2g}$ transition at 300 K is found to be increased by about 700% compared with the initial intensity at 10 K and then decreased at higher temperatures due to the intense non-radiative transition. It is suggested for Ba$_5$AlF$_{13}$:Mn$^{4+}$ that the increased emission intensity is due to expansion of the host lattice and the enhancement of the lattice vibration modes with increasing temperature.$^{24}$

3. It is observed that all the emission peaks show a tiny red shift and become gradually broader with increasing temperature (Fig. 7b). This is mainly due to the expansion of the unit cell and the enhancement of the vibration modes of the MnF$_6^{2-}$ octahedra in a hot environment.$^{25}$

4. The shifts of emission peaks and the changes in the relative emission intensity may induce variations of the chromatic coordinates of the phosphor. The dependences of the chromatic coordinates upon the temperature are calculated in Table 1 and shown in Fig. 7c. The $x$ values slightly decrease, while the $y$ values slightly increase, with increasing temperature. The variations in chromatic coordinates are caused by the red-shift of emission bands and the enhancement of anti-Stokes bands.

Table 1 Calculated CIE values, the ratio $R$ of the anti-Stokes emission intensity to the Stokes emission intensity

| Temperature | $x$   | $y$   |
|-------------|------|------|
| 10 K        | 0.696| 0.304|
| 90 K        | 0.695| 0.305|
| 210 K       | 0.694| 0.306|
| 300 K       | 0.691| 0.309|
| 390 K       | 0.683| 0.317|
| 510 K       | 0.670| 0.330|
temperature and the temperature dependent decay times can be written by the following equation:26

\[
\tau = \frac{\tau_{\text{stat}} \left(1 + \exp\left(-\frac{\hbar \omega}{kT}\right)\right) + 3 \exp\left(-\frac{\Delta'}{kT}\right)}{1 + \frac{\tau_{\text{dyn}}}{\tau_{\text{stat}}} \exp\left(-\frac{\hbar \omega}{kT}\right) \left(\frac{W_{\text{SO}}}{\Delta'}\right)^2 + 3 \exp\left(-\frac{\Delta'}{kT}\right)}
\]

where \(\Delta'\) represents the energy difference between the \(^2E_g\) and \(^4T_{2g}\) states which can be calculated from the excitation spectrum. \(\Delta\) is the energy difference between the minimum energy of the \(^2E_g\) and \(^4T_{2g}\) states. \(\hbar \omega\) is considered as a free parameter for the effective energy of phonons and \(W_{\text{SO}}\) is an average spin-orbit parameter. \(\frac{\tau_{\text{stat}}}{\tau_{\text{dyn}}}\) is the ratio of the radiative decay times induced by static and dynamic processes. In addition, \(\frac{1}{\tau_{\text{dyn}}}\) is explicitly independent of temperature.24

The temperature dependent decay times are well fitted to eqn (6) and the fit result is shown by the solid red curve in Fig. 10a. The best fit result gives the parameters \(\Delta' = 5150 \text{ cm}^{-1}\), \(\Delta = 3170 \text{ cm}^{-1}\), \(\hbar \omega = 339 \text{ cm}^{-1}\), \(W_{\text{SO}} = 24 \text{ cm}^{-1}\), \(\tau_{\text{stat}} = 0.311 \text{ ms}\), and \(\frac{\tau_{\text{stat}}}{\tau_{\text{dyn}}} = 7.3\). The results of the temperature dependent decay times of the \(^2E_g\) state indicate that an additional relaxation pathway (the spin-allowed \(^4T_{2g} \rightarrow ^4A_{2g}\) transition) due to the spin–orbit interaction of \(^2E_g\) and \(^4T_{2g}\) states occurs with increasing temperature. As calculated, the obtained value of the radiative lifetime \(\tau_{\text{stat}}\) corresponding to \(^4T_2 \rightarrow ^4A_2\) is 0.311 ms, which is much shorter than the observed \(^2E \rightarrow ^4A_2\) transition. Moreover, the effective spin–orbit coupling energy (24 cm\(^{-1}\)) is much smaller than the spin–orbit coupling energy of the spin–orbit interaction Hamiltonian generated by vibronic overlap integrals between the involved states as products of the electronic and vibronic wave functions.21

4. Conclusions

Ba\(_2\)AlF\(_{13}\):Mn\(^{4+}\) nanoparticles were developed by the two-step coprecipitation method. Well-crystallized particles were obtained with sizes ranging from 300 to 500 nm. The phosphors can be effectively excited by near UV – blue light and show bright red emission colors with several sharp lines of emission in the wavelength region 60–660 nm. An intense ZPL emission at 620 nm is observed even at room temperature, which can be attributed to the incorporation of Mn\(^{4+}\) ions into highly distorted octahedral lattice sites. The temperature dependent luminescence indicates that the Ba\(_2\)AlF\(_{13}\):Mn\(^{4+}\) red phosphor shows significant anti-thermal quenching behaviour to increase its emission intensity at 300 K relative to 10 K. In addition, based on the temperature dependent decay curves, a modified dynamic model was constructed, indicating that an additional relaxation pathway (the spin-allowed \(^4T_{2g} \rightarrow ^4A_{2g}\) transition) occurs with increasing temperature.

Conflicts of interest

There are no conflicts to declare.

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