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Effects of change of the cation M$^{2+}$ on crystal structure and optical properties of divalent samarium-doped $\text{MAl}_2\text{Si}_2\text{O}_8$ ($\text{M}=\text{Ca, Sr, Ba}$)

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Abstract

In order to investigate the effects of cation ion change on crystal structure and optical properties of divalent samarium-doped $\text{MAl}_2\text{Si}_2\text{O}_8$, the $\text{Sm}^{2+}$ doped triclinic $\text{CaAl}_2\text{Si}_2\text{O}_8$ (CASO), monoclinic $\text{SrAl}_2\text{Si}_2\text{O}_8$ (SASO) and $\text{BaAl}_2\text{Si}_2\text{O}_8$ (M:BASO) as well as hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$ (H:BASO) have been synthesized using polymerizable-complex technique under reducing atmosphere. At room temperature, under the N-UV or blue excitation, $\text{Sm}^{2+}$ doped SASO, M:BASO and H:BASO showed strong red emission, which widen the group of novel red-emitting materials. Their emission bands of $\text{Sm}^{2+}$ consists of a broad 4f-5d transition band and sharp f-f transition lines. The correlation between the crystal structure and the 4f-4f transition emission intensity of $\text{Sm}^{2+}$ as well as the excitation peaks
of 5d energy level is deeply discussed, and the theoretical analysis is in good agreement with our experimental result. These are essential to understand the relationship between the crystal structure and luminescence properties, which are fundamental to design luminescent materials of Sm systems.

1. Introduction

The alkaline-earth feldspars MAI$_2$Si$_2$O$_8$ (M=Ca, Sr, Ba) were reported to be very suitable host lattices for the luminescent divalent rare earth ion especially the Eu$^{2+}$ ions$^{1-8}$. Among the various rare earth ions, Sm$^{2+}$ doped inorganic materials have been found important applications in lighting, display and persistent spectral hole-burning (PSHB)$^{9-13}$. Sm$^{2+}$ ions doped inorganic materials have been attracted more and more attention because they have the advantages of 4f-5d broad excitation and emission bands as well as the sharp f-f transition emission$^{9-14}$. The Sm$^{2+}$ generally has a broad continuum excitation band in the range from 200 to 500 nm. And its emission is composed of the 4f-5d broad band and deep red 4f$^6$-4f$^6$ sharp emission. However, optical properties of Sm$^{2+}$ doped alkaline-earth feldspars MAI$_2$Si$_2$O$_8$ (M=Ca, Sr, Ba) have not been reported.

On the other hand, the luminescence of divalent samarium ions is sensitive to the crystalline environment of the lattice site that it occupies$^{15}$. The relative position between the lowest-lying 4f$^5$5d$^1$ excited states and the 4f$^6$ ($^5$D$_0$) level governs whether the emission displays 4f$^6$$\rightarrow$4f$^6$ sharp
line and/or 4f⁵5d¹→4f⁶ broad band. It has been reported that the 4f-5d excited broad band is dependent on many factors such as the crystal field strength, the coordination number and the covalence of the bonds. Understanding the relationship between these factors and the 4f-5d transition of Sm²⁺ is of great importance due to the potential technological applications as functional photonic materials. We will choose the systematic alkaline-earth feldspars MAI₂Si₂O₈ (M=Ca, Sr, Ba) as the host lattices to investigate the effects of the crystal structure on the 4f-5d excitation band due to their characteristic structural properties. In these host lattices, firstly, the number of the M²⁺ site occupied by Sm²⁺ is different. In CaAl₂Si₂O₈, Ca²⁺ includes four different 2i sites, but only one kind of M²⁺ (Sr²⁺ or Ba²⁺) site exists in the SASO, M-BASO and H-BASO. So the effects of the number of the occupied sites on the 4f-5d transition can be obtained. Secondly, the symmetry of the M²⁺ is different. The Ba²⁺ site of H-BASO is central symmetry while the others are non-central symmetry. Thus the effects of the symmetry on the photoluminescence properties of Sm²⁺ can be shown. Thirdly, the SASO is monoclinic and isostructural with the M-BASO. They are similar to each other except the different cation site. So the effects of the cation ions on the 4f-5d of Sm²⁺ can be obtained. Fourthly, the H-BASO and the M-BASO are allomorphism. They are different in crystalline form without change in chemical constitution. So the effects the crystal
structure with the same chemical constitution on the f-d transition peak can be investigated.

In order to obtain more exact photoluminescence data and high-efficiency phosphor emission, it is necessary to utilize solution-based techniques for synthesis. We used Pechini-type sol-gel process\(^{19}\) (PSG, also known and called as polymerizable-complex technique) to synthesize the Sm doped MA\(_{2}\)Si\(_2\)O\(_8\) (M=Ca, Sr, Ba). If precursor powders are prepared using PSG, all the component ions can be evenly dispersed in the precursors, leading to the formation of high-purity phosphors with a uniform dispersion of Sm ions activators.

In our paper, the Sm\(^{2+}\) doped triclinic CaAl\(_2\)Si\(_2\)O\(_8\) (CASO), monoclinic SrAl\(_2\)Si\(_2\)O\(_8\) (SASO) and BaAl\(_2\)Si\(_2\)O\(_8\) (M-BASO) as well as hexagonal BaAl\(_2\)Si\(_2\)O\(_8\) (H-BASO) have been synthesized using polymerizable-complex technique under reducing atmosphere. The photoluminescence properties of Sm\(^{2+}\) in the systematic host lattices have been reported. Furthermore, the important chemical bonds such as the environmental factor (h\(_e\)) and parameter (F\(_C\)) were calculated using the dielectric theory of complex crystals. The effects of the crystal structure on the 4f-5d transition and f-f emission intensity of Sm\(^{2+}\) were discussed.

2. Experimental section

2.1. Sample Preparation: Unless otherwise stated, all reagents were purchased from Sigma-Aldrich. The MA\(_{2}\)Si\(_2\)O\(_8\) (M=Ca, Sr, Ba) powder
samples were prepared by a pechini-type sol-gel process (PSG, also known and called as polymerizable-complex technique), which can give the highest possible homogeneity for the material\textsuperscript{19}. The doping level of Sm ions was 5.0 mol % in MAI\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}:Sm. The mixtures were heated in a hydrogen-nitrogen (5\% H\textsubscript{2}+95\% N\textsubscript{2}) atmosphere.

The raw materials were Sm\textsubscript{2}O\textsubscript{3}, Ca(NO\textsubscript{3})\textsubscript{2} \cdot 4H\textsubscript{2}O, Ba(NO\textsubscript{3})\textsubscript{2}, Sr(NO\textsubscript{3})\textsubscript{2}, Al(NO\textsubscript{3})\textsubscript{3} \cdot 9H\textsubscript{2}O, tetraethyl orthosilicate (Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}, TEOS) and citric acid as the chelating agent. The 0.05M Sm(NO\textsubscript{3})\textsubscript{3} solution was prepared by dissolving Sm\textsubscript{2}O\textsubscript{3} in the diluted HNO\textsubscript{3} and adding appropriate volume of de-ionized water. The 0.25M M(NO\textsubscript{3})\textsubscript{2} (M=Ca, Sr, Ba), Al(NO\textsubscript{3})\textsubscript{3} solutions and 1M citric acid solution were prepared using the de-ionized water. Briefly, a stoichiometric volumes of M(NO\textsubscript{3})\textsubscript{2} (M=Ca, Sr, Ba) and Al(NO\textsubscript{3})\textsubscript{3} solutions were dissolved in an aqueous solution of citric acid (citric acid/M\textsuperscript{2+}=2:1, molar ratio) under vigorous stirring to form solution “A”. Then TEOS was dissolved using some ethanol under stirring to form solution “B”. Then A and B were mixed together and stirred for several hours at room temperature. The resultant mixture was heated up to 120 °C and kept at the temperature for 4 h to produce solid gels. The solid gels were prefired at 1200°C for 4 h. After being fully ground, Sm: M-BASO (M=Ca, Sr) samples were annealed at 1400°C in the reducing atmosphere for 6 h and single hexagonal and monoclinic phases of Sm: BASO were obtained between 1350 to 1650 °C in the reducing atmosphere for 6 h.
2.2. Characterizations

The phase purity of the as prepared phosphor was checked by powder x-ray diffraction (XRD) analysis by using a D/MAX 2500 instrument (Rigaku) with a Rint 2000 wide angle goniometer and Cu Kα1 radiation (λ = 1.54056 Å) at 40 kV and 100 mA. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a fluorescence spectrophotometer (Photon Technology International) equipped with a 60 W Xe-arc lamp as the excitation light source. All the measurements were taken at room temperature.

3. Theoretical method

The dielectric theory of complex crystals was used to calculate the chemical bond parameters of inorganic compounds quantitatively. In this theory, the complex crystals with crystal formula \( A_{a_1}^1 A_{a_2}^2 \cdots A_{a_i}^i B_{b_1}^1 B_{b_2}^2 \cdots B_{b_j}^j \) can be written as a linear combination of the sub-formula of various binary crystals when the crystal structure is known. The sub-formula of any type of chemical bond A-B in the multi-bond crystal \( A_{a_1}^1 A_{a_2}^2 \cdots A_{a_i}^i B_{b_1}^1 B_{b_2}^2 \cdots B_{b_j}^j \) ... can be expressed by the following formula:

\[
\frac{N_{(b'_{i-1}-a')}}{N_{(a'_{i-1}-b')}} A_i \frac{N_{(d'-b')}}{N_{(c'b')}} B_j = A_{a'_i} B_{b'_j}
\]  

(1)

where
\[ m_j = \frac{N_{(B^{j-1})} \times a_i}{N_{Cd}}, n_j = \frac{N_{(A^{j-1})} \times b_j}{N_{CB}} \]  

(2)

And the bond sub-formula equation is given by:

\[ A_{a_1}^1 A_{a_2}^2 \cdots A_{a_i}^i B_{b_1}^1 B_{b_2}^2 \cdots B_{b_j}^j = \sum_{i,j} A_{a_i}^i B_{b_j}^j \]

(3)

where \( A_{a_i}^i, B_{b_j}^j \) stands for the different constituent elements or different sites of the same element in the crystal formula, and \( a_i, b_j \) represents the number of the corresponding element. \( N_{(B^{j-1})} \) is the number of \( B^j \) ions in the coordination group of a \( A^i \) ion, and \( N_{Cd} \) represents the nearest coordination number of \( A^i \) ion. This means that the complex crystal is decomposed into the sum of different binary crystals like \( A_{a_i}^i B_{b_j}^j \).

Once the different binary crystals are obtained, the covalency of any \( \mu \) type binary bond can be defined as:

\[ f_c^\mu = \frac{E_h^{\mu 2}}{E_g^{\mu 2}} \]

(4)

where

\[ (E_g^{\mu})^2 = (E_h^{\mu})^2 + (C^\mu)^2 \]

(5)

and

\[ E_h^{\mu} = 39.74/(d^{\mu})^{2.48} \]

(6)

\[ C^\mu = 14.4b^{\mu} \exp(-k^\mu r_0^{\mu})[(Z_A^{\mu})^n - \frac{n}{m}(Z_B^{\mu})^n]/r_0^{\mu} \quad (n > m) \]

(7)

\[ C^\mu = 14.4b^{\mu} \exp(-k^\mu r_0^{\mu})[\frac{m}{n}(Z_A^{\mu})^n - (Z_B^{\mu})^n]/r_0^{\mu} \quad (n < m) \]

(8)

Here, \( d^{\mu} \) is the bond distance (in Å) and \( r_0^{\mu} \) is half of the bond distance. \( k^\mu \) is the Thomas-Fermis screening wavenumber of valence electrons and \( a_b \) is the Bohr radius. \( b^\mu \) is proportional to the square of the
average coordination number. \((Z_A^\mu)^*\) and \((Z_B^\mu)^*\) are the number of effective valence electrons of the cation and anion in the \(\mu\) type bond, respectively.

For the chemical bond of type \(\mu\), the polarizable coefficient \(\alpha_0^\mu\) can be obtained from the Lorentz-Lorenz equation

\[
\frac{(\varepsilon^\mu - 1)}{(\varepsilon^\mu - 2)} = \left(\frac{4\pi}{3}\right)\alpha_0^\mu
\]

Hence, the polarizability of the chemical bond volume \((\text{Å}^3)\) is given by:

\[
\alpha_b^\mu = \alpha_0^\mu v_b^\mu
\]

More detail calculation process can be referred to the reference \(^{25}\).

4. Result and discussion

4.1. Crystal Phase Formation

Figure 1. XRD patterns of Sm-doped MA\(_{2}\)Si\(_2\)O\(_8\) samples prepared in reducing
atmosphere. (a) CaAl$_2$Si$_2$O$_8$:Sm; (b) SrAl$_2$Si$_2$O$_8$:Sm; (c) monoclinic BaAl$_2$Si$_2$O$_8$:Sm; (d) hexagonal BaAl$_2$Si$_2$O$_8$:Sm

Figure 1. shows X-ray diffraction (XRD) patterns of Sm-doped MAI$_2$Si$_2$O$_8$ samples prepared in reducing atmosphere. It is clear that all the diffraction peaks of four Sm-doped compounds can be readily indexed to the corresponding standard data for triclinic phase of CaAl$_2$Si$_2$O$_8$ (JCPDS 48-1454), monoclinic phase of SrAl$_2$Si$_2$O$_8$ (JCPDS 38-1454) and BaAl$_2$Si$_2$O$_8$ (JCPDS 38-1450) as well as the hexagonal phase of BaAl$_2$Si$_2$O$_8$ (JCPDS 28-0124), respectively. No other impurities can be detected. In addition, the refined crystallographic unit cell parameters of the calcined products were calculated using the software Jade 5.0 and listed in Table 1.

Table 1: Unit cell parameters of Sm-doped MAI$_2$Si$_2$O$_8$ samples

<table>
<thead>
<tr>
<th>compound</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>α(°)</th>
<th>β(°)</th>
<th>γ(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-BASO:5%Sm</td>
<td>5.2942</td>
<td>5.2942</td>
<td>7.7836</td>
<td>90</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>Pure H-BASO$^a$</td>
<td>5.2955</td>
<td>5.2955</td>
<td>7.7817</td>
<td>90</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>M-BASO:5%Sm</td>
<td>8.6316</td>
<td>13.0444</td>
<td>14.4053</td>
<td>90</td>
<td>115.11</td>
<td>90</td>
</tr>
<tr>
<td>Pure M-BASO$^b$</td>
<td>8.6268</td>
<td>13.045</td>
<td>14.408</td>
<td>90</td>
<td>115.22</td>
<td>90</td>
</tr>
<tr>
<td>SASO:5%Sm</td>
<td>8.3705</td>
<td>12.9671</td>
<td>14.2559</td>
<td>90</td>
<td>115.25</td>
<td>90</td>
</tr>
<tr>
<td>Pure SASO$^c$</td>
<td>8.392</td>
<td>12.967</td>
<td>14.260</td>
<td>90</td>
<td>115.43</td>
<td>90</td>
</tr>
<tr>
<td>CASO:5%Sm</td>
<td>8.16785</td>
<td>12.87079</td>
<td>14.17677</td>
<td>93.2473</td>
<td>115.731</td>
<td>91.1248</td>
</tr>
<tr>
<td>Pure CASO$^d$</td>
<td>8.173</td>
<td>12.869</td>
<td>14.165</td>
<td>93.113</td>
<td>115.913</td>
<td>91.261</td>
</tr>
</tbody>
</table>

$^a$reference 4; $^b$reference 18 ; $^c$reference 17; $^d$reference 16

4.2. Photoluminescence Properties.

The photoluminescence properties of Sm$^{2+}$ in different host lattices are quite different because of their different environmental factor. Divalent Sm$^{2+}$ has the 4f$^6$ electron configuration. Under irradiation with UV to blue light, it can be excited into the 4f$^6$5d$^1$ continuum, from which the
ions rapidly relax to the lowest excited state\textsuperscript{9-13}. Just as the Eu\textsuperscript{2+} or Ce\textsuperscript{3+} ions, the f-d luminescence wavelength of phosphors employing Sm\textsuperscript{2+} changes greatly with the type of the host crystal\textsuperscript{1, 26}.

4.2.1. Characteristic luminescence of Sm\textsuperscript{2+} in MA\textsubscript{2}Si\textsubscript{2}O\textsubscript{8} (M=Ca, Sr, Ba):Sm
Figure 2. Photoluminescence emission and excitation spectra of Sm-doped MAI₂Si₂O₈ (M= Ba, Sr, Ca) samples related to the luminescence centre ions Sm²⁺ at room temperature.

Figures 2 shows the excitation and emission spectra of Sm doped
CASO, SASO, M-BASO and H-BASO samples at room temperature with the initial samarium concentration of 5 mol%. Different excitation wavelength produces different photoluminescence spectra. For CASO:Sm, Figure 2(a) shows the broad excitation band monitored by 689 nm with the peak at 375 nm. In the emission spectra under the excitation at 375 nm, a weaker $^5D_0 \rightarrow ^7F_0$ transition of Sm$^{2+}$ at 698.5 nm can be found (Figure 2(b)). Unusual luminescence of Sm$^{3+}$ in CASO can be monitored. As can be shown in Figure 2(b), the sharp emission lines at 565, 601, 648 nm come from the f:f transitions of Sm$^{3+}$, which can be assigned to $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$, respectively. It indicates the existence of Sm$^{3+}$ in CASO.

Figures 2(d), 2(f) and 2(h) show that Sm doped SASO, M-BASO and H-BASO samples exhibit efficient deep red emission under irradiation with UV light. For SASO: Sm, the excitation spectrum (Figure 2(c), $\lambda_{ex}=687$ nm) consists of a broad band from 250 to 500 nm with a maximum at 359.5 nm. This is assigned to 4f-5d transition of Sm$^{2+}$. As is shown in Figure 2(d), under the excitation into the 4f$^6$5d$^1$ states with the wavelength at 360 nm, the obtained emission spectra of SASO: Sm show a broad band emission from 600 to 750 nm overlapped with the f-f transitions of Sm$^{2+}$. The peak of the broad band emission is 662 nm assigned to f-d transition of Sm$^{2+}$. The sharp emission bands consists of three groups of lines at 687, 702 and 727 nm corresponding to the
$^{5}D_0\rightarrow^{7}F_0$, $^{5}D_0\rightarrow^{7}F_1$ and $^{5}D_0\rightarrow^{7}F_2$ transitions of Sm$^{2+}$, respectively. The dominant line is about 687 nm ($^{5}D_0\rightarrow^{7}F_0$ transition of Sm$^{2+}$ ions), which shows that Sm$^{2+}$ ions occupy the crystallographic sites without central symmetry in the host.

Table 2. The excitation and emission peak positions of Sm$^{2+}$ in the samples MAI$_2$Si$_2$O$_6$: 5\% Sm (M= Ba, Sr, Ca) ($^{*}$ indicates the strongest peak position of the excitation and emission spectra.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Excitation (f→d) (nm)</th>
<th>Emission (nm) f→f transition ($^{7}D_0\rightarrow^{7}F_J$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASO:Sm</td>
<td>375$^{*}$</td>
<td>689.5$^{*}$</td>
</tr>
<tr>
<td>SASO:Sm</td>
<td>359.5$^{*}$</td>
<td>687$^{*}$, 702, 727</td>
</tr>
<tr>
<td>M-BASO:Sm</td>
<td>365$^{*}$</td>
<td>685$^{*}$, 700.5, 727</td>
</tr>
<tr>
<td>H-BASO:Sm</td>
<td>329$^{*}$</td>
<td>683.5, 698$^{*}$, 725.5</td>
</tr>
</tbody>
</table>

The excitation and emission spectra of M-BASO:Sm show in Figure 2(e) and 2(f). The broad excitation band with the peak at 365 nm extends from 250 to 500 nm. And the broad f-d transition emission of Sm$^{2+}$ ranges from 600 to 750 nm with the peak at 660 nm. The sharp emission bands consists of three groups of lines at 685, 700.5 and 727.5 nm corresponding to the $^{5}D_0\rightarrow^{7}F_0$, $^{5}D_0\rightarrow^{7}F_1$ and $^{5}D_0\rightarrow^{7}F_2$ transitions of Sm$^{2+}$, respectively. The optical properties of M-BASO:Sm are similar to those of SASO: Sm. This is because that the crystal structure of M-BASO is close to that of SASO:Sm , thus crystal environment of Sm$^{2+}$ in M-BASO is near to SASO:Sm. However, compared with that of SASO:Sm, a red-shift of the excitation for M-BASO:Sm can be found and the reason will be discussed in the discussion part.
As can be shown in Figures 2(g) and 2(h), the sample H-BASO:Sm shows different excitation and emission spectra. The spectra are quite different with the photoluminescence properties of Sm doped SASO and M-BASO samples. Two dominate excitation peaks at 329 nm and 423 nm can be found, which can be assigned to the 4f-5d transition of Sm$^{2+}$. The emission bands consist of a broad band emission from 550 to 650 nm with the peak at 603 nm. The sharp emission bands consists of three groups of lines at 683.5, 698 and 725.5 nm correspond to the $^5D_0\rightarrow^7F_0$, $^5D_0\rightarrow^7F_1$ and $^5D_0\rightarrow^7F_2$ transitions of Sm$^{2+}$, respectively. The strongest emission is at 698 ($^5D_0\rightarrow^7F_1$ of Sm$^{2+}$), which indicates that the Sm$^{2+}$ ions occupy the crystallographic sites with central symmetry in the host.

Figure 3. CIE (commission International de l'Eclairage 1931) chromaticity coordinates of Sm doped CASO, SASO, M-BASO and H-BASO.
Table 3. CIE values of Sm doped CASO, SASO, M-BASO and H-BASO.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CIE (excitation wavelength)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASO:Sm</td>
<td>(0.573, 0.407) (374nm)</td>
</tr>
<tr>
<td>SASO:Sm</td>
<td>(0.680, 0.319) (360 nm)</td>
</tr>
<tr>
<td>M-BASO:Sm</td>
<td>(0.635, 0.350) (365nm)</td>
</tr>
<tr>
<td>H-BASO:Sm</td>
<td>(0.616, 0.357) (330 nm)</td>
</tr>
</tbody>
</table>

Figure 3 shows the CIE (commission International de l’Ecairage 1931) chromaticity coordinates of Sm doped CASO, SASO, M-BASO and H-BASO. For Sm-doped CASO, the emission light excited at 375 nm shows orange-red because it mainly comes from the emission of Sm$^{3+}$. For Sm doped SASO, M-BASO and H-BASO, as can be shown in Figure 2 and Table 3, excited at n-UV light, their CIE values are B(0.680, 0.319), C(0.635, 0.350) and D(0.616, 0.357), respectively. All of them yield strong deep red emission, which may be used as the red phosphors in the phosphors-converted light-emitting diodes.

4.2.2. Crystal structure and spectra of Sm doped $\text{MAI}_2\text{Si}_2\text{O}_8$ (M=Ca, Sr, Ba)

4.2.2.1. The relationship between the crystal structure and the f-f transition intensity of Sm$^{2+}$

From the above analysis, it has been clearly shown that the f-d transition energy of Sm doped SASO, M-BASO and H-BASO can
produce f-d transition emission accompanied by some strong f-f transitions of Sm$^{2+}$, however, the f-f emission intensity are quite different. Their comparison of the emission intensity under the excitation of 360 or 460 nm can be shown in Figure 4. The clear order of the strongest f-f emission intensity of Sm$^{2+}$ is H-BASO$>$M-BASO$>$SASO$>$CASO. We will make our focus on the spectra analysis of Sm doped H-BASO, M-BASO and SASO to try to find out the relationship between the crystal structure and their PL properties because their strong f-d and f-f transition of Sm$^{2+}$ at room temperature.

Figure 4. Comparison emission intensity of Sm doped CASO, SASO, M-BASO and H-BASO under the f-d transition energy excitation.
As is well known, the relative intensity of f-f transitions is influenced by the crystalline environment due to the different symmetry of the occupied sites \(^9,^{10,27-30}\). The crystal structure of MASO\((M=\text{Ca and Ba})\) has been shown in Figure 5. In the Sm doped MASO \((M=\text{Ca and Ba})\) systematic samples, the Sm ions occupy the site of \(M^{2+}\) ions, therefore, the f-f
transition intensity is mainly influenced by the symmetry of the M$^{2+}$ sites. Just as the Eu$^{3+}$ emission, the intensities of different $^5D_0-^7F_j$ transitions of Sm$^{2+}$ depend on the local symmetry of the crystal field of the Sm$^{2+}$ ions$^{9-13}$. The $^5D_0-^7F_0$ transition is hypersensitive, while the $^5D_0-^7F_1$ transition is insensitive to the crystal field environment. For instance, in a site with inversion symmetry, the $^5D_0-^7F_1$ transition is dominant, while in a site without inversion symmetry, the $^5D_0-^7F_0$ electronic transition becomes the strongest one. The intensity of $^5D_0-^7F_0$ transition is much higher than that of $^5D_0-^7F_1$, which is strong evidence that Sm$^{2+}$ ions mainly occupy the lattice site without inversion symmetry$^9$. From the crystal structure and the skeleton construction of MASO (Figure 5), we can see that only in the Sm-doped H-BASO sample, Sm occupy the centered site with six identity oxygens (O2), which is inversion symmetry, so the intensity of $^5D_0-^7F_1$ transition of Sm$^{2+}$ in H-BASO is the strongest among the four samples.

The space groups of M-BASO and SASO are I 12/c1 (No. 15)$^{17, 18}$. Both of the occupied sites of Ba$^{2+}$ in M-BASO and Sr$^{2+}$ in SASO are 8f. The symmetry of Ba$^{2+}$ in M-BASO crystal is similar to that of Sr$^{2+}$ in SASO crystal, but the intensity of $^5D_0-^7F_0$ transition of Sm$^{2+}$ of M-BASO:Sm is about 2 time stronger than that of SASO:Sm, which can be shown in Figures 4(b) and 4(d). In their crystal structure, as can be shown in Figures 5(c) and 5(d), there is one 8f site of Ba with seven
different nearest neighbors atoms including two types of Ba-O1, one Ba-O2, one Ba-O3, one Ba-O4, one Ba-O7 and one Ba-O8 bonds. This type of symmetry produces the strong emission of the \( ^5D_0 \rightarrow ^7F_0 \) transition of \( \text{Sm}^{2+} \). It has been found that the photoluminescence intensity ratio between \( ^5D_0 \rightarrow ^7F_2 \) and \( ^5D_0 \rightarrow ^7F_1 \) emission of \( \text{Eu}^{3+} \) \( (I(\text{Eu}^{3+}) = I(\text{Eu}^{3+})/I(\text{Eu}^{3+})) \) increases with increasing of the distortion degree of \( \text{LnO}_6 \) or \( \text{LnO}_7 \) polyhedron from that of an ideal octahedron. So, just as the \( \text{Eu}^{3+} \), the transition intensity ratio between \( ^5D_0 \rightarrow ^7F_0 \) and \( ^5D_0 \rightarrow ^7F_1 \) emission of \( \text{Sm}^{2+} \) \( (I(\text{Sm}^{2+}) = I(\text{Sm}^{2+})/I(\text{Sm}^{2+})) \) is influenced by the distortion degree of \( \text{LnO}_n \) polyhedron from that of an ideal polyhedron\(^{27,28}\). Their ratio values of \( I(\text{Sm}^{2+})/I(\text{Eu}^{3+}) \) for SASO:Sm, M-BASO and H-BASO are about 2.21, 3.34 and 0.95, respectively. The distortion degree can be calculated using the standard deviation of environmental factor of the individual bond (EFSD) \( \sigma(h_{i}) \), which can be expressed as below:

\[
\sigma(h_{i}) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (h_{i} - \delta)^2} \quad (11)
\]

where \( h_{i} = (f_{i}^{\alpha} \alpha_{i}^{\beta})^{1/2} Q_{\alpha}^{\beta} \quad (12) \)

and \( \delta = \frac{1}{N} \sum_{i=1}^{N} h_{i} \quad (13) \)

Table 4. The environmental factor of any individual bond between the centre-M\(^{2+}\) atom and its nearest coordination atom \( (h_{i}) \) in the monoclinic crystals M-BASO and SASO, their standard deviation of the seven M-O environmental factors \( (\sigma(h_{i}) \) as well as the emission intensity ratio between \( ^5D_0 \rightarrow ^7F_0 \) and \( ^5D_0 \rightarrow ^7F_1 \) \( (I(\text{Sm}^{2+})/I(\text{Eu}^{3+})) \) in the hexagonal crystal H-BASO and
monoclinic crystals M-BASO and SASO.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Central ion</th>
<th>Bond type</th>
<th>( f_c )</th>
<th>( \alpha_s )</th>
<th>( Q_8 )</th>
<th>C.N.</th>
<th>( h_{i,c} )</th>
<th>( \sigma(h_{i,c}) )</th>
<th>( \frac{I(5D_0 \rightarrow 7F_0)}{I(5D_0 \rightarrow 7F_1)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SASO</td>
<td>Sr(^{2+})</td>
<td>Sr-O1</td>
<td>0.0318</td>
<td>0.1810</td>
<td>1.1429</td>
<td>2</td>
<td>0.08671</td>
<td>0.03379</td>
<td>2.21</td>
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<td></td>
<td></td>
<td>Sr-O2</td>
<td>0.0696</td>
<td>0.3123</td>
<td>0.8571</td>
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<td>0.12636</td>
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<tr>
<td></td>
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<td>Sr-O3</td>
<td>0.0650</td>
<td>0.5346</td>
<td>0.8571</td>
<td>1</td>
<td>0.15977</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sr-O4</td>
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<td>0.6209</td>
<td>0.8571</td>
<td>1</td>
<td>0.17072</td>
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<tr>
<td></td>
<td></td>
<td>Sr-O7</td>
<td>0.0646</td>
<td>0.5603</td>
<td>0.8571</td>
<td>1</td>
<td>0.16306</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Sr-O8</td>
<td>0.0650</td>
<td>0.5306</td>
<td>0.8571</td>
<td>1</td>
<td>0.15917</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-BASO</td>
<td>Ba(^{2+})</td>
<td>Ba-O1</td>
<td>0.0304</td>
<td>0.2402</td>
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<td>2</td>
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<td>0.07348</td>
<td>3.34</td>
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<tr>
<td></td>
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<td>Ba-O2</td>
<td>0.0655</td>
<td>0.4451</td>
<td>0.8571</td>
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<td>Ba-O3</td>
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<td>0.6692</td>
<td>0.8571</td>
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<td>0.6809</td>
<td>0.8571</td>
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<td>0.17681</td>
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<tr>
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<td></td>
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<td>0.6437</td>
<td>0.8571</td>
<td>1</td>
<td>0.17246</td>
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<tr>
<td>H-BASO</td>
<td>Ba(^{2+})</td>
<td>Ba-O2</td>
<td>0.1047</td>
<td>1.1695</td>
<td>1.000</td>
<td>6</td>
<td>-</td>
<td>0</td>
<td>0.951</td>
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</table>

The related chemical parameters, such as the covalency \( f_c \), the polarizability of the chemical bond volume \( \alpha_s \), and the present charge of the ligand in the binary crystals, are listed in Table 4. According to the equations (11)-(13), their standard deviation of the seven M-O environmental factors \( \sigma(h_{i,c}) \) of MO\(_7\) or MO\(_6\) polyhedron in the SASO, M-BASO and H-BASO can be calculated to be 0.03379, 0.07348 and 0 respectively. The \( \sigma(h_{i,c}) \) value of M-BASO is 2.2 times larger than that of SASO. Generally, the \( I(5D_0 \rightarrow 7F_0)/I(5D_0 \rightarrow 7F_1) \) value of Sm\(^{2+}\) increases with increasing of \( \sigma(h_{i,c}) \).\(^{27,28}\) Therefore, the \( I(5D_0 \rightarrow 7F_0)/I(5D_0 \rightarrow 7F_1) \) of Sm\(^{2+}\) in the crystal M-BASO is stronger than that in the crystal SASO or H-BASO, and \( I(5D_0 \rightarrow 7F_0)/I(5D_0 \rightarrow 7F_1) \) of H-BASO:Sm is the lowest.

4.2.2.2. The relationship between the crystal structure and the f-d transition energy of Sm\(^{2+}\)
Figure 6 shows the comparisons of 4f-5d transition excitation spectra in Sm$^{2+}$ in H-BASO, M-BASO and SASO. (The intensity of H-BASO is reduced 6 times; and that of SASO is enlarged 1.5 times.) The lowest band comes from the Sm doped H-BASO (red line). The broad bands of Sm doped M-BASO and SASO have a blue-shift comparing with that of H-BASO. The 4f-5d transition band of Sm-SASO (blue line) has a blue-shift comparing with that of M-BASO (black line).

As is well known, the 4f-5d transition energy is greatly influenced by the crystalline environmental$^{21, 22, 26, 31}$. This is because that the excited
states such as 5d are not shielded from the surrounding electronic shell, so the 5d electron has a strong interaction with the neighboring anions in the compound. The interactions for the $4f^65d$ configuration, which may be important for optical spectrum simulations, are as follows:\[32\]:

$$H = H_0 + H_{\text{coul}}(ff) + H_{so}(f) + H_{cf}(f) + H_{cf}(d) + H_{so}(d) + H_{\text{coul}}(fd)$$  \hspace{1cm} (14)

Where $H_0$ is the central-field interaction which includes the kinetic energy of electron and the Coulomb interaction between the $4f^6$ core and the electrons; $H_{\text{coul}}(ff)$, $H_{so}(f)$ and $H_{cf}(f)$ are Coulomb, spin-orbit and crystal-field interactions for the $4f^6$ core; $H_{cf}(d)$ and $H_{so}(d)$ are crystal field and spin orbit interactions for the single 5d electron; $H_{\text{coul}}(fd)$ is the Coulomb interaction between the $4f^6$ core and the 5d electron. The order of magnitude of the energy splitting caused by these interactions is as follow:

$$H_0 \{H_{\text{coul}}(ff), H_{cf}(d)\} H_{\text{coul}}(fd) H_{so}(f) H_{so}(d) H_{cf}(f)$$  \hspace{1cm} (15)

The interactions $H_{so}(d)$ and $H_{cf}(f)$ can be generally ignored. In our systematic samples the central ion is Sm$^{2+}$ with the electron $4f^6$ configuration, the lowest $4f^6 \rightarrow 4f^55d$ energy ($E_{\text{exp}}(4f^6 - 4f^55d)$) is determined by five parts: the energy centroid of the 5d orbital ($E_C$), the Coulomb, spin-orbital interactions between 4f and 4f electrons ($E_{\text{coul}}(ff), E_{so}(f)$), the Coulomb interactions between 4f and 5d electrons ($E_{\text{coul}}(fd)$) and the effect of the crystal field ($E_{cf}(d)$). Figure 7 shows a schematic energy diagram of the $4f^6 \rightarrow 4f^55d$ configuration of Sm$^{2+}$ in
any host lattice.

![Schematic Diagram](image)

Figure 7. A schematic energy diagram of $4f^6 \rightarrow 4f^5 5d$ configuration of Sm$^{2+}$ in any host lattice.

From the diagram (Figure 7), the lowest $4f^6 \rightarrow 4f^5 5d$ transition energy of Sm$^{2+}$ can be obtained as follows:

$$E_{\text{exp}} (4f^6 - 4f^5 5d) = E_C - E_{\text{Coul}}(ff) - E_{so}(f) - E_{\text{Coul}}(fd) - E_{\text{cf}}(d) \quad (16)$$

In our case, all of the luminescence centre ions are Sm$^{2+}$, it is expected that $E_{\text{Coul}}(ff)$ and $E_{so}(f)$ are unchanged in the MASO (M=Sr and Ba) crystals. The energy difference among Sm-doped SASO, H-BASO and M-BASO mainly comes from the difference of the other three parts of equation (16): $E_C$, $E_{\text{Coul}}(fd)$ and $E_{\text{cf}}(d)$. $E_C$ and $E_{\text{Coul}}(fd)$ are related to the environmental factor $h_e^{31}$ and $E_{\text{cf}}(d)$ is concerned with the environmental parameter $F_c^{22}$. The values of $h_e$ can be calculated using the below equations:
\( h_e = \left( \sum_{\mu} \mu \alpha_\mu^Q \mu^2 \right)^{\frac{1}{2}} \)  

(17)

Where \( Q_\mu^Q \) stands for the presented charge of the nearest anion in the chemical bond, and \( \alpha_\mu^Q \) is the polarizability of the chemical bond volume in the \( \mu \) type of chemical bonds\(^{31} \). Also, the relationship between the environmental factor \( (h_e) \) and the environmental factor of any individual bond between the centre atom and their nearest coordination atom \( (h_{e_i}) \) can be expressed by

\[
h_e^2 = \sum_{i=1}^{N} (h_{e_i}^2)
\]

(18)

The values of the environmental parameter \( F_c \) can be obtained as follows:

\[
F_c = \frac{\bar{E}_h \bar{Q}_I}{N}
\]

(19)

Where \( \bar{E}_h \) is the average homopolar part of the energy gap. \( \bar{Q} \) is the average present charge of the anions, and \( \bar{I} \) is the average bond ionicity between the central ion and the nearest neighbors.

According to the equations (18) and (19), the values of the environmental factor \( h_e \) and the environmental parameter \( F_c \) as well as their related chemical bond parameters are calculated and listed in Table 8. The \( h_e \) values of Sm doped H-BASO, M-BASO and SASO are 0.8573, 0.4028 and 0.3710, respectively. Generally, an increase of \( h_e \) leads to a decrease of the energy centroid of the 5d orbital \( (E_c) \)^{31}. Thus the order of their \( E_c \) values is \( E_c(H - BASO) > E_c(M - BASO) > E_c(SASO) \), and the
order of the $E_{\text{cov}}(fd)$ value is just reverse. It has been shown that the $E_{\text{cf}}(d)$ increases with increasing of $F_C$, so the order of the $E_{\text{cf}}(d)$ value is $E_{\text{cf}}(H - BASO) > E_{\text{cf}}(SASO) > E_{\text{cf}}(M - BASO)$. Finally, according to the equation (16), it can be judged that among the three samples the lowest 4f-5d transition energy of Sm doped H-BASO is the lowest, which coincides with the experimental data (423 nm). For the other two crystal M-BASO and SASO, their difference between the environmental factors ($h_e$) ($\Delta(h_e)=0.0318$) is near to the difference between $F_C(\Delta(h_e)=0.0553)$.

On the other hand, the magnitude of $H_0$ is larger than others in equation (14). Thus the difference of the $E_{\text{exp}}(4f^6 - 4f^55d)$ value is mainly determined by the difference of $E_C$, so the lowest 4f-5d energy of Sm-doped SASO is a little larger than that of Sm-doped M-BASO, which is consistent with the experimental result.

### Table 5. The values of the corresponding crystal factors ($F_C$) and environmental factor ($h_e$) of the central ions $M^{2+}$ for H-BASO, SASO and M-BASO samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Central ion</th>
<th>Bond type</th>
<th>$E_k$</th>
<th>$f_i$</th>
<th>$Q_B$</th>
<th>C.N.</th>
<th>$F_C$</th>
<th>$h_e$</th>
</tr>
</thead>
<tbody>
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<td>SASO</td>
<td>Sr$^{2+}$</td>
<td>Sr-O1</td>
<td>3.4944</td>
<td>0.9682</td>
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<td>2</td>
<td>0.4278</td>
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<tr>
<td></td>
<td></td>
<td>Sr-O2</td>
<td>4.3145</td>
<td>0.9304</td>
<td>0.8571</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sr-O3</td>
<td>3.1692</td>
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<tr>
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<td>Sr-O7</td>
<td>3.0862</td>
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<tr>
<td>M-BASO</td>
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5. Conclusion

The Sm$^{2+}$ doped triclinic CaAl$_2$Si$_2$O$_8$ (CASO), monoclinic SrAl$_2$Si$_2$O$_8$ (SASO) and BaAl$_2$Si$_2$O$_8$ (M-BASO) as well as hexagonal BaAl$_2$Si$_2$O$_8$(H-BASO) have been synthesized using polymerizable-complex technique under reducing atmosphere. At room temperature, under the N-UV or blue excitation, Sm$^{2+}$ doped SASO, M-BASO and H-BASO showed strong red emission. Their strongest emission spectra mainly come from the $^5D_0\rightarrow^7F_0$ transition of Sm$^{2+}$ in the H-BASO crystal and the $^5D_0\rightarrow^7F_1$ transition of Sm$^{2+}$ in SASO and M-BASO, respectively. The calculated standard deviation of environmental factor of the individual bond of Sm disclosed the reason why the emission intensity ratio($I(^5D_0\rightarrow^7F_0)/I(^5D_0\rightarrow^7F_1)$) of Sm$^{2+}$ in SASO is stronger than that in M-BASO and that of H-BASO is the lowest. The lowest excitation energy of 5d energy levels of Sm$^{2+}$ have a blue-shift in the order H-BASO<M-BASO<SASO. The physical reason for spectral and energy level changes is analyzed in detail to be a comprehensive result from the shift of the energy centroid of the 5d orbital, the Coulomb interaction between 4f and 5d electrons, and the crystal-field splitting of 5d energy level. The theoretical analysis is in good agreement with our experimental result.

Acknowledgments

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References


