Color-Tunable Eu$^{2+}$ Activated Oxysilicate Phosphors with Oxyapatite Structure

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Citation

Abstract
Color-tunable Eu$^{2+}$ activated oxysilicate phosphors with a general formula M$_{3.85}$La$_6$ (SiO$_4$)$_6$O:Eu$^{2+}_{0.15}$ (M = Mg, Ca, Sr, Ba) were synthesized for the first time by solid-state reaction at high temperature under reducing atmosphere. The influence of alkaline earth metal ions on the crystal structure and photoluminescence characteristics have been investigated by the measurement of XRD and photoluminescence characteristics. The results have indicated that all the phosphors were oxyapatite structure belonging to $P_{43/m}$ space group and cell parameters increase in order of Mg<Ca<Sr<Ba. According to the photoluminescence spectra, the peak wavelength and FWHM of emission bands have been changed by varying M ions in the host lattices, resulting in the emission color have been changed. The detailed explanations have been well suggested by crystal structure and covalent effect.

1. Introduction

Alkaline earth silicates are important luminescent host materials because of their excellent chemical and thermal stability and stable crystal structures. On the other hand, Eu$^{2+}$ ion as an activator has always attracted much attention for its broadband luminescence spectra originated from the allowed transition between its 5$d$ and 4$f$ levels. Because Eu$^{2+}$ is likely to be introduced into the alkaline earth silicate lattice and stabilized in the host due to its ionic radius close to that of alkaline earth ions, the fluorescence of Eu$^{2+}$-activated binary and ternary silicates has been studied for years. In particular, the ternary alkaline earth and rare earth silicates with oxyapatite structure, such as Ca$_2$RE$_8$(SiO$_4$)$_6$O$_2$ (RE = Y, Gd, La), have been widely investigated and reported to be efficient host lattices for luminescence of various ions.

It is well known that the structure of oxyapatite is characterized by the presence of two sites for cations in the host lattice, which are the nine-coordinated 4f site with C3 point symmetry and the seven-coordinated 6h site with CS point symmetry. Both sites are very suitable to accommodate activators, such as rare earth and transition metal ions because of their low symmetry features. Phosphate apatites substituted by rare earths and other cations have been extensively used as phosphors in fluorescent lamps, for instance the blue emitting Sr$_5$(PO$_4$)$_3$Cl:Eu$^{2+}$ or the white emitting Ca$_3$(PO$_4$)$_3$(F, Cl):Sb$^{3+}$, Mn$^{2+}$. 
Thus, oxysilicates with oxyapatite structure have attracted researchers’ attention.

Our previous work showed that Eu$^{2+}$ in the $\text{Sr}_{x-y}\text{La}_{10-x}(\text{SiO}_4)_6\text{O}_{3-x/2}:\text{Eu}^{2+}$ ternary silicates exhibited excellent luminescence properties.

As mentioned above, luminescence of Eu$^{2+}$ ions arises from the 4f-5d transition where 5d orbitals are exposed to the significant interaction with the surrounding atoms and ions. Thus silicate hosts containing different alkaline earth will have different effects on the crystal field which will influence the luminescence properties of Eu$^{2+}$. So far, studies on the Eu$^{2+}$ doped ternary alkaline earth-rare earth silicate oxyapatite phosphors have been rather limited. In present work, Eu$^{2+}$ doped silicate oxyapatites with different alkaline earth were prepared by a solid state reaction at high temperature under reducing atmosphere and their photoluminescence behaviors have been investigated.

2. Experiments Procedures

A series of samples, $\text{M}_{3.85}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ (M = Mg, Ca, Sr, Ba), have been prepared by using MgCO$_3$ (3N), CaCO$_3$ (3N), SrCO$_3$ (3N), BaCO$_3$ (3N), La$_2$O$_3$ (4N), SiO$_2$ (4N) and Eu$_2$O$_3$ (4N) as raw materials. The raw materials were weighted by stoichiometric ratio. After being thoroughly mixed and ground in an agate mortar, the mixtures were then pressed to form pellets and sintered at 1400°C for 6h under reducing atmosphere (N$_2$+H$_2$ (10%).

The phase purity of synthesized powder samples were determined by X-ray powder diffraction (D8 ADVANCE, Bruker) using Cu Kα ($\lambda$=1.5405Å) at room temperature. Spectrofluorometer (Fluorolog-3-P, Jobin Yvon) equipped with 450W Xe-arc lamp was used for the photoluminescence measurement at room temperature. All photoluminescence spectra were corrected for the photomultiplier sensitivity and all excitation spectra for the intensity of the excitation source.

3. Results and Discussion

The XRD patterns of the as-synthesized samples with different alkaline earth and trivalent rare earth ions are given in Fig. 1. The lines are indexed and compared with the JCPDS standard cards. All the diffraction peaks of $\text{M}_{3.85}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ (M = Mg, Ca, Sr, Ba) are in good agreement with those of Ca$_2$La$_8$(SiO$_4$)$_6$O$_2$ (JCPDS No. 29-337). And the diffraction peaks of Sr$_{3.85}$Y$_6$(SiO$_4$)$_6$O:Eu$_{0.15}$ and Sr$_{3.85}$Gd$_6$(SiO$_4$)$_6$O:Eu$_{0.15}$ are in good agreement with Ca$_4$Y$_6$(SiO$_4$)$_6$O (JCPDS No. 27-0093) and Ca$_4$Gd$_6$(SiO$_4$)$_6$O (JCPDS No.28-0212) respectively. The results suggest that silicates with oxyapatite structure were successfully synthesized. On the other hand, diffraction peaks shift a little to smaller angles as the radii of alkaline earth and rare earth ions increase.

The XRD patterns of the as-synthesized samples with different alkaline earths are given in Figure 1. The lines are indexed and compared with the JCPDS files. All the diffraction peaks of $\text{M}_{3.85}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ (M = Mg, Ca, Sr, Ba) are in good agreement with those of Ca$_2$La$_8$(SiO$_4$)$_6$O$_2$ (JCPDS No. 29-337) except for an unknown peak in the XRD
pattern of Mg_{3.85}La_{6}(SiO_{4})_{6}O:Eu_{0.15}. 2-theta values gradually shift to lower angular in the order of Mg, Ca, Sr, Ba, indicating larger and larger cell parameters in the order of Mg < Ca < Sr < Ba, when increasing ions size.  

Fig. 2 shows photoluminescence excitation (PLE) and emission (PL) spectra of M_{3.85}La_{6}(SiO_{4})_{6}O:Eu_{0.15} (M = Mg (MLSOE), Ca (CLSOE), Sr (SLSOE), Ba (BLSOE)). The excitation bands are broad and extend from 280 to 470 nm, depending on the type of alkaline earth ions in the host. This suggests that all four Eu^{2+} activated alkaline earth silicates can be excited by near ultraviolet to blue radiation. Excited by 365 nm light, all the phosphors give rise to broad emission bands centered at 555 nm, 505 nm, 496(566) nm and 507 nm respectively for MLSOE, CLSOE, SLSOE and BLSOE samples. The characteristic broad bands of the PLE and PL spectra provides evidence that europium ions in these samples are present in divalent state and that those bands originate from 5d-4f transition.

Moreover, these emission bands are asymmetric. As previously reported 10, there are two sites (4f(I) and 6h(II)) for cations in apatite structure, and cation at 6h site is more covalent than the one at 4f site. As commonly admitted, Eu^{2+} at higher covalent site show longer emission and excitation wavelength 11. Thus, in the PL of M_{3.85}La_{6}(SiO_{4})_{6}O:Eu_{0.15}, we can attribute the shorter wavelength emission to Eu^{2+} ions at 4f (Eu^{2+} (I)) sites and the longer wavelength emission to Eu^{2+} ions at 6h (Eu^{2+} (II)) sites. The PL spectra of all samples have been decomposed by Gaussian fitting method and the obtained peak wavelength of the two emission bands have been given in Fig. 3 as a function of the radius (type) of alkaline earth ions in the host. One can note that the longer wavelength emission band shows a blueshift with increasing the alkaline earth radius but Sr^{2+} is an exception. This phenomenon can be explained by the crystal field theory 12.

According to the crystal field theory, the crystal field strength decreases with an increase of bond length by replacing smaller ions with larger ones. The related equation 13 is as follows:

\[ Dq \propto 1/R^5 \]

where \( Dq \) is the strength of crystal field, \( R \) is the bond length between a center ion and ligand ions. Thus, the blueshift of Eu^{2+} emission which is proportional to \( Dq \), obeys the sequence of Mg, Ca, and Ba. In the case of the Sr^{2+}-containing sample (SLSE), however, the difference between the size of cation and the diameter of Eu^{2+} ions is zero (\( \Delta r_M = |r_{M^{2+}} - r_{Eu^{2+}}| \); \( \Delta r_{Sr} = 0.046nm, \Delta r_{Ca} = 0.013nm, \Delta r_{Ba} = 0.022nm \), so the symmetry of ligand ions surrounding Eu^{2+} ions is better than the samples containing Ca^{2+} and Ba^{2+} (CLSE and BLSE), leading to the smaller lattice distortion 12 and the stronger crystal field. As a result, the redshift is observed.

As for the emission bands at shorter wavelength, the phenomenon is different. Blueshift occurs in the sequence of Mg^{2+}, Ca^{2+} and Sr^{2+} whereas from Sr^{2+} to Ba^{2+} a slight redshift is observed. This phenomenon can be explained in terms of two competing factors: the crystal field and the covalence degree. In the case of samples containing Mg^{2+}, Ca^{2+} and Sr^{2+} (MLSOE, CLSOE and SLSOE), the difference between the size of these alkaline earth ions in (I) site and the diameter of Eu^{2+} ion is small. Therefore, the Eu^{2+} ions located in (I) sites are dominantly affected by the crystal field. As a result, the blueshift of Eu^{2+} (I) emission occurs with the decreasing \( Dq \). For the Ba^{2+}-containing sample (BLSOE), however, the Eu^{2+} ions in (I) site experience a larger nephelauxetic effect 12 due to the larger bond length. According to the nephelauxetic effect theory we know that the covalence of Eu-O bonds increases with the involved alkaline earth ions according to the following order: Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}. In other words, in the Ba^{2+}-containing sample (BLSE), the covalence of Eu-O bonds is the strongest, causing negative charges easy to transfer to Eu^{2+} ions and thus decrease the difference between the 4f and 5d levels 12. Consequently, a redshift of the Eu^{2+} (I) emission is observed compared with the Sr^{2+}-containing sample (SLSOE).

It can be observed from figure 2 that BLSE exhibits considerably high excitation and emission intensities. This is attributed to large overlapping of two emission bands. Emission peaks wavelength and FWHM of M_{3.85}La_{6}(SiO_{4})_{6}O:Eu_{0.15} were listed in table 1.
BLSE has the lowest wavelength difference and FWHM, leading to the highest emission peak intensity.

<table>
<thead>
<tr>
<th>Samples</th>
<th>MLSOE</th>
<th>CLSOE</th>
<th>SLSOE</th>
<th>BLSOE</th>
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<tbody>
<tr>
<td>λ\text{exc}/nm</td>
<td>530</td>
<td>497</td>
<td>486</td>
<td>500</td>
</tr>
<tr>
<td>FWHM/µm</td>
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<td>61</td>
<td>61</td>
<td>48</td>
</tr>
<tr>
<td>λ\text{em}/nm</td>
<td>571</td>
<td>533</td>
<td>558</td>
<td>522</td>
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<tr>
<td>FWHM/µm</td>
<td>95</td>
<td>92</td>
<td>93</td>
<td>66</td>
</tr>
<tr>
<td>∆\lambda=λ\text{em}-λ\text{exc}/nm</td>
<td>44</td>
<td>40</td>
<td>82</td>
<td>20</td>
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<tr>
<td>FWHM/µm</td>
<td>112</td>
<td>79</td>
<td>143</td>
<td>61</td>
</tr>
<tr>
<td>Color Coordinates (x,y)</td>
<td>(0.3922,0.5010)</td>
<td>(0.2252,0.4699)</td>
<td>(0.3382,0.4647)</td>
<td>(0.1737,0.5384)</td>
</tr>
</tbody>
</table>

The calculated color coordinates are presented in figure 3. In accordance with the emission spectra, the emission colors of BLSE and CLSOE are located in the green region and SLSOE and MLSOE trend to yellow region in CIE 1931 chromatic diagram. These indicate that the emission color also can be controlled by changing divalent cation.

![Figure 3. CIE 1931 chromatic diagram of M_{1-x}La_{x}(SiO_{4})_6O:Eu^{2+}, (M = Mg, Ca, Sr, Ba) under 365 nm excitation.](image)

4. Conclusions

In conclusion, M_{1-x}La_{x}(SiO_{4})_6O:Eu^{2+}, (M = Mg, Ca, Sr, Ba) phosphors have been synthesized by solid-state reaction at high temperature under reducing atmosphere. These phosphors show broad excitation and emission bands due to 5d-4f transition of Eu^{2+} ion. The emission bands are asymmetric and two emission bands are observed after Gaussian fitting. The shorter wavelength emission is due to Eu^{2+} ions at 4f (Eu^{2+} (I)) sites and the longer wavelength emission to Eu^{2+} ions at 6h (Eu^{2+} (II)) sites. The longer wavelength emission bands show a blueshift with increasing the radius of the involved alkaline earth ions due to the decrease in crystal field effect but Sr^{2+} is an exception due to the zero difference between the ionic radii of Eu^{2+} and Sr^{2+}. On the other hand, the shorter wavelength emission is influenced by two competing factors: crystal field and covalent degree. A blueshift is observed in the sequence of Mg^{2+}, Ca^{2+} and Sr^{2+} due to the decrease in crystal field while for Ba^{2+}-containing sample, a redshift occurs due to the increase in the nephelauxetic effect.

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