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► **To cite this version:**

Shuanglong Yuan, Luting Wang, Zhaofeng Cui, Yunxia Yang, Huidan Zeng, et al.. Color-tunable Eu^{2+} activated oxysilicate phosphors with oxyapatite structure. *Journal of Materials Sciences and Applications*, 2015, 1 (2), pp.33-37. hal-01201718

HAL Id: hal-01201718

<https://hal.science/hal-01201718>

Submitted on 20 Oct 2015

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Journal of

**Materials Sciences
and Applications****Keywords**Oxysilicates,
Phosphor,
Oxyapatite Structure,
Color-Tunable

Received: February 4, 2015

Revised: March 9, 2015

Accepted: March 10, 2015

Color-Tunable Eu²⁺ Activated Oxysilicate Phosphors with Oxyapatite Structure

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CitationShuanglong Yuan, Luting Wang, Zhaofeng Cui, Yunxia Yang, Huidan Zeng, François Cheviré, Franck Tessier, Guorong Chen. Color-Tunable Eu²⁺ Activated Oxysilicate Phosphors with Oxyapatite Structure. *Journal of Materials Sciences and Applications*. Vol. 1, No. 2, 2015, pp. 33-37.**Abstract**

Color-tunable Eu²⁺ activated oxysilicate phosphors with a general formula M_{3.85}La₆(SiO₄)₆O:Eu²⁺_{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_{63/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, result 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^{1,2}. On the other hand, Eu²⁺ 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^{3,4}. Because Eu²⁺ 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 ions⁵, the fluorescence of Eu²⁺-activated binary and ternary silicates has been studied for years^{1,2}. In particular, the ternary alkaline earth and rare earth silicates with oxyapatite structure, such as Ca₂RE₈(SiO₄)₆O₂ (RE = Y, Gd, La), have been widely investigated and reported to be efficient host lattices for luminescence of various ions⁶.

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 4*f* site with C₃ point symmetry and the seven-coordinated 6*h* site with C_S point symmetry⁷. Both sites are very suitable to accommodate activators, such as rare earth and transition metal ions because of their low symmetry features^{7,8}. Phosphate apatites substituted by rare earths and other cations have been extensively used as phosphors in fluorescent lamps, for instance the blue emitting Sr₅(PO₄)₃Cl:Eu²⁺ or the white emitting Ca₅(PO₄)₃(F, Cl):Sb³⁺, Mn²⁺.

Thus, oxysilicates with oxyapatite structure have attracted researchers' attention.

Our previous work showed that Eu^{2+} in the $\text{Sr}_{x-y}\text{La}_{10-x}(\text{SiO}_4)_6\text{O}_{3-x/2}:\text{Eu}^{2+y}$ ternary silicates exhibited excellent luminescence properties⁹.

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, $\text{M}_{3.85}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$), have been prepared by using MgCO_3 (3N), CaCO_3 (3N), SrCO_3 (3N), BaCO_3 (3N), La_2O_3 (4N), SiO_2 (4N) and Eu_2O_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 $\text{Cu K}\alpha$ ($\lambda=1.5405\text{\AA}$) 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 $\text{M}_{3.85}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) are in good agreement with those of $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$ (JCPDS No. 29-337). And the diffraction peaks of $\text{Sr}_{3.85}\text{Y}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ and $\text{Sr}_{3.85}\text{Gd}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ are in good agreement with $\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{O}$ (JCPDS No. 27-0093) and $\text{Ca}_4\text{Gd}_6(\text{SiO}_4)_6\text{O}$ (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.

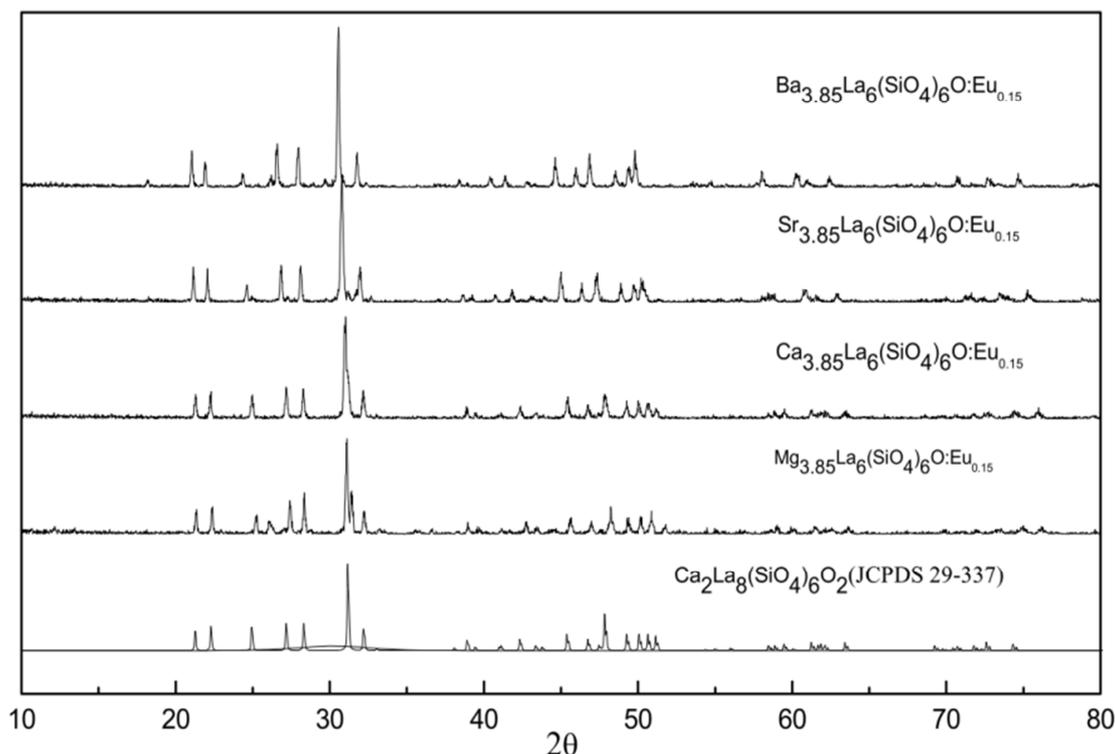


Figure 1. XRD patterns of the samples

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 $\text{M}_{3.85}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) are in good agreement with those of $\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2$ (JCPDS No. 29-337) except for an unknown peak in the XRD

pattern of $Mg_{3.85}La_6(SiO_4)_6O:Eu_{0.15}$. 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 $M_{3.85}La_6(SiO_4)_6O:Eu_{0.15}$ ($M = Mg$ (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.

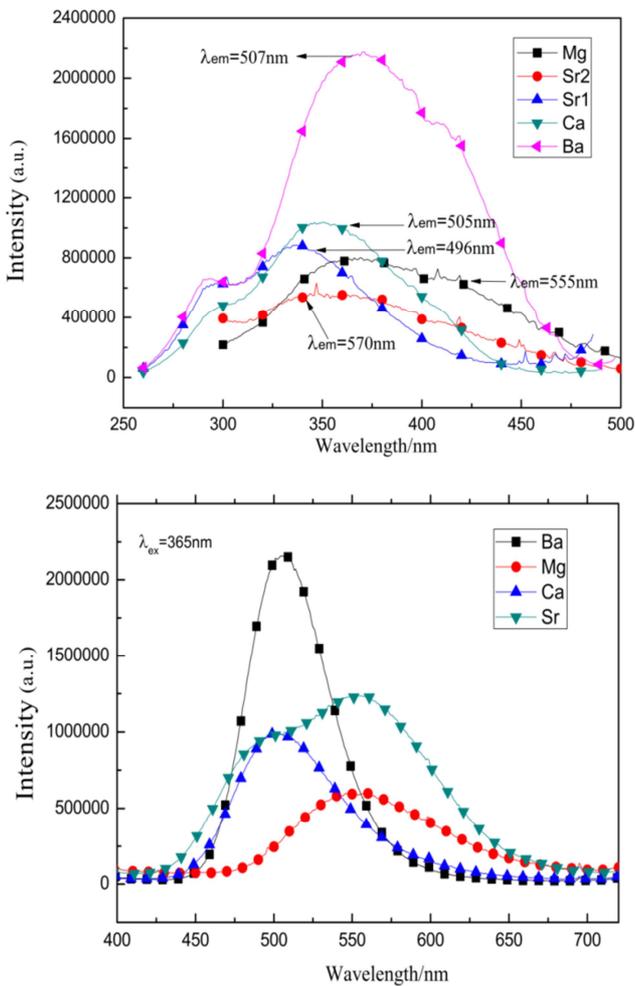


Figure 2. PLE (a) and PL (b) spectra of $M_{3.85}La_6(SiO_4)_6O:Eu_{0.15}$ ($M=Mg, Ca, Sr, Ba$)

Moreover, these emission bands are asymmetric. As previously reported¹⁰, 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 wavelength¹¹. Thus, in the PL of $M_{3.85}La_6(SiO_4)_6O:Eu_{0.15}$, 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 theory¹².

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 equation¹³ 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 site and the diameter of Eu^{2+} ions is zero ($\Delta r_M = |r_M^{2+} - r_{Eu^{2+}}|$; $\Delta r_{Mg} = 0.046nm$, $\Delta r_{Ca} = 0.013nm$, $\Delta r_{Sr} = 0nm$, $\Delta r_{Ba} = 0.022nm$), 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 distortion¹² 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 effect¹² 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 $5d$ levels¹². 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 $M_{3.85}La_6(SiO_4)_6O:Eu_{0.15}$ were listed in table 1. Apparently,

BLSE has the lowest wavelength difference and FWHM, leading to the highest emission peak intensity.

Table 1. Emission peaks wavelength and FWHM of $\text{M}_{3.85}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ under 365 nm excitation.

Samples	MLSOE	CLSOE	SLSOE	BLSOE
$\lambda_{\text{Eu(I)}}$ /nm	530	497	486	500
FWHM _{Eu(I)} /nm	60	61	61	48
$\lambda_{\text{Eu(II)}}$ /nm	571	533	558	522
FWHM _{Eu(II)} /nm	95	92	93	66
$\Delta\lambda = \lambda_{\text{Eu(II)}} - \lambda_{\text{Eu(I)}}$	44	40	82	20
FWHM/nm	112	79	143	61
Color Coordinates (x,y)	(0.3922,0.5010)	(0.2252,0.4699)	(0.3382,0.4647)	(0.1737,0.5384)

The calculated color coordinates are presented in figure 3. In accordance with the emission spectra, the emission colors of BLSOE 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.

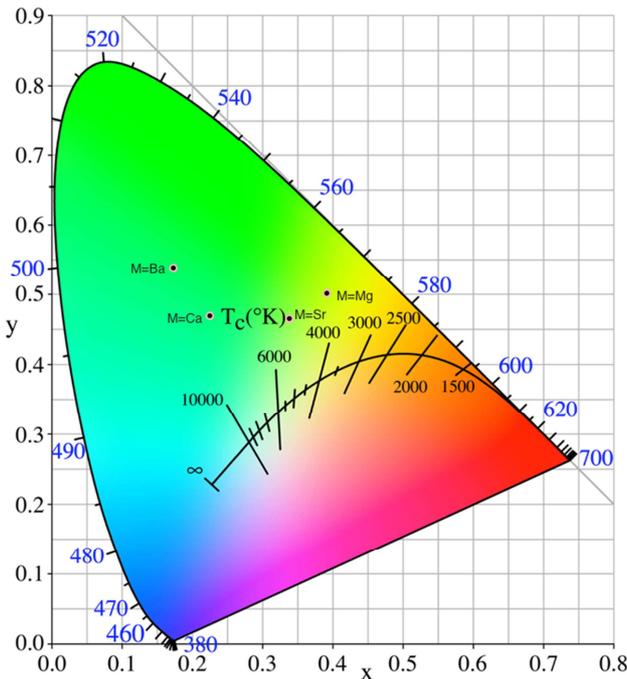


Figure 3. CIE 1931 chromatic diagram of $\text{M}_{3.95}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.05}$ ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) under 365 nm excitation.

4. Conclusions

In conclusion, $\text{M}_{3.85}\text{La}_6(\text{SiO}_4)_6\text{O}:\text{Eu}_{0.15}$ ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) 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.

Acknowledgement

This work is financially supported by the Fundamental Research Funds for the Central Universities (WD1314055).

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