

# The New Rare Earth Chlorosilicate Phosphor

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**Abstract:** Recently trivalent Europium doped phosphors have been extensively studied due to the potential applications. The new rare earth chlorosilicate phosphor  $\text{La}_3(\text{SiO}_4)_2\text{Cl}$  doped with  $\text{Eu}^{3+}$  is prepared through high temperature solid state reaction in reducing atmosphere. Their photoluminescence characterization studied. In Photoluminescence spectra, emission peaks are observed at 617nm with an excitation 280 nm studied. Europium activated sample exhibit persistent phosphorescence.

**Keywords:** Rare earth, Phosphors, Activator, Phosphorescence, Silicate,  $\text{Eu}^{3+}$

## 1. Introduction

A large number of  $\text{Eu}^{3+}$  activated phosphors have drawn considerable attention in view of their application as red phosphors in color television tubes and field emission displays. For these applications, phosphors exhibiting pure red emission with a high efficiency are required Rare earth (RE) Chlorosilicates have been widely researched as various luminescent materials in lighting, and display, optoelectronic devices, etc. [1,2]. Among them  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions are the most popular activators with transitions of 4f-4f and 4f-5d, respectively, which are sensitive to the crystal field in the lattices.

Silicate hosts have rigid frameworks with covalent Si-O bonds. Especially halide-containing silicates have many excellent properties such as chemical and physical stability, and preferable thermal stabilities. This makes it a suitable host lattice for luminescence materials in lighting [3-6]. In other words Silicates are stable in oxygen atmosphere. Many silicates are largely inert to common reagents, they have high degree of structural and compositional flexibility, their frameworks can be much more heat tolerant than organic frameworks.

In general electronic transitions are influenced by the symmetry of luminescent centers. If inversion symmetry is present, the electric-dipole transitions are forbidden, so that the emission is restricted to magnetic-dipole  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition. If inversion symmetry is absent, forced electric-dipole transitions are allowed. The red emission of  $\text{Eu}^{3+}$  is due to radiative transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  [7]. In this special case they are restricted to the transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_2, ^7\text{F}_4, ^7\text{F}_6$ . The broad absorption and reflection spectra of the  $\text{Eu}^{3+}$  ion in oxides is ascribed to a charge-transfer transition in which an electron is promoted from the highest-filled oxygen-orbital to the 4f shell of the  $\text{Eu}^{3+}$  ion

In present work  $\text{La}_3(\text{SiO}_4)_2\text{Cl}:\text{Eu}^{3+}$  phosphor is prepared through solid state reaction.

## 2. Experimental

$\text{La}_3(\text{SiO}_4)_2\text{Cl}:\text{Eu}^{3+}$  is prepared through solid state reaction. Ingredients used were  $\text{La}_2\text{O}_3$ ,  $\text{LaOCl}$ ,  $\text{Eu}_2\text{O}_3$  and Silicic acid ( $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ). Typical molar ratios used for preparing the phosphors are given.

$\text{LaOCl}:\text{Eu}_2\text{O}_3:\text{La}_2\text{O}_3:\text{Silicic acid}$   
0.94 : 0.06: 1 : 2

All constituents in the stated proportions, were mixed together. The mixture on thoroughly grinding was transferred to furnace for heating at 800 C for 12 to 14 hrs. To confirm the structure of the synthesized phosphors, powder photographs were obtained using Philips diffractometer, PW 1710. Photoluminescence spectra were recorded on Hitachi F-4000 spectro-fluorimeter with spectral slit width of 1.5 nm in the range 220-700 nm.

## 3. Result and Discussion

XRD Pattern of given phosphor is shown in fig 1. The pattern matches with ICDD no.79-0111. This phosphor having monoclinic structure.

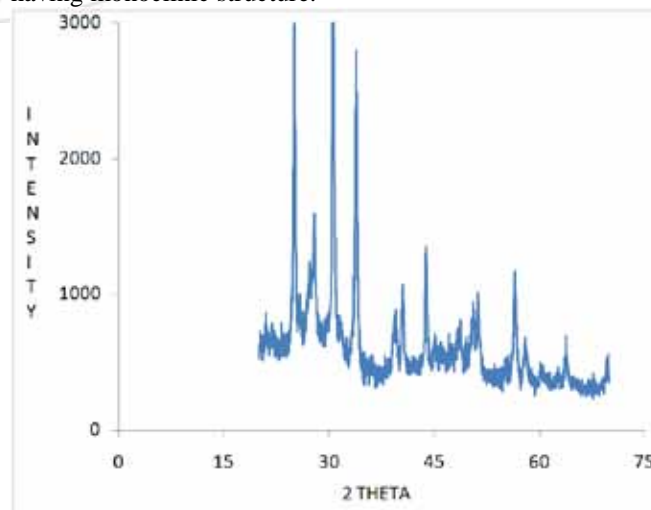
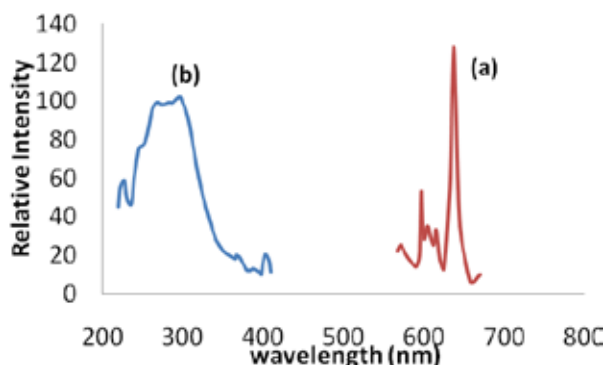


Figure 1: XRD Pattern of  $\text{La}_3(\text{SiO}_4)_2\text{Cl}:\text{Eu}^{3+}$  phosphor

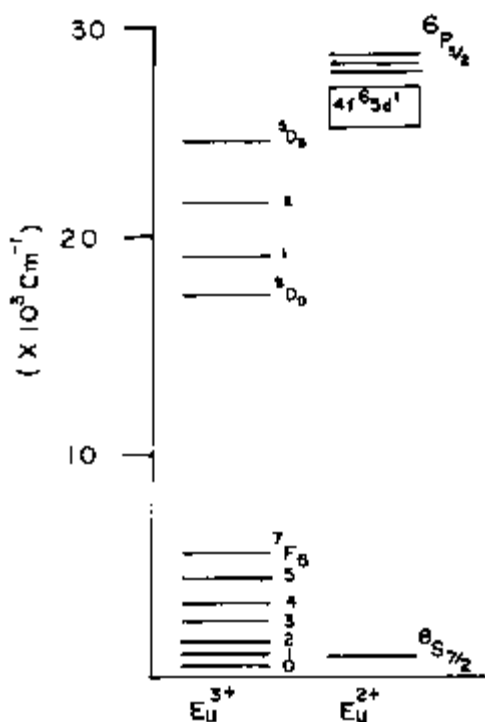
Fig 2 shows PL spectra for  $\text{La}_3(\text{SiO}_4)_2\text{Cl}:\text{Eu}^{3+}$ . Strong emission (**Fig. 2, curve a**) is with maximum around 617 nm. Excitation spectrum (**Fig. 2, curve b**) is very broad, stretching from 210 nm to 410 nm with broad maxima around 270 nm and 298 nm with prominent shoulders at about 230 and 332 nm.



**Figure 2:** PL Spectra of  $\text{La}_3(\text{SiO}_4)_2\text{Cl}:\text{Eu}^{3+}$

Curve (a) shows emission for 280 nm excitation,  
Curve (b) shows excitation for 617 nm emission

$\text{Eu}^{3+}$  emission usually occurs from  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  transitions. There are three transitions (**Fig. 3**) [8-10] which are of prime importance  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  (around 570 nm),  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  (around 595 nm) and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  (around 610 nm). The first one is strongly forbidden transition and yet observed with appreciable intensity in some hosts.  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition is forbidden as electric dipole, but allowed as magnetic dipole. This is the only transition when  $\text{Eu}^{3+}$  occupies a site coinciding with a centre of symmetry. When  $\text{Eu}^{3+}$  ion is situated at a site, which lacks the inversion symmetry, then the transitions corresponding to even values of  $j$  (except 0) are electric dipole allowed and red emission can be observed.  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition can also be observed as magnetic dipole allowed transition. Further, all the lines corresponding to these transitions split.



**Figure 3:** Energy Level Diagram of  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ion

In this special case they are having the transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ,  $^7\text{F}_4$ ,  $^7\text{F}_6$ . The broad absorption and reflection spectra of the  $\text{Eu}^{3+}$  ion in oxides is ascribed to a charge-transfer transition in which an electron is promoted from the highest-filled oxygen-orbital to the 4f shell of the  $\text{Eu}^{3+}$  ion.

#### 4. Conclusion

The red-emitting  $\text{La}_3(\text{SiO}_4)_2\text{Cl}$  doped with  $\text{Eu}^{3+}$  phosphor has been synthesized by a solid-state reaction. The Photoluminescence emission spectra show broad-absorption band in the range of 210–410 nm. The PL spectra exhibit broad band but asymmetric red emission centering at 617 nm. The results indicate that the  $\text{La}_3(\text{SiO}_4)_2\text{Cl}$  doped with  $\text{Eu}^{3+}$  phosphor is a promising candidate as a red component.

#### References

- [1] A. Bril and W. L. Wanmaker, *J. Electrochem. Soc.*, **111**, 1363–1964.
- [2] Levine and F. C. Palilla, *Appl. Phys. Lett.*, **5**, 118–1964.
- [3] Y.L. Yang, X.M. Li, W.L. Feng, W.L. Li, C.Y. Tao, *J. Alloys Comp.* 505 (2010) 239–242.
- [4] C.X. Qin, Y.L. Huang, H.J. Seo, *J. Alloys Comp.* 534 (2012) 86–92.
- [5] H. He, X.F. Song, R.L. Fu, Z.W. Pan, X.R. Zhao, Z.H. Deng, Y.G. Cao, *J. Alloys Comp.* 493 (2010) 401–405.
- [6] G. Blasse and A. Bril, *J. Chem. Phys.*, **47**, 5442–1967
- [7] H. Yu, Y.W. Lai, G.M. Gao, L. Kong, G.H. Li, S.C. Gan, G.Y. Hong, *J. Alloys Comp.* 509 (2011) 6635–6639.
- [8] Blasse G. (1966), *J. Chem. Phys.* 45, 2356.
- [9] Blasse G. & Bril A. (1966), *Phil. Res. Rept.* 21, 368; (1966), *J. Chem. Phys.* 45, 2350.
- [10] Blasse G. & J.de Vries. (1967), *J. Electrochem. Soc.* 114, 875