



## THERMAL ANALYSIS AND LUMINESCENCE PROPERTIES OF THE EUROPIUM DOPED $\text{Sr}_2\text{SiO}_4$ PHOSPHOR

Chaudhari Dilip B<sup>1</sup>, Zambare Pradip Z.<sup>2</sup>, A. P. Zambare<sup>3</sup> and Mahajan O. H.<sup>4</sup>

<sup>1</sup>Department of Physics, ASC College, Bhalod (M. S.), India.

<sup>2</sup>Department of Physics, S. V. S's D. R. College, Dondaicha, (M. S.), India.

<sup>3</sup>Department of Physics, Agasti Arts, Com. & D. R. Sci. College Akole, India.

<sup>4</sup>Department of Physics, M. J. College Jalgaon, (M.S.), India.

### Abstract

The thermal analysis for  $\text{Sr}_2\text{SiO}_4$  phosphor during solid state diffusion method is investigated using an isothermal method. The starting materials Strontium carbonate  $\text{SrCO}_3$  and silicate  $\text{SiO}_3$  are used to prepare  $\text{Sr}_2\text{SiO}_4$  Phosphor TG/DTA and XRD analysis suggest a direct reaction between  $\text{SrCO}_3$  and  $\text{SiO}_2$  powders. The conversion ratios of the  $\text{Sr}_2\text{SiO}_4$  starting materials are calculated from the weight loss. Based on the reaction kinetic isothermal analysis,  $\text{Sr}_2\text{SiO}_4$  formation is corroborated as controlled by the Brounshtein-Ginstling's diffusion-controlled model. The purpose of this study is to elucidate the reaction mechanism and reaction kinetics of formation of  $\text{Sr}_2\text{SiO}_4$  in a solid-state diffusion. The precursors were examined using thermal and X-ray diffraction analysis to determine the optimum reaction range. The isothermal analysis was adopted to understand the reaction mechanism and kinetics. Using the microstructural observations accompanied by the kinetics, a reaction model for the formation of  $\text{Sr}_2\text{SiO}_4$  via the solid-state reaction is proposed. The emission spectra shows broad band peaking at 612 nm for the excitation wavelength 254 nm. Color co-ordinates of  $\text{Sr}_2\text{SiO}_4: 1.0\% \text{Eu}^{3+}$  are  $x = 0.67$  and  $y = 0.32$ , it is in red color region.  $\text{Sr}_2\text{SiO}_4: 1.0\% \text{Eu}^{3+}$  phosphor is very appropriate red emitting phosphor for white-emitting diodes.

### Introduction:

Alkaline earth silicate is a significant luminescent material because of its outstanding chemistry and thermal stabilization, facile synthesis and cheap raw material ( $\text{SiO}_2$ ), so it has

been widely applied in phosphor for lamp. Since it can be excited efficiently by LED chips, there have been many reported about this material applied in phosphor for white LED [1-4]. However, it has problems of low color stability with increasing applied current, low color rendering index, and low color reproducibility [5,6]. Another new type of phosphor- $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$  has attracted researchers' attention [7-10].  $\text{Sr}_2\text{SiO}_4$  provides the broadband absorption in UV/Blue region due to low symmetry of the crystallographic sites. In addition, the  $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$  phosphor has a higher luminous efficiency, CRI and color stability than YAG [10, 11], and giving rise to a new phosphor approach for white LED applications. Therefore,  $\text{Sr}_2\text{SiO}_4$  is a suitable host lattice for phosphor applications  $\text{Sr}_2\text{SiO}_4$  powder is usually prepared in a solid-state reaction by heating mixed strontium and silicon salts at elevated temperatures. Knowledge of the fundamental reaction kinetics and mechanism are important when optimizing the solid-state process for phosphor applications. In this study,  $\text{Sr}_2\text{SiO}_4$  powders were prepared via solid-state reaction by heating mixed precursors at elevated temperatures. The purpose of this study is to explain the reaction mechanism and reaction kinetics of formation of  $\text{Sr}_2\text{SiO}_4$  in a solid-state reaction. The precursors were examined using thermal and X-ray diffraction analysis to determine the optimum reaction range. The isothermal analysis was adopted to understand the reaction mechanism and kinetics. Using the microstructural observations accompanied by the kinetics, a reaction model for the formation of  $\text{Sr}_2\text{SiO}_4$  via the solid-state reaction is proposed.

**Experimental Methods and Materials:**

$\text{Sr}_2\text{SiO}_4$  phosphor was synthesized by the solid state reaction method. Strontium carbonate ( $\text{SrCO}_3$ , Aldrich Chemicals, 99.9%), and silicon dioxide ( $\text{SiO}_2$ , -325 mesh, Aldrich Chemicals, 99.6%) were mixed in their stoichiometric ratio according to the  $\text{Sr}_2\text{SiO}_4$  chemical formula. A Stoichiometric mixture of these powders was thoroughly homogenized in agate mortar for 1hr. and then transferred to alumina crucibles. The homogenized mixture was heated in air at  $1200^\circ\text{C}$  for 4h in a muffle furnace with heating rate of  $300^\circ\text{C/hr}$ . Finally cool down to room temperature by furnace shut off. All samples were prepared by same technique.

Thermo gravimetric analysis (TG, DTA, DTG, and DSC) of precursor of  $\text{Sr}_2\text{SiO}_4$  was carried out in nitrogen atmosphere in  $30\text{--}1200^\circ\text{C}$  temperature range using a Perkin Elmer, Diamond TG/DTA instrument. The initial mass of sample taken for recording the TG/DTA curves was 64.778 mg and hold for 1.0 min at  $300^\circ\text{C}$ , and then heating rate was maintained at  $100^\circ\text{C/min}$ . The phase composition and phase structure were characterized by X-ray diffractograms (XRD) using an automated Rigaku Miniflex X-ray diffractometer (D Max III VC, Japan). The photoluminescence

excitation and emission spectra were measured by Spectrofluorophotometer (SHIMADZU, RF – 5301 PC) equipped with a 150 W Xenon lamp as excitation source. All the spectra were recorded at room temperature. The emission and excitation spectra of  $\text{Sr}_2\text{SiO}_4$  phosphor were recorded for excitation at  $256\text{ nm}$  and for emission at  $468\text{ nm}$ .

Results and discussion:

Fig 1 a) and b) illustrates the DTA and TGA curves for the  $\text{Sr}_2\text{SiO}_4$  precursors heated at rate of  $10^\circ\text{C/min}$ . The TG-DTA analysis showed two stages of weight loss accompanied by two endothermic peaks. The corresponding endothermic peak at  $100$  and  $450^\circ\text{C}$  in DTA curve, corresponding to the weight loss shown in TG, was due to precursor dehydration. An apparent weight loss occurred at around  $700^\circ\text{C}$ , and no further weight loss was found at temperatures higher than  $980^\circ\text{C}$ . To explain the broad endothermic peak at around  $820^\circ\text{C}$ , the DTA/TG analysis for pure strontium carbonate and silicon dioxide ( $\text{SiO}_2$ ) were also performed. According to our experimental results, the silicon dioxide seemed to be stable in comparison with strontium carbonate in the range of  $25^\circ\text{C}$  to  $1000^\circ\text{C}$ .

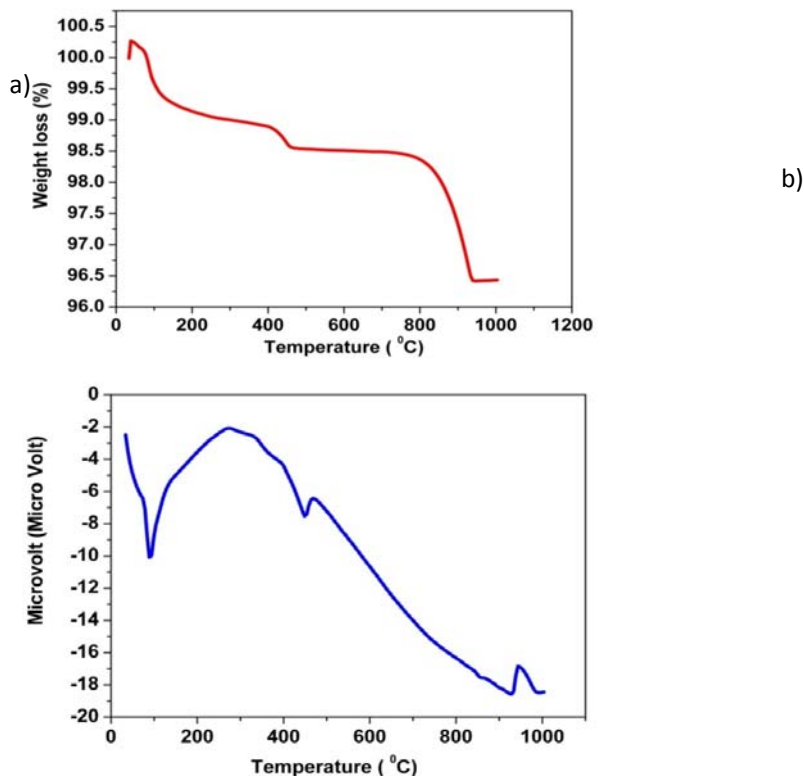
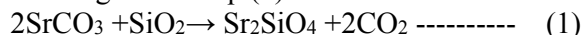


Fig.1 a) and b) shows TG and DTA of Precursor of  $\text{Sr}_2\text{SiO}_4$ .

The results are not shown here. As a result, the endothermic peak at  $820^\circ\text{C}$  shown in Fig. 2 was attributed to reactive strontium carbonate reacting with stable silicon oxide, thereby

leading to the formation of  $\text{Sr}_2\text{SiO}_4$ . The total weight loss measured from TG experiment amounted to 24.7%, which was closed to the theoretical weight loss of this reaction. The net equation of the reaction involving  $\text{SrCO}_3$  and  $\text{SiO}_2$  is given in Eq. (1).



During the reaction indicated in Eq. (1), the conversion ratio of  $\text{Sr}_2\text{SiO}_4$  can be calculated from the weight loss of the samples. The mixed  $\text{Sr}_2\text{SiO}_4$  precursors were isothermally heated at these temperatures for various periods of time and then quenched to room temperature. The weight difference  $_W$  of each specimen before and after the heating process was recorded. The conversion ratio of  $\text{Sr}_2\text{SiO}_4$  formation under each

heating condition was calculated by Eq. (2). The reaction was nearly completed at 800 °C after 60 min. In addition, it was noted that for the same reaction period, the conversion increased with a rise in the heating temperature. Heating specimens at 700 °C for 120 min increased conversion ratio to about 71%. After reacting for 120 min, the conversion ratios at 750 °C and 800 °C were 95% and 97%, respectively.

**XRD Analysis :**

The structure and phase purity of the synthesized  $\text{Sr}_2\text{SiO}_4$  phosphor was investigated by X-Ray Diffraction Method. Results are shown in Fig. 2 and all diffraction peaks can be well indexed based on the JCPDS data card No. 39-1256.

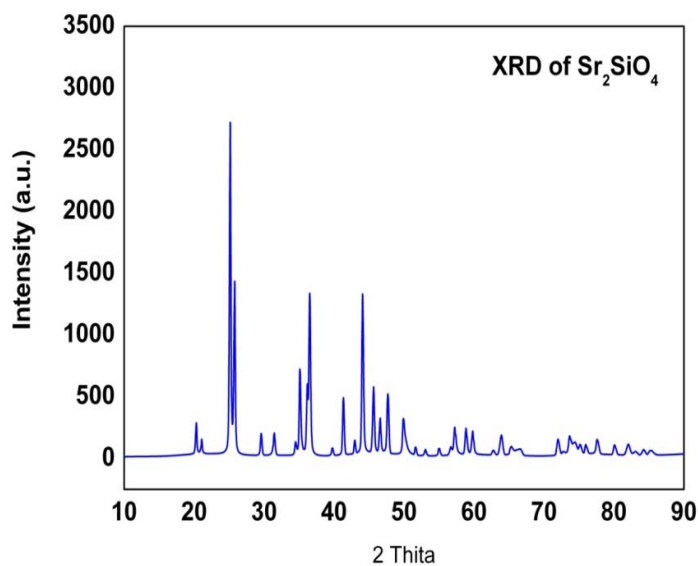


Fig. 2 shows XRD of  $\text{Sr}_2\text{SiO}_4$  at temperature 1200 °C.

All diffraction patterns were obtained using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54051 \text{ \AA}$ ), at 30 kV and 15 mA. Measurements were made from  $2\theta = 10^\circ$  to  $80^\circ$  with steps of  $0.02^\circ$ . The crystallite size of powders samples were calculated from X-ray peak broadening of the diffraction using Scherer's formula. The calculated average crystallite size of the  $\text{Sr}_2\text{SiO}_4$  phosphor is 22 nm. The XRD patterns of the powders revealed that the structure of  $\text{Sr}_2\text{SiO}_4$  is orthorhombic.

#### **Luminescence properties:**

The excitation spectra recorded at 612 nm emission shows peak around 274 nm is due to charge transfer band between  $\text{O}_2^-$ —  $\text{Eu}^{3+}$  as shown in fig. 3. The electron transfers to partially filled 4f orbit of  $\text{Eu}^{3+}$  from 2p full orbit. This transfer leads to oxidation of  $\text{O}_2^-$  to  $\text{O}^-$  and reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ .

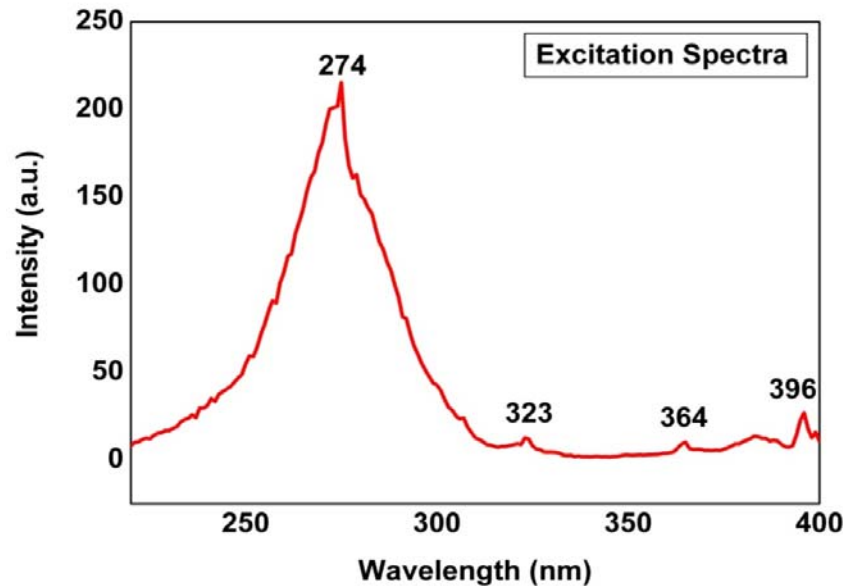


Fig. 3 Shows Excitation spectra of  $\text{Sr}_2\text{SiO}_4: \text{Eu}^{3+}$

Thus the phosphor can be efficiently excited by mercury lamp [12]. Peaks at 376, 382, and at 393 nm are due to  ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$ ,  ${}^7\text{F}_0 \rightarrow {}^5\text{G}_5$  and  ${}^7\text{F}_0 \rightarrow {}^5\text{G}_6$  respectively. In  $\text{Eu}^{3+}$  there are two types of excitation charge transfer band and 4f-4f

transition. The filled  ${}^5\text{S}_2$  and  ${}^5\text{P}_6$  orbital shield the 4f orbital. Thus the influence on the optical transition by host lattice within the 4fn configuration is small and 4f-4f transition is sharp lines [12].

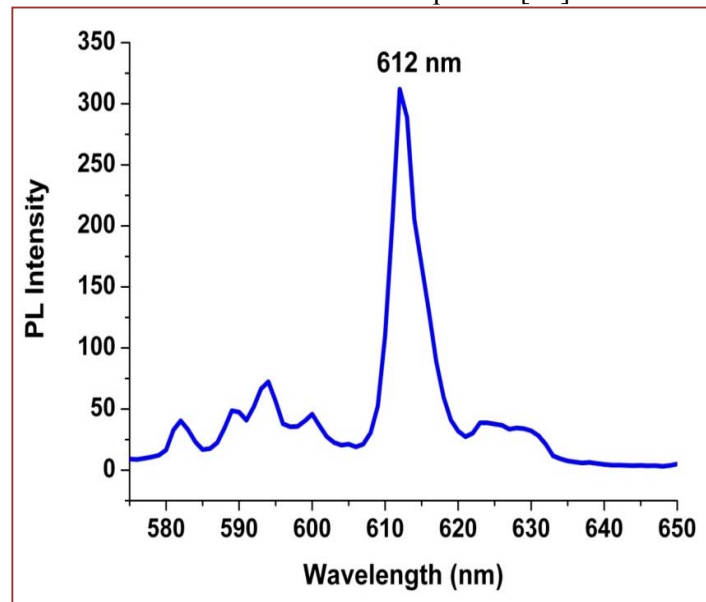


Fig. 4 Shows Emission spectra of  $\text{Sr}_2\text{SiO}_4: \text{Eu}^{3+}$

Fig. 4 shows the excitation and emission spectra of  $\text{Sr}_2\text{SiO}_4: \text{Eu}^{3+}$ . The emission spectrum was recorded with 393 nm excitation. The peaks in the emission spectra are due to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $j=1, 2, 3, 4, \dots$ ). Major peaks are observed in red region. The peaks at 589-593, 612-619 nm are due to

radiative transitions from  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ . The couple arises due to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}$  transition level at 254 nm characteristic excitation of  $\text{Eu}^{3+}$  ion.  $\text{Eu}^{3+}$  ion substitutes  $\text{Sr}^{2+}$  ions in the host lattice which may lead to emission at 593 and 612 nm [13].



Fig.5. CIE for 2.0 mol %  $\text{Eu}^{3+}$  doped  $\text{Sr}_2\text{SiO}_4$  phosphor

Fig.5. Illustrates the CIE chromaticity diagram for the emissions of pure and  $\text{Eu}^{3+}$ , (1.0 mol %) doped  $\text{Sr}_2\text{SiO}_4$ . The colour co-ordinates for the 1.0 %  $\text{Eu}^{3+}$ , doped  $\text{Sr}_2\text{SiO}_4$  phosphors were  $x = 0.67$  and  $y = 0.32$ . This phosphor having colour tenability from red to white light and this phosphor has potential an application in the lighting system.

#### Conclusion:

The reaction mechanism and kinetic analysis for the formation of  $\text{Sr}_2\text{SiO}_4$  are investigated in this study. The process of formation of  $\text{Sr}_2\text{SiO}_4$  is assumed to be a direct reaction between  $\text{SrCO}_3$  and  $\text{SiO}_2$  via the TG/DTA and XRD analysis. The conversion of  $\text{Sr}_2\text{SiO}_4$  from the starting materials increases with an increase in the heating temperature and heating time. For the ceramic reaction involving  $\text{SrCO}_3$  and  $\text{SiO}_2$ , the three-dimensional solid-state reaction model is considered. The formation of  $\text{Sr}_2\text{SiO}_4$  is confirmed to be governed by a diffusion controlled mechanism via reaction kinetic isothermal analysis. According to the Brounshtein-Ginstling model, The colour co-ordinates for the 1.0 %  $\text{Eu}^{3+}$ , doped  $\text{Sr}_2\text{SiO}_4$  phosphors were  $x = 0.67$  and  $y = 0.32$ . This phosphor having colour tenability from red to white light and this phosphor has potential an application in the lighting system.

#### References

1. Lim M A, Park J. K., Kim C. H., J. Mater Sci Lett, 22(2003), 1351-1353.
2. Liu Jie, Lian Hongzhou, SUN Jiayue, Chem Lett, 34(10), (2005) 1340-1343.
3. Zeng Q., Tanng H. Egoshi K., Appl Phys Lett, 88(051996) (2006), 1-3.
4. Yang Zhiming, Liu Yufeng, Acta Phys Sin, 55(09) (2006) 4946-4950.
5. J.S. Kim, P.E. Jeon, J.C. Choi, H.L. Park, Appl. Phys. Lett. 84 (2004) 2931–2933.
6. H. Zhang, T. Horikawa, H. Hanzawa, A. Hamaguchi, K.I. Machida, J. Electrochem. Soc. 154 (2007) J59–J61.
7. G. Blasse, P.E. Wanmaker, J. Vrugt, Philips Res. Rep. 23 (1968) 189–200.
8. J.S. Yoo, S.H. Kim, W.T. Yoo, G.Y. Hong, K.P. Kim, J. Rowland, P.H. Holloway, J. Electrochem. Soc. 152 (2005) G382–G385.
9. A. Nag, T.R.N. Kutty, J. Mater. Chem. 14 (2004) 1598–1604.
10. J.K. Park, M.A. Lim, C.H. Kim, H.D. Park, J.T. Park, S.Y. Choi, Appl. Phys. Lett. 82 (2003) 683–685.
11. J.S. Kim, J.Y. Kang, P.E. Jeon, J.C. Choi, H.L. Park, T.W. Kim, Jpn. J. Appl. Phys. 43 (2004) 989–992.
12. QIAO Yanmin, ZHANG Xinbo, YE Xiao, CHEN Yan, GUO Hai. Journal of rare earths, 27, 323, (2009).
13. I.M. Nagpure, Subhajit Saha, S.J. Dhoble, Journal of luminescence, 129, 898-905, (2009).
14. Roshani Singh and S.J. Dhoble, Adv. Mat. Lett., 2 (2011) 341.
15. Color Calculator version 2, software from Radiant Imaging, Inc, (2007).
16. K.N. Shinde and S.J. Dhoble, Adv. Mat. Lett.,