Positron annihilation studies of Eu and Dy doped $\alpha'$-Sr$_2$SiO$_4$

S K Gupta, K Sudarshan*, S K Sharma, P K Pujari and V Natarajan
Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

*E-mail: kathis@barc.gov.in

Abstract: Sr$_2$SiO$_4$ is an important inorganic host for lanthanide doped white light emitting diodes (LEDs). Strontium silicate (Sr$_2$SiO$_4$) samples doped with 1.0 mol % of Eu$^{3+}$ and Dy$^{3+}$ content were prepared via sol-gel route and characterized by X-ray diffraction (XRD), Raman spectroscopy and positron annihilation spectroscopy (PAS). The concentration of the dopant ion and the temperature of annealing were optimized for maximum luminescence intensity. The positron annihilation lifetime and coincidence Doppler broadening (CDB) measurements indicated that the local environment around the positron annihilation site is different in Eu$^{3+}$ doped and Dy$^{3+}$ doped samples. The results could be explained based on the different local site occupancy of Eu$^{3+}$ and Dy$^{3+}$ in the matrix.

1.0 Introduction

Oxide-based hosts have received considerable attention for use in flat-panel displays due to their luminescent characteristics, stability in high vacuum, and the absence of corrosive gas emission under electron bombardment, as compared to currently used sulfide-based phosphors [1]. Therefore, oxide-based phosphors are likely to emerge as the choice for field emission diodes (FED) green or red phosphors. Among these, strontium silicate is an excellent matrix due its stable crystal structure, good mechanical strength and high thermal stability provided by the tetrahedral silicate (SiO$_4$)$^{2-}$ group [2]. Sr$_2$SiO$_4$ has attracted current interest due to its special structural features and potential application in developing white LEDs. GaN (400 nm chip) coated with Sr$_2$SiO$_4$: Eu$^{2+}$ was shown to exhibit better luminous efficiency than that of industrially available products such as InGaN (460 nm chip) coated with YAG:Ce [3]. The optical band gap of alkaline earth silicate is 4.7eV and therefore these materials are characterized by good transmission properties in the visible part of the electromagnetic spectrum. Strontium silicate exists in monoclinic ($\beta$-Sr$_2$SiO$_4$) phase at low temperatures and in orthorhombic ($\alpha'$-Sr$_2$SiO$_4$) phase at high temperatures with a transition temperature of $\sim$85 °C [4]. It has been reported that the crystal structures of $\alpha'$-Sr$_2$SiO$_4$ (orthorhombic), and $\beta$-Sr$_2$SiO$_4$ (monoclinic), are very similar. In $\beta$$\rightarrow$$\alpha'$ transition a small rotation in SiO$_4$ tetrahedra cause appearance of (100) plane, which is absent in $\beta$ form [4, 5]. In both the phases there are two different Sr sites: one having coordination number 9 and the other with coordination number 10. The ten coordinated Sr(1) sites form linear three-membered rows of (Si–O–Sr(1)–O–Sr(2)) whereas the nine coordinated Sr(2) sites form zig-zag chains of (Sr(1)–O–Sr(2)–O–Sr(1)) along the b-axis [3]. Pictorial representation of the structure is given in figure 1.

It is known that the luminescence properties are strongly influenced by the presence of lattice defects [6] like mono vacancy, vacancy cluster, voids or pores which are formed naturally during synthesis. The positron annihilation spectroscopy is a powerful and sensitive tool to identify the
defects in the solids, distinguish the type of defects and provide relevant information about the size and environment around the defects [7].

In the present work, $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Dy}^{3+}$ phosphors are synthesized by sol–gel method using tetraethyl orthosilicate as precursor. The samples were characterized by XRD for phase purity. The positron annihilation lifetimes and coincidence Doppler broadening of annihilation radiation has been measured and the results are discussed.

2.0 Experimental

2.1. Sample preparation:
All the chemicals used in the sample preparation were of Analytical reagent (AR) grade and procured from Sigma Aldrich. The alkaline earth silicate samples were prepared via a sol-gel route using tetraethyl orthosilicate (TEOS) and strontium nitrate. For preparation of lanthanide doped sample (1.0 mol %), appropriate quantities of $\text{Eu(NO}_3)_3$, and $\text{Dy(NO}_3)_3$ were added to the hydrolyzed TEOS solution. The details of synthesis are mentioned in our earlier work [8, 9].

2.2. Instrumentation:
The phase purity of the prepared phosphors was confirmed by X-ray diffraction (XRD). The measurements were carried out on a STOE X-ray diffractometer equipped with Ni filter, scintillation counter and graphite monochromator. The diffraction patterns were obtained using monochromatic Cu-K$_\alpha$ radiation ($\lambda = 1.5406\text{Å}$) keeping the scan rate at 1sec/step in the scattering angle range ($2\theta$) of 10° to 60°. The K$_{\alpha 2}$ reflections were removed by a stripping procedure to obtain accurate lattice constants.

Positron annihilation life time spectroscopy (PALS) measurements were carried out by using a fast-fast coincidence system with plastic scintillation detectors. The time resolution of lifetime spectrometer was 260 ps ($^{60}\text{Co}$) with time calibration of 25 ps/channel. $^{22}\text{Na}$, (10 $\mu\text{Ci}$) deposited and dried between two kapton films of thickness 8 micron was used as positron source. The positron source was completely immersed in powder samples to stop all positrons in the sample. For each of the three spectra $~10^6$ counts were recorded. The computer program, PATFIT-88 was used for the analysis of the spectra. Two HPGe detectors each having resolution of 1.1 keV at 514 keV of $^{85}\text{Sr}$, located at 180° relative to each other were used to record two annihilation photons $E_1$ and $E_2$ emitting from a single event. The sum and difference in the energy of the two gamma-rays is plotted. The details of the coincidence Doppler broadening system and data analysis are reported in ref [10].

3.0. Results and discussion

3.1. Structural analysis: Powder X-ray Diffraction (PXRD)
The purity and crystallinity of the as-prepared $\text{Sr}_2\text{SiO}_4$ and $\text{Sr}_2\text{SiO}_4:Ln^{3+}$ ($Ln = \text{Eu}, \text{Dy}, \text{Sm}$) samples were characterized using powder X-ray diffraction (XRD). As seen from the XRD pattern in figure 2, the diffraction peaks of both $\text{Sr}_2\text{SiO}_4$ and $\text{Sr}_2\text{SiO}_4:Ln^{3+}$ ($Ln = \text{Eu and Dy}$) samples could be indexed to the orthorhombic phase of $\alpha'_-$ $\text{Sr}_2\text{SiO}_4$ (JCPDS card No. 39-1256). Incorporation of lanthanide ion has not changed the XRD pattern and no impurity peaks were observed confirming that doping has not distorted the structure of strontium silicate and dopants are efficiently dissolved in the $\text{Sr}_2\text{SiO}_4$ host lattice by replacing the $\text{Sr}^{2+}$ because of the similar ionic radius and very small level of doping (1.0 mol %).

3.3. Positron annihilation spectroscopic studies
From the coincidence Doppler broadening spectroscopic measurements, the momentum distribution ratio curves of $\text{Sr}_2\text{SiO}_4$, and $\text{Eu}^{3+}$, $\text{Dy}^{3+}$ doped $\text{Sr}_2\text{SiO}_4$ with respect to silicon as reference are shown in figure 3. It is clearly seen from the figure 3 that the shape of the momentum ratio curves in all cases are similar but the heights of the peaks differs considerably in the case of $\text{Dy}^{3+}$ doped $\text{Sr}_2\text{SiO}_4$. The similar shape of
the curves indicates that the elements around the site of positron annihilation in each case are similar. The peak around $10 \times 10^{-3} \text{ m}_0 c$ in ratio curves of different oxide samples with respect to silicon is attributed to the positron annihilations with 2p electrons of oxygen [11].

Figure 1: Pictorial representation of 9- and 10-coordinated Sr$^{2+}$ in strontium silicate

Figure 2: XRD pattern Sr$_2$SiO$_4$ and Sr$_2$SiO$_4$:Ln$^{3+}$ (Ln = Eu and Dy)

The positron annihilation lifetime spectra could be fitted to three components. The lifetime of the long lived component was 1-1.2 ns with ~1% intensity. The origin of this component is not clear. The two other major components observed are given in table 1 along with the respective intensities. As seen from Table 1, $\tau_1$ in Sr$_2$SiO$_4$ increased from 184 ps to 212 on Eu doping and to 236 ps on Dy doping. The increase in $\tau_1$ is higher than seen due to oxygen vacancies. In general, life time changes are in the range of 10 ps for oxygen vacancies, 10-20 ps in the case of oxygen clusters and 30-50 ps for cation vacancies [12]. The lifetime changes suggest that the changes are due to cation vacancies. However, the change in lifetime upon Dy doping is more drastic than Eu doping. Similar results are observed in the case of coincidence Doppler broadening measurements too. The second lifetime component is similar both in Eu and Dy doped samples but is higher than that in the undoped sample. This lifetime could be due to vacancy clusters with contributions expected from the positron annihilations from surface of the particles.

Table 3: Positron life time values with their intensity

| Sample          | $\tau_1$ (ps) | $\tau_2$ (ps) | $I_1$ (%) |
|-----------------|---------------|---------------|-----------|
| Sr$_2$SiO$_4$   | 183.6 ±2.2    | 343.8 ±3.8    | 48.3 ±1.0 |
| Eu- doped       | 212.5 ±1.9    | 395.0 ±7.1    | 67.0 ±1.0 |
| Dy- doped       | 235.9 ±1.9    | 399.6 ±8.6    | 70.9 ±1.1 |

It has been reported from time resolved fluorescence spectroscopy (TRFS) studies that Eu(III) ions occupy both Sr(1) (10 coordinated) and Sr(2) sites (9 coordinated), whereas Dy(III) ions occupy only Sr(2) (9 coordinated) sites [8, 9]. Though lanthanide doping is expected to increase the cation vacancies there by increasing the positron annihilation lifetimes, the nature of vacancies could be different due to preferential occupation of Dy in only the 9-coordinated sites. This would leave more cation vacancies at Sr(1) site with 10 oxygens around in the Dy sample. This might be the
4. Conclusions
The positron annihilation studies in Eu$^{3+}$ and Dy$^{3+}$ doped Sr$_2$SiO$_4$ showed that though positrons are annihilating from the cation vacancies in these samples, the local environment around the annihilation site is different in both the cases. The results are consistent with the reported time resolved fluorescence results where it has been shown Dy preferentially occupies 9-coordinated site of the Sr$_2$SiO$_4$ matrix. This results in more cation vacancies in 10-oxygen coordinated site in the lattice in Dy doped sample and it manifests as larger peak in the coincidence Doppler broadening momentum ratio curve as well as large positron lifetime.

References:
[1] Gupta S K, Sahu M, Krishnan K, Saxena M K, Natarajan V and Godbole S V 2013 J. Mater., Chem. C 1 7054
[2] Denault K A, Brgoch J, Gaultois M W, Mikhailovski A, Petry R, Winker H, Denbaars S P and Seshadri R 2014 Chem. Mater. 26 2275
[3] Nag A and Kutty T R N 2004 J. Mater. Chem. 14 1598
[4] Catti M, Gazzoni G and Ivaldi G 1983 Acta Crystallogr. Sect. C. 39 29.
[5] Hyde B G, Seller J R and Stenberg L 1986 Acta Crystallogr. Sect. B. 42 423.
[6] Lin Y-H, Li M, Nan C-W and Zhang Z 2007 J. Am. Ceram. Soc. 90 2991.
[7] Kuramoto E, Tsutsumi T, Ueno K, Ohmura M and Kamimura Y 1999 Comput. Mater. Sci. 14 28.
[8] Gupta S K, Mohapatra M, Kaity S, Natarajan V and Godbole S V 2012 J. Lumin. 132 1329
[9] Gupta S K, Kumar M, Natarajan V and Godbole S V 2013 Opt. Mater. 35 2320
[10] Sharma S K, Sudarshan K, Maheshwari P, Dutta D, Pujari P K, Shah C P, Kumar M and Bajaj P 2011 Eur. Phy. J. B 82 335.
[11] Sharma S K, Pujari P K, Sudarshan K, Dutta D, Mahapatra M, Godbole S V, Jayakumar O D and Tyagi A K 2009 Solid State Communications 149 550.
[12] Vance E R, Hanna J V and Hadley J H 2012 Adv. Appl. Ceram. 111 94.