Thermoluminescence Studies of Ce^{3+} Doped Sr_2SiO_4 Phosphor

Monika Somani[a)], M. Saleem, M. Mittal, P. K. Sharma

Department of Physics, Govt. Autonomous Holkar Science College, Indore, 452001, India
[a)]monikasomani88@gmail.com

Abstract: Hereby, Ce^{3+} doped Sr_2SiO_4 phosphor prepared by high temperature solid state reaction (SSR) method has been addressed. The phosphor was characterized by XRD for structure and phase confirmation. The XRD data analysis revealed that the phosphor is single phased in nature and has crystallized into the orthorhombic structured (Pmnb). The study of surface morphology was carried out using scanning electron microscopy (SEM) and observation of the micrograph so obtained revealed the agglomeration process in the sample preparation with growth in average particle size due to the diffusion facilitated by sintering at high temperature compared to the average particle size calculated from XRD. Further elemental verification of the synthesized phosphor was done using energy dispersive analysis of x-ray diffraction (EDX) and the spectrum analysis revealed the presence of all the constituents without presence of any foreign element. The phosphor was investigated for Thermoluminescence (TL) properties. The TL spectrum displayed three peaks after deconvolution observed at around 249.72 ˚C,226.51˚C,and 27318 ˚C respectively. TL parameters such as activation energy (E), shape factor (μ) were also calculated with the help of TL glow curve.

Keyword: Phosphor, XRD, Morphology, Thermoluminescence.

INTRODUCTION

In the last few decades nano-materials have become important in the field of luminescence due to the enhancement in optical properties than their bulk counter parts because of their quantum size effect and an increased surface to volume ratio. Trivalent rare earth (RE^{3+}= Dy^{3+}, Ce^{3+}) doped phosphors has made rapid development. Silicate based and rare earth ion doped phosphors haveattracted attention of researchers due to their exceptional performance compared to the aluminate based phosphors in the sense of theirexcellent physical and high chemical stability, low power consumption, persistent glow, reliability and water resistant character[1, 2].Strontium silicate is an important host in case of luminescence materialsand has been actively investigated for its luminescent from their application point of view such as the development of displays and luminescence device [3, 4].

Thermoluminescence is an important tool for estimating the trap depth present in solids.The convenient discussion on thermoluminescence starts with the assumption that there is the presence of localized and discrete energy levels within the band gap. As the study of thermoluminescence is supplemented by kinetic analysis, analysis of glow-peaks for kinetic parameters is a prime importance. A method applicable to an isolated peak may not provide a valid result. Since most kinetic analysis methods apply for isolated peaks, it is necessary to consider the case where multiple subsidiary peaks are examined within the limits of the dominant one in such a manner so that the collection appears to be single [5].

The long lasting phosphor materials, materials with large size are prepared using solid-state reaction technique and in order to obtain much smaller particles, the larger phosphor particles need to be grinded further, which can easily introduce additional defects and greatly reduce the luminescence efficiency. The optical properties of luminescent materials not only are closely related to its native crystal structure but also to its morphology.

This paper reported Ce^{3+}doped Sr_2SiO_4 phosphor synthesized by high temperature solid state reaction method. The Structuralcharacterizationof the prepared sample was investigated by XRD, SEM and EDX and optical analysis were also done on the basis of Thermoluminescence (TL).

EXPERIMENTAL DETAILS

The polycrystalline $Sr_2SiO_4:Ce^{3+}$ phosphor was synthesized by high temperature solid state reaction method. The starting materialwere $SrCO_3$ (99.99%), SiO_2 (99.99%) and Ce_2O_3 (99.99%). The raw material were weighted in stoichiometric ratio and thoroughly mixed in a mortar-pestle for 3 h. The mixture was then calcined at a temperature of 800˚C for 4 h. The calcined powder was again ground for two hours and the fine powder so obtained was annealed at 1100 ˚C for 3h [6].

The phase formation and hence the structure of the sample was investigated by XRD characterization technique using Bruker D8 advanced [Cu K_α radiation (λ=1.54060Å)] over the 2θ range of 20˚ to 80˚. Elemental composition and the formation of phosphor were confirmed by SEM and EDX. Scanning electron micrographs and energy dispersive spectrum analysis of X-ray diffraction were obtained using SEM instrument model JEOL JSM-5600 with a resolution of 3.5 nm, magnification power of × 18–300,000 kV (in 136 steps), acceleration voltage of 0.5–30 kV (53 steps), and energy dispersive spectrometer, model INCA Oxford. The Thermoluminescence glow curve recorded by TLD recorder 1009I by Nucleonix (Nucleonix Pvt. Ltd. Hyderabad, India).

RESULTS AND DISCUSSIONS

The X-ray powder diffraction (XRD) patterns of Ce^{3+} doped Sr_2SiO_4 phosphor obtained by SSR method is shown in Figure. 1. From the study of the XRD spectrum of the phosphor, it is revealed that the prepared phosphor was single phase and has crystallized into the orthorhombic structure with space group Pmnb. Further. Within the bound of the characterization, no extra reflection is observed that indicates the sample purity and its single phase nature. The XRD patterns were found to match well with the joint committee powder diffraction standard data (JCPDS) file (39-1256) [7].The lattice parameters calculated were nearly, a= 5.6689, b= 7.0765, c= 9.7364 From the XRD spectrum, it is concluded that the intense and sharp characteristic peak indicates the highly crystalline nature of the synthesized phosphor. At the same time, the narrowness of the FWHM of the characteristic peaks reveals the larger average particle size. The average crystalline size of the prepared phosphor was calculated using Debye Sherrer formula[8].

$t = 0.9\lambda/\beta \cos\theta$

Where T is crystalline size, λ is wavelength (for Cu KαÅ), β is FWHM and θ is Bragg's angle. The calculated average crystalline size of the phosphor was 63nm.

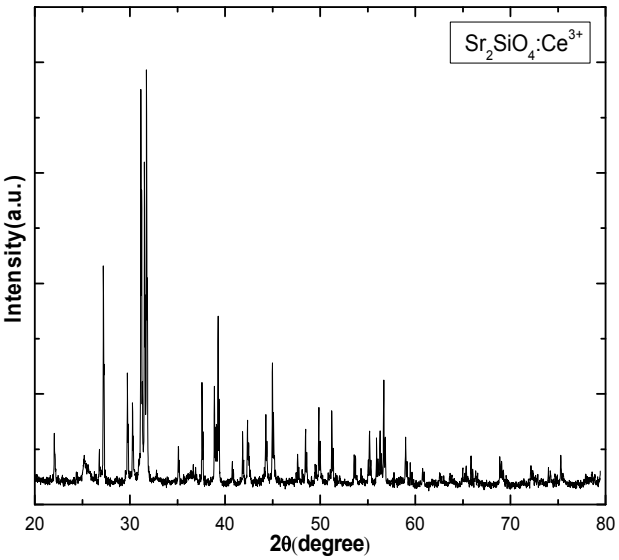

FIGURE 1.XRD pattern of Sr_2SiO_4: Ce^{3+} phosphor.

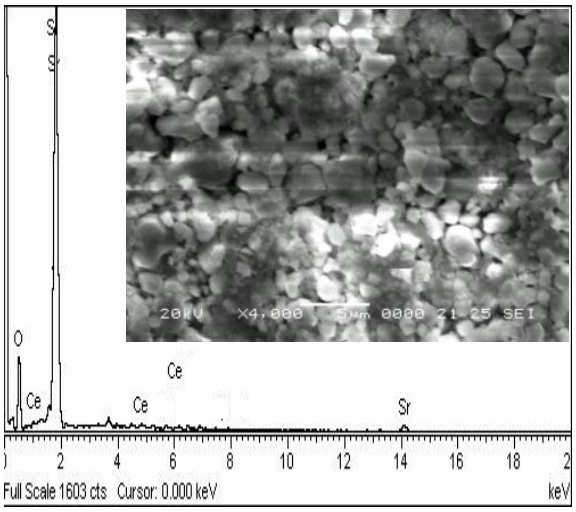

FIGURE 2. EDAX and SEM (inset) of Sr_2SiO_4: Ce^{3+} phosphor.

The phosphor was subjected for surface analysis studies as the luminescence properties of the phosphor also depends upon the surface morphology of the phosphor, particle size and shape. The morphology study of the Ce^{3+} doped Sr_2SiO_4 phosphor was investigated using scanning electron microscopy. The SEM image of the phosphor is displayed as the inset of the Fig 2. The micrograph of the as synthesized phosphordisplay irregular shapes of the

particles but close observation reveals that all the particles tend to achieve spherical shape. Further the SEM image indicates that particles are homogeneously distributed. The development of the grain in the sample suggests that in the sample formation, aggregation has occurred. The sample though crystalline in nature, there is no definite grain boundaries developed and all the particles are well separated from each other. The average size of the particles in the phosphor has been calculated using ImagJ software and was found to be 1.3 μm [9].

The surface morphology studies are as important as the verification of the constituent elements of the sample and their concentration. The loss of any integral element of the sample heavily influences the physical properties of the sample and so is the case with any foreign impurity. To clear this confusion, EDAX characterization has been carried out. The EDAX spectrum of the phosphor has been shown by the Figure 2. The careful observation of the spectrum that there is no loss of the any of the integral component of the sample and within the limits of the experiment, no foreign element is found to be present.

Thermoluminescence is thermally stimulated emission of light, when the material is irradiated with ionizing radiations i.e. UV radiation. This technique is one of the possible ways to investigation the trap states of the materials. Thermoluminescence records the glow intensity as a function of temperature. Figure: 3shows the TL glow curve for of Ce^{3+} doped Sr_2SiO_4phosphor for different UV exposure times that exhibited only one prominent TL peak at around 265 ^oC indicating that only one set of traps was activated within the particular temperature range. All four peaks had an almost similar structure with slightly variation in the peak position.

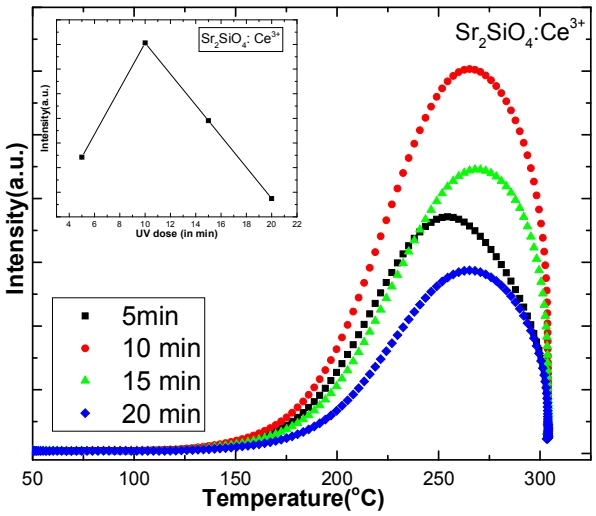

FIGURE 3. Thermo-luminescence (TL) glow curve, (inset-UV exposure time vs intensity) of Sr_2SiO_4: Ce^{3+} phosphor sample.

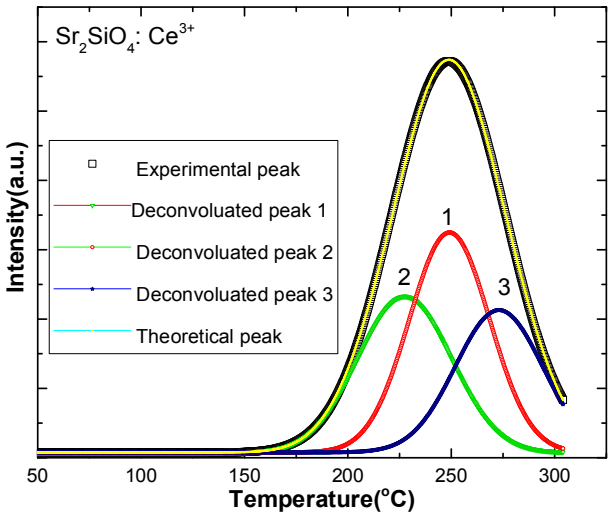

FIGURE 4. Deconvoluted glow curve of Sr_2SiO_4: Ce^{3+} phosphor.

In order to study the different kinetic parameters from deconvoluted TL glow curves shows in Figure.4,peakshape method [5]was used which gives the trap depth in terms of $\delta = T_2-T_m$, $\tau = T_m-T_1$, $\omega = T_2-T_1$. The geometrical factor μ_g can be calculated as $\mu_g=\delta/\omega$. This method is mainly based on the temperatures T_m, T_1, T_2, where T_m is the temperature corresponding to the maximum intensity and T_1, T_2 are the temperatures at half of the maximum intensity on the ascending and descending parts of the peak, respectively. The expression deduced by Chen's, valid for any kinetics is

$$E_\alpha = C_\alpha\left(\frac{kT_m^2}{\alpha}\right) - b_\alpha(2kT_m)$$

For general order of kinetics, the value of the C_α and b_α are calculated as

$C_\tau = [1.15+3(\mu_g-0.42)]$, $b_\tau = [1.58+4.2(\mu_g-0.42)]$

$C_\delta = [0.976+7.3(\mu_g-0.42)]$, $b_\delta = 0$

$C_\omega = [2.52+10.2(\mu_g-0.42)]$, $b_\omega = 1$

Table -1 shows the different parameters of TL glow curve. Theoretically, the value of symmetry factor (μ_g) for first and second order kinetics is 0.42 and 0.52 respectively. The activation energy E or trap depth which is the thermal energy required to liberate the trapped electrons and holes can be determine by the Chen's equation. The calculation reveals the values for the trap depth as 1.54eV, 1.19eV and 1.58eV in the Sr_2SiO_4; Ce^{3+} phosphor.

TABLE: - 1 The kinetic parameter for Sr_2SiO_4: Ce^{3+} phosphor estimated from Chen's glow peak method.

Peak	T_1(°C)	T_m(°C)	T_2(°C)	E_ω	E_τ	E_δ	μ_g	Kinetic Order	Activation Energy (eV)
1	226	249.72	272.42	1.55	1.53	1.54	0.48	2	1.54
2	198.96	226.51	254.56	1.20	1.20	1.19	0.50	2	1.19
3	247.68	273.18	300.22	1.64	1.50	1.62	0.51	2	1.58

SUMMARY

In conclusion, the Sr_2SiO_4: Ce^{3+} phosphor was successfully synthesized by high temperature solid state reaction method that crystallized in single phased orthorhombic structure (*Pmnb*). The surface morphology reveals the uniform distribution of particles and agglomeration process in the synthesis tenure of the phosphor. EDAX confirmed the composition of the sample and hence facilitated the doping effect studies on the luminescence. TL properties of UV irradiated phosphor displayed a singleglow peak which on deconvolution revealsvalue of trap depths to be1.54eV, 1.19eV, 1.58eV.

ACKNOWLEDGEMENTS

UGC-DAE-CSR, as an institute is acknowledged for providing characterization facilities. Authors are thankful to Dr. M. Gupta, Dr. D. M. Phase for their guidance and useful discussions. Special thanks to Dr. D. P. Bisen for TL characterization, SOS of physics, Pt. Ravishankar Shukla University, Raipur (CG).

REFERENCE

1. G. Zhu,Y. Wang, Q. Wang, X. Ding, W. Geng, Y.Shi, Journal of Luminescence, 154 (2014) 246.
2. V. B. Pawade, S. J. Dhoble, Journal of Luminescence ,145 (2014) 626.
3. Y. H. Lin, Z. L. Tang, Z. T. Zhang, X. X. Wang, J. Y. Zhang, J. Mater. Sci. Lett.20(2001) 1505.
4. S. A. Studenikin, M. Cocivera, Thin solid Film,394(2001) 264.
5. R. Chen, S.A.A. Winer, J. Appl. Phys. 41 (1970) 5227.
6. Q. Yanmin, Z. Xinbo, Y. Xiao, C. Yan, G.Hai, J. Rare Earths, 27(2009) 323.
7. JCPDS File Number 39-1256, JCPDS International Center for Diffraction Data.
8. M. Saleem and D. Varshney, J. Alloy. Comp., 708 (2017) 309.
9. M. Saleem and D. Varshney, RSC Advances, 8 (2018) 1600.
10. H. Y. Chen, M. H. Weng, S. J. Chang, R. Y. Yang, Ceram.Int. **38** (2012) 125.