RSC Advances

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC
Advances
Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

Anomalous Luminescent Properties in ZnO and $SrAl_2O_4$ Composites

V. P. Singh[a], P. Mohanty[a], S. P. Lochab[b] and Chandana Rath*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

We have reported earlier in ZnO-$SrAl_2O_4$ composite synthesized through solution combustion route that by dispersing 20wt% of ZnO in $SrAl_2O_4$ matrix and calcining at 700 ^oC, a stable hexagonal phase of $SrAl_2O_4$ at RT is established which is generally a high temperature phase of $SrAl_2O_4$ reported in literatures [*singh et al*. 2014 *Dalton Transactions* (Ref. 19)]. Increasing the calcination temperature of composite to 1200 ^oC, hexagonal phase transforms to stable, monoclinic phase of $SrAl_2O_4$. In addition, we have observed anomalous luminescent properties in these composites. In photoluminescence spectra, we observe near band edge emission and defect band emission (DBE) corresponding to ZnO without any signature of emission corresponding to $SrAl_2O_4$ in both the composites. The DBE peak is found to be stronger in monoclinic phase than that observed in hexagonal phase of $SrAl_2O_4$, indicates more defects in the former composite. Combining the excitation and emission properties, we propose a tentative model to illustrate the mechanism of excitation and emission processes involved in composites.
Thermoluminescence studies show a common glow peak at ~323 ^oC in both composites and an additional glow peak at ~158 ^oC in composite with monoclinic phase. Additional glow peak further confirms more defects in monoclinic phase than that of hexagonal phase corroborating with PL and XRD results. With increasing γ- irradiation dose, the additional glow peak shows a linear dosimetric response. The composite with monoclinic phase seems to be suitable for dosimetric application which will be confirmed after doing more measurements in future.

Introduction

Optical ceramic composites are of great interest for the photonic devices. Most common approach for the development and easy manipulation of such composites with enhanced luminescent properties is to combine the filler of particular optical properties with ceramic host matrix. Transition metal oxides like ZnO, TiO_2, MgO, and GeO_2 etc have been considered as most common filler for the next-generation light-emitting devices.[1-4]Among them, ZnO has its own importance due to its green emission in visible region which is applicable for greenish white light emitting phosphor for low-voltage vacuum display devices with a relatively high luminescent efficiency.[1,5,6] Reason behind the green luminescence in ZnO is due to the radiative recombination involving the intrinsic defect centers.[7,8]Moreover, ZnO improves the UV shielding in different host as encapsulating material.[9] Recent research work emphasizes on the formation of transition metal oxide based ceramic composite which shows improvement in optical properties as well as catalytic behavior of transition metal oxide.[10]For example, there are few reports where ZnO is used as filler material in the host of $ZnGa_2O_4$, $ZnAl_2O_4$, $CaAl_2O_4$, YbF_3 and Y_2O_3.[11-16] Among the above hosts, the spinels like $ZnGa_2O_4$, $ZnAl_2O_4$ and $CaAl_2O_4$ containing a large number of intrinsic defects have been reported for improvement of catalyst and luminescent behavior.[11-14,17]Composite of spinels with TiO_2 shows enhanced luminescence intensity. Persistent luminescent for 3 h after turning off the light source for photocatalytic reaction has been observed in $CaAl_2O_4/TiO_{2-x}N_y$: (Eu, Nd) composite.[18-20]$SrAl_2O_4$ with TiO_2 has been used in solar cell as it has an improved efficiency and light down-converting properties of phosphors in presence of Eu, Dy rare earths.[21]Better emission in spinel is due to the presence of high concentration of cationic vacancies and a large proportion of intrinsic disorder.[22]As a consequence, intrinsic defects in the spinel act as trapping centers for electrons and holes created by irradiation. Compared to other spinel**s**, $SrAl_2O_4$ has been proven to be an efficient host material

---

[a] *Vinay Pratap Singh, School of Materials Science and Technology, Indian Institute of Technology, Banaras Hindu University, Varanasi, 221005, India. Fax: 05422368707; Tel: +919452008891; E-mail: vinay.phy@gmail.com*
[*a] *Dr.Chandana Rath , School of Materials Science and Technology, Indian Institute of Technology, Banaras Hindu University, Varanasi, 221005, India. Fax: +91-542-5422368707; Tel: +91 9451058153; E-mail: chandanarath@yahoo.com*
[a] *P. Mohanty, School of Materials Science and Technology, Indian Institute of Technology, Banaras Hindu University, Varanasi, 221005, India. Fax: 05422368707; Tel: +917275795176; E-mail: pankaj22.mohanty@gmail.com*
[b] *Dr. S. P. Lochab, Inter-University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110067, India.; E-mail: lochab@iuac.res.in*

for photo luminescence, cathodoluminescence and plasma display panel phosphors in visible region.[23] The integration of ZnO with $SrAl_2O_4$ rich in intrinsic defects may make them possible to achieve excellent photoluminescence (PL) properties. Due to large lattice mismatch between ZnO and $SrAl_2O_4$, new defects generated at ZnO/$SrAl_2O_4$ interface, may further improve the luminescent. However, the preparation of $SrAl_2O_4$ is quite troublesome as without using any flux it requires high temperature.[24]Therefore, in order to use $SrAl_2O_4$ as a phosphorescent material in visible region, we have attempted to make composites of $SrAl_2O_4$ and ZnO at room temperature (RT) so that luminescent properties of each entity can be exploited.

Here, we report the luminescent properties of composite of 20% ZnO dispersed in $SrAl_2O_4$ synthesized through combustion technique and post calcined at 700 and 1200 °C. For the best of our knowledge, we have stabilized high temperature hexagonal phase at RT for the first time after calcining the composite at 700 °C. After calcining at 1200 °C, the hexagonal phase is transformed to monoclinic phase which is generally a stable RT phase of $SrAl_2O_4$. Surprisingly, the luminescent behavior of composite is dominated by ZnO showing near band edge emission in UV range and broad emission band in visible range.

Synthesis and Characterizations

ZnO, $SrAl_2O_4$ and ZnO-$SrAl_2O_4$ composite with 20 wt% of ZnO were synthesized by solution-combustion technique. 20 wt% of ZnO was dispersed in $SrAl_2O_4$ matrix and the above composite was calcined at 700 °C and 1200 °C. Detailed description of synthesis of composites was given elsewhere.[25] ZnO, $SrAl_2O_4$ and ZnO(20%)-$SrAl_2O_4$ composite calcined at 700 °C and 1200°C were denoted as ZnO(A) and ZnO(B); SAO(A) and SAO(B); composite(A) and composite(B) respectively throughout the manuscript. We characterized the material using UV-visible spectrophotometer, Photoluminescence(PL) spectroscopy and Thermoluminescence(TL) spectroscopy. Optical band gap was estimated by using double beam UV-visible spectrophotometers SHIMADZU-2600. PL study was carried out using third and fourth harmonic of a pulsed Nd: YAG laser (Spitlight600, Innolas, Germany,) as a light source (355 and 266 nm wavelength) with Ocean Optics QE65000 as dispersing device for emission spectra. Xenon lamp in wave length range 280-900 nm (Horiba Jobin Yvon Spectrofluorometer, FluoroMax®-4), was used for recording exitation spectra. For TL study, Co^{60} source was used to perform γ irradiations. The small pieces of sample were exposed to γ rays using 5 Gy/min dose rate at room temperature. TL measurements were carried out using a heating rate of 5 °C/s. TL glow curves were recorded for each sample using a Harshow TLD reader (Model 3500) fitted with a 931B photo multiplier tube (PMT).

Results and discussion

In our previous work, we have shown that ZnO(%)-SAO composite, calcined at 700 °C, with increasing concentration of ZnO from 0 to 20%, monoclinic phase of SAO transforms to hexagonal phase at 20 % of ZnO.[25] Further, we have demonstrated that with increasing calcination temperature from 700 °C to 1200 °C, hexagonal phase again transforms to monoclinic.[25] Moreover, XRD pattern of ZnO(20%)-SAO composite calcined at 700 °C named as Composite(A) shows wurtzite structure of ZnO ($P6_3mc$) and the hexagonal phase ($P6_322$) of SAO. ZnO(20%)-SAO composite calcined at 1200 °C named as Composite(B) illustrate monoclinic phase ($P2_1$) of SAO as well as the wurtzite structure of ZnO ($P6_3mc$) with improved crystalinity. ZnO plays an important role behind the monoclinic to hexagonal phase transformation and stablization of hexagonal phase at RT. Adding ZnO in SAO, one may expect two possibilities: one is the replacement of Sr by Zn and the other would be the replacement of Al by Zn. Although, the valency of Zn and Sr are same, due to large difference in the ionic radius of Zn^{2+} (0.60 to 0.745A) and Sr^{2+} (1.32A), the nine fold coordination of Zn in the undistorted $[Al_2O_4]^{2-}$ framework leads to severely collapsed structure at RT and hence crystallizes in monoclinic structure. If Zn replaces Al, oxygen vacancy is produced which varies with concentration of ZnO. At lowest concentration of ZnO, SAO always shows monoclinic phase at RT which demonstrates that at lower concentration of ZnO,

Fig. 1 Photoluminescence spectra of (a) pristine ZnO(A) and ZnO(B), (b) pristine SAO(A) and SAO(B) and (c) composite(A) and composite(B) calcined at 700°C and 1200 °C, respectively after using the excitation wavelength 266nm.

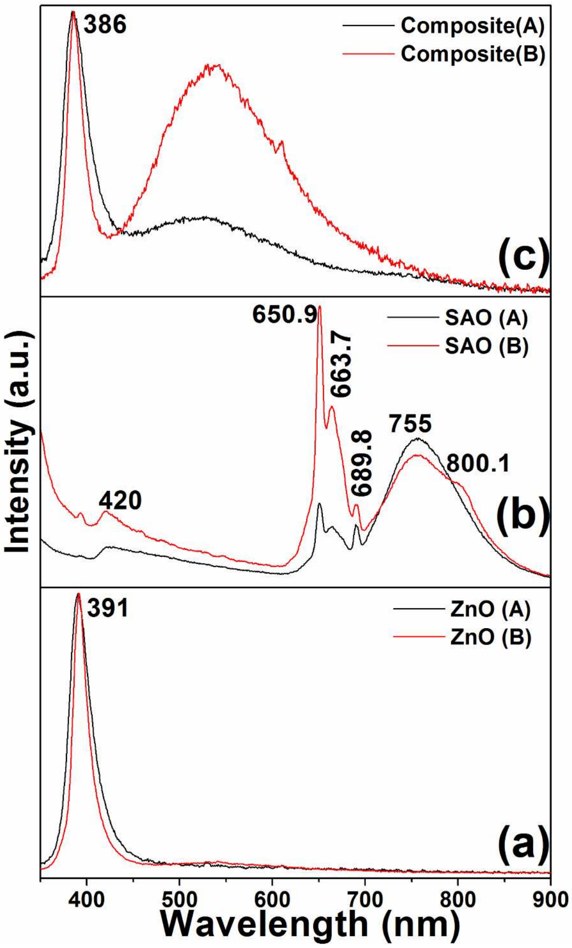
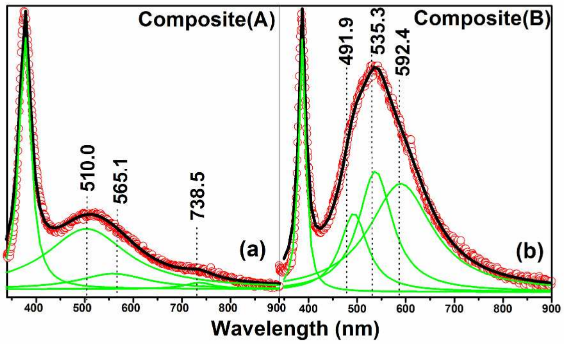


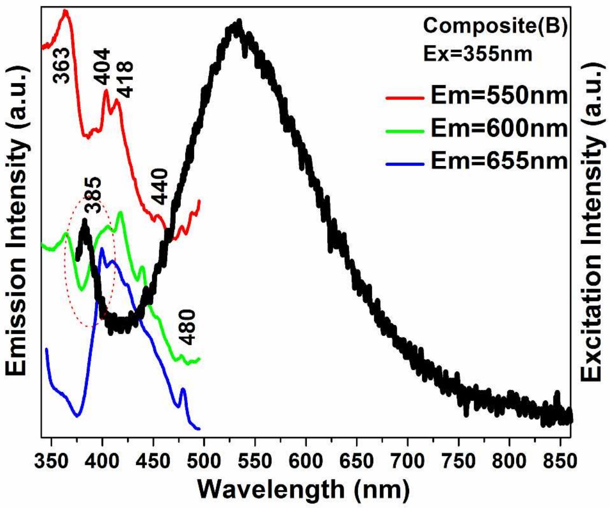
Fig. 2 Overlapping bands in emission spectra (using Ex=266nm) of (a) composite(A) and (b) composite(B) are deconvoluted into



separate bands by Lorenzian fitting.

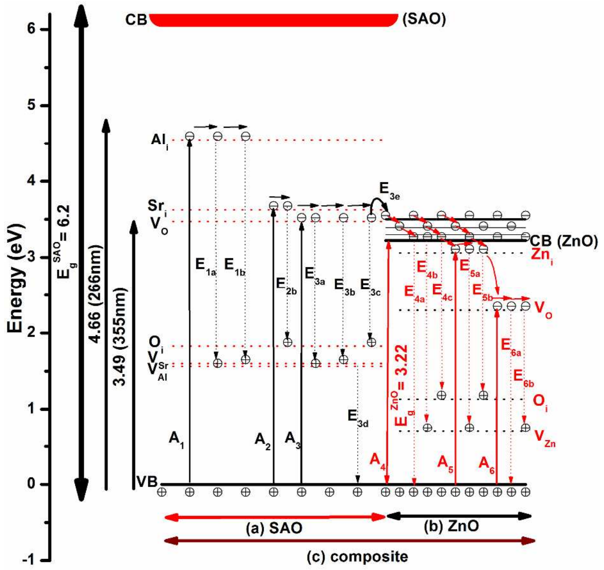
even if Zn replaces Sr and/or Al, the phase of SAO does not change. Therefore, oxygen vacancy formation due to replacement of Al does not play any important role in the phase formation at a low concentration of ZnO. With gradual increase in ZnO content in SAO, more and more oxygen vacancies are produced and both monoclinic and hexagonal phases coexist upto 15 % of ZnO composite. At 20 % of ZnO composite, the oxygen vacancies are sufficient enough to stabilize the hexagonal phase. After calcining at 1200°C, although oxygen vacancies would be filled up in some extent, formation of Sr vacancies at high temperature would be more probable origin behind the hexagonal to monoclinic phase transformation. Sr vacancies are generally produced after calcining SAO at high temperature reported in the literature.[26] Further, the vacancies responsible for phase transformation is supported by photoluminescent and thermoluminescent measurements.

Fig. 3 Emission spectrum of composite(B) samples(after exciting at Ex=355nm) along with the excitation spectra for emission at 550, 600 and 655nm.



Absorbance measurement as a function of wavelength of light in composites do**es** not show significant changes in the band gap compared to pristine ZnO (figure is not shown here). Photoluminescence spectra at RT for ZnO, SAO and composites are shown in Fig. 1 after exciting at 266 nm. Two bands appear in the photoluminescence spectrum of ZnO: one sharp and intense band appears at 391 nm which is due to near band edge (NBE) in UV region and other band in green region due to defect related deep band emission (DBE), as shown in Fig. 1(a). Former one has been widely regarded as recombination through free excitons and later is mostly due to intrinsic defects.[27]With increase in calcination temperature, we did not see any change in DBE peak intensity. In Fig. 1(b), the luminescent spectra of SAO(A) sample shows four emission peaks at 420, 650, 664, 690 nm and a broad band in the range of 700-900 nm. Intensity of former emission peaks are enhanced and a shoulder on the broad band at 800.12 nm appears after calcining at 1200°C. The broad emission band could be due to intrinsic defects.[28,29]Sharp peaks seem to be the spectral lines of Sr.[29] Near band edge (NBE) emission at 386 nm and a broad defect band emission (DBE) in the range of 440 to 800 nm corresponding ZnO are observed in luminescent spectra of composite**,** shown in Figure 1(c). By normalizing NBE emission peak intensity, we observe an increase in DBE intensity with increasing the calcination temperature from 700°C to 1200 °C. Both spectra are further deconvoluted and are shown in Fig. 2. It is observed that DBE constitutes three emission peaks such as 510, 565, 738.5 nm and 492, 535, 592 nm in composite(A) and composite(B), respectively. All these emission peaks of composite(A) are blue shifted in composite(B). One may highlight here that although ZnO incorporation induces hexagonal to monoclinic phase transformation in SAO, there is no indication of emission peaks corresponding to SAO rather the NBE and DBE of ZnO predominates the luminescent behavior in composites. Further, the DBE in composite(B) becomes more intense at the expense of NBE peak after exciting with 355 nm laser source (fig. 3). Intensity ratio of I_{DBE}/I_{NBE} is found to be increased from 0.808 to 2.014 after increasing excitation wavelength from 266 to 355 nm in composite(B). We have carried out excitation spectra with respect to the emission at 550, 600 and 655 nm and are shown along with emission spectra in Fig. 3. Excitation spectra for emission at 550nm demonstrate an intense band at 363 nm and few weak peaks at 404, 418, 440 and 480 nm. While the former band confirms the band-to-band excitation, weak band confirms excitation of electrons from VB

Fig. 4 The proposed energy band diagram of electron transfer in ZnO-SAO composites after excitation.



to intermediate defect states present in the band gap. Excitation spectra for emission at 600nm shows increase in intensity of the band at 440 and 480 nm along with a decrease in intensity of the band located at 363 nm. Excitation spectra corresponding to the 655 nm emission peak show a less intense peak located at 363nm and a broad band in the range of 375 to 490 nm accompanied with the peaks at 404, 418, 440 and 480 nm. Thus, from the excitation spectra corresponding to emission monitored at 550, 600 and 655 nm, we confirm that the intensity of peak responsible for NBE of ZnO decreases and intensity of the broad band above 385 nm increases which is responsible for DBE. Looking at emission spectra obtained by using 266 and 355 nm in composite(B), one may note that by exciting the sample with energy close to the band gap of ZnO (3.2 eV), more electrons relax through intermediate defect states of ZnO than direct band to band transition. The anomalous change in DBE peak in composites could not be explained considering the defect states of ZnO alone because, we have not observed any defect band emission either in ZnO(A) or ZnO(B). Therefore, defect band emission corresponds to ZnO in composites is associated with the monoclinic/hexagonal phase of SAO having different native defects. The excited electrons from defect states of SAO are deexcited through the defect states of ZnO emitting photons of energy in the range of visible region. The intensity of DBE increases in composite(B), confirms more native defects. More native defects in monoclinic phase reported in literature is further confirmed from the PL data shown in Fig. 1.[30-32]By exciting with 355nm, more electrons transfer their energy through the defect states of ZnO and hence defect band intensity in composite(B) is enhanced.

Based on the photo luminescence data, we propose a tentative model to illustrate the mechanism of excitation and emission processes observed in composite(B) in fig.4. In the band diagram, we have specified the energy level of V_{Sr},V_{Al},V_O, Sr_i, Al_i and O_i corresponding to SAO and V_{Zn},V_O,Zn_i and O_i corresponding to ZnO. Exciting with photons of energy 4.66/3.49eV (266/355nm), electrons may show band to band excitation and the formation of excitons. The relative absorption processes of electrons are represented by A_1, A_2, A_3, A_4, A_5 and A_6 in the band diagram. Excited electrons are deexcited directly to the valence band or trapped by the defect states of SAO (Sr_i, Al_i and V_O) and/or by defect states of ZnO (Zn_i, V_o, O_i and V_{Zn}). There could be a possibility of emission of electrons from donor levels Al_i, (emission processes are represented by E_{1a},E_{1b}), from Sr_i (represented by E_{2a}) and from Vo (represented by E_{3a}, E_{3b} and E_{3c}) as there is evidence of emission peaks 420nm, 651, 664, 690, 755 nm in SAO observed by exciting at 266/355 nm. However, we do not find any emission peaks of SAO in composite(B). One may note that although there is a possibility of donor states of SAO to be populated by excitation of electrons, emission only occurs through the defect states of ZnO (The process E_{3e}). This is only possible by transfer of energy from the donor levels of SAO to the lower energy levels of ZnO which includes the CB of ZnO and deep defect levels such as Zn_i and V_O. The relative emission processes are E_{4a}, E_{4b}, E_{4c}, E_{5a}, E_{5b} and E_{6a}, E_{6b}. We conclude that intense white light emission is accompanied with the phase transition from hexagonal to monoclinic phase of SAO in presence of ZnO, is an important finding.

Fig. 5 Thermoluminescence spectra of composite(A) (a) before and (b) after γ irradiation and composite(B) (c) before and (d) after γ irradiation.

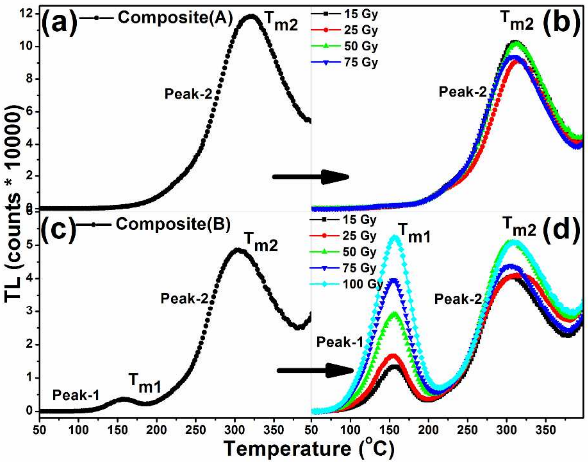
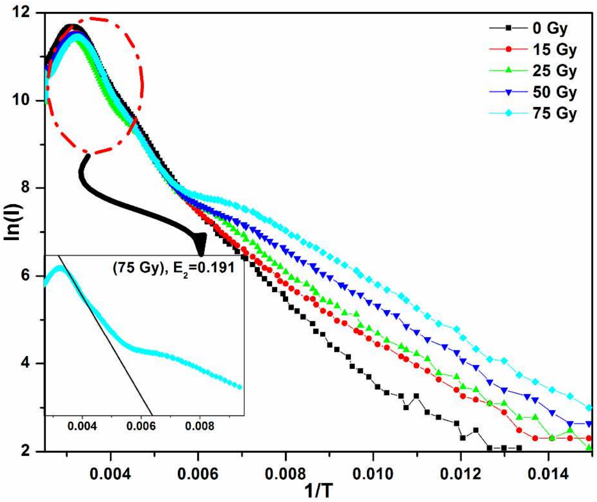
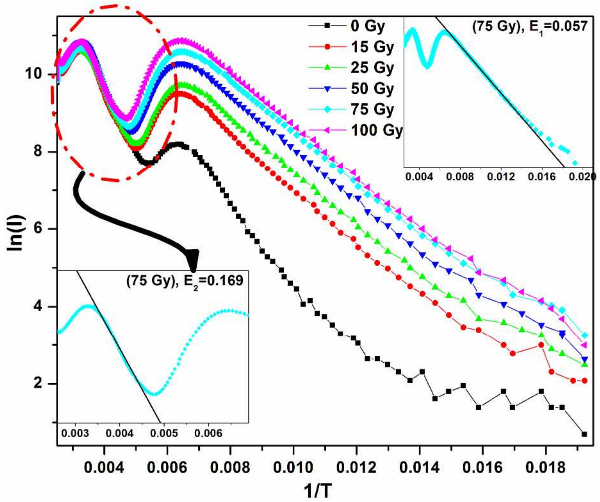


Fig. 6 Calculation of activation energy *E* of traps for composite(A) with respect to the TL glow peak-**2**.



Thermoluminescence (TL), a reliable technique to study defects, has been carried out in order to compare defects in composite(A) and composite(B). Fig. 5 shows the thermoluminescence (TL) spectra of composites before and after γ irradiation. A well resolved broad and intense single glow peak with maxima at ~323 °C is observed in the composite(A). In addition to glow peak at ~323 °C, TL glow curve of composite(B) exhibits one more peak with maxima at ~158 °C. The peaks observed at low temperature and high temperature are denoted as peak-1 and peak-2, respectively. The maximum intensity observed for peak-1 & 2 at ~158 °C and ~323 °C denoted as T_{m1} and T_{m2}, respectively (Fig. 5). The intensity of peak-1 is very low compared to the peak-2 in composite(B). After irradiation with gamma (γ) rays, for a dose range of 15–75 Gy, the intensity of peak-1 in composite(B) increases without changing the shape of glow curve. In contrary,

Fig. 7 Calculation of the activation energy *E* of traps for composite(B) with respect to the TL glow peak-1 and glow peak-2.

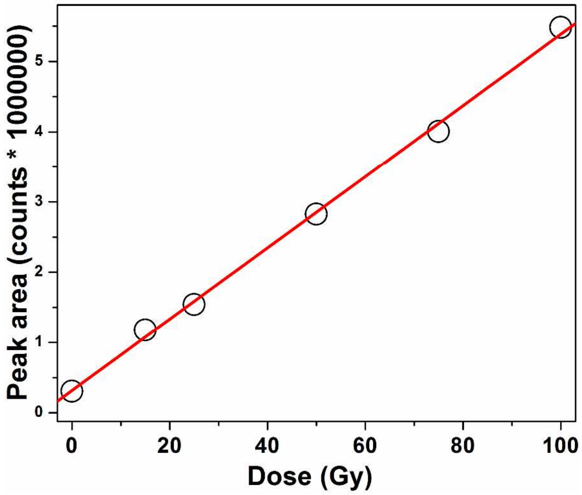


the intensity and curve shape of peak-2 in both the samples does not show significant change in intensity even after increasing dose range. The increasing trend in intensity of peak-2 for composite(B), can be understood by the fact that more and more traps responsible for the glow peak are getting filled with electrons after increasing the irradiation dose. The trapped electrons afterward annihilate with holes by thermal stimulation and gives rise to glow peak as observed in composite(B). It has been reported that electron traps are basically the lattice point defects which form during synthesis or heat treatment and create the charge noncompensation so that the electrons or holes can be trapped at these charge defects by the coulomb attraction.[33] We thus confirm that composite(B), with monoclinic phase is having more defects than the composite(A) with hexagonal phase.[25] T_{m1} and T_{m2}, do not change with increase in dose in both composites. This is a characteristic of all first-order TL curves. From the first-order TL curves, depth of trap energy level in both composites can be calculated using the initial rise method.[34] The formula for calculation is as follows:

$$I(t) = -\frac{dn}{dt} = \mathrm{sn}\exp\{-\frac{E}{kT}\} \qquad (1)$$

Where k is the Boltzmann's constant, the term *s* is called the frequency factor and *n* is for trapped electrons. Plotting ln(*I*) versus 1/*T*, a straight line is expected in the initial rise temperature range of glow peaks, from which the activation energy, *E* of trap is readily found. Using equation 1, from Fig. 6, activation energy, *E,* of trap for the composite(A) is found to be about 0.1840 ± 0.0044 eV corresponding to TL glow peak-2. Similarly from Fig. 7, activation energy for trap depths are calculated to be 0.0637 ± 0.0091 eV and 0.1628 ± 0.0270 eV corresponding to the peak-1 & peak-2, respectively for composite(B). While same type of defect center are responsible for TL glow peak-2 in both the composites, new type of defect centers emerges in composite(B) with respect to the peak-1. The extra glow peak well corroborates with the enhanced DBE observed in composite(B) accompanied with excess of native defects. The total energy of defect free $SrAl_2O_4$ and $SrAl_2O_4$ containing V_O, V_{Al} or V_{Sr} defects are *ca.* -432, -430, -425 or -345 keV, respectively.[26] Thus, one may note that formation of V_{Sr} relatively needs high temperature. TL glow peak-2 in both the composites must be due to V_O which is present in both composites. However, peak-1 in composite(B) may be attributed to V_{Sr} which appears due to the elevated calcination temperature, resulting in monoclinic phase. The increase in peak area or intensity of TL glow peak-1 in composite(B) with irradiation dose may be applied in the field of radiation dosimeter. Fig. 8 shows the integrated peak area as a function of γ irradiation dose in the range from 0Gy to 100Gy corresponding to TL glow peak-1 of composite(B). The composite(B) exhibits a remarkable linear dosimetric response in the dose range of 0Gy to 100Gy, which shows no indication of saturation response. For dosimeter applications, a linear dependence on the dose is highly desirable. Therefore, composite(B) is found to be more suitable for the application of long lasting phosphor and may be explored for radiation dosimeter in future.

Fig. 8 The linear response of integrated thermoluminescence of composite(B) as a function of γ irradiation dose with respect to the TL glow peak-**1**.



Conclusions

We stabilized hexagonal phase of SAO at room temperature by incorporating 20% of ZnO in SAO matrix and post-calcined at 700 °C. Calcining at 1200°C, hexagonal phase transformed to monoclinic phase which is a stable phase of SAO generally observed at RT. From the photoluminescence spectra, near band edge emission and defect band emission in visible range corresponding to ZnO were observed in ZnO-SAO composite without showing any signature of SAO. We revealed from photoluminescence spectra that with increasing calcination temperature of composite, defect band emission increased. PL showed the higher concentration of defects for monoclinic SAO in composite. TL study further confirmed increase in number of defect centers in monoclinic phase compared to the hexagonal phase of SAO. We proposed a energy band diagram responsible for defect band emission observed in both the composites.

Acknowledgements

V.P. Singh acknowledges CSIR, India for providing senior research fellowship. CR acknowledges Prof. D. Pandey and Prof. R.K. Sinha for fruitful discussions.

References

1. A.B. Djurisic, Y.H. Leung, W.C.H. Choy, K.W. Cheah and W.K. Chan, *Appl. Phys. Lett.,* 2004, 84, No. 14.
2. N.M. Bahadur, T. Furusawa and M. Sato, *Materials Research Bulletin,* 2010, 45, 1383.
3. S. Das, S. Chakrabarti and S. Chaudhuri, *J. Phys. D: Appl. Phys.* 2005, 38, 4021.
4. Z. Gu, F. Liu, X. Li and Z.W. Pan, *Cryst. Eng. Comm.,* 2013, 2904.
5. K. Morimoto, in: S. Shionoya, W.M. Ren, (Eds.), Phosphor Handbook, *CRC Press,* Cleveland, 1999, p. 561.
6. E.G. Bylander, *J. Appl. Phys.,* 1978, 49, 3.
7. Y.G. Wang, S.P. Lau, X.H. Zhang, H.W. Lee, S.F. Yu, B.K. Tay and H.H. Hng, *Chemical Physics Letters,* 2003, 375, 113.
8. K. Vanheusden, C.H. Seager, W.L. Warren, D.R. Tallant and J.A. Voigt, *Appl. Phys. Lett.,* 1996, 68, 403.
9. Y.Q. Li, S.Y. Fu and Y.W. Mai, *Polymer,* 2006, 47, 2127.
10. J.M. Lin, C.L. Cheng, H.Y. Lin and Y.F. Chen, *Optics Letters,* 2006, 31, No. 21, 3173.
11. M. Zhong, Y. Li, I. Yamada, and J.J. Delaunay, *Nanoscale*, 2012, 4, 1509.
12. Hou, F. Meng and J. Sun, *Nanoscale Research Letters*, 2013, 8, 144.
13. R.K. Verma, A.K. Singh, D.K. Rai and S.B. Rai, *Materials Chemistry and Physics* 2012, 135, 298.
14. R.K. Verma, K. Kumar and S.B. Rai, *Journal of Luminescence,* 2011, 131, 988.
15. W. Zhang, S. Xiao, X. Yang and X. Jin, *Funct. Mater. Lett.* 2013, 06, 1350002.
16. R.V. Yadav, R.K. Verma, G. Kaur and S.B. Rai, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* 2013, 103, 216.
17. Y. Zhuang, J. Uedaa and S. Tanabeb, *J. Mater. Chem. C*, 2013, 1, 7849
18. H. Li, S. Yin and T. Sato, *Nanoscale Res. Lett.,* 2011, 6, 5.
19. H. Li, S. Yin, Y. Wang and T. Sato, *Journal of Catalysis,* 2012, 286, 273.
20. H. Li, S. Yin, Y. Wang and T. Sato, *Journal of Molecular Catalysis A: Chemical*, 2012, 363–364, 129.
21. H. Sun, L. Pan, X. Piao and Z. Sun, *J. Mater. Chem. A,* 2013, 1, 6388.
22. V.T. Gritsyna, Y.G. Kazarinov, V.A. Kobyakova and K.E. Sickafus, *Radiat. Effects Defects in Solids,* 2002, 157, 659.
23. K.D. Budd, *US Patent,* 1995, 5418062.
24. P. Escribano, M. Marchal, M.L. Sanjuan, P. Alonso-Gutierrez, B. Julian and E. Cordoncillo, *J. Solid State Chem.* 2005, 178, 1978.
25. V.P. Singh, S.B. Rai, H. Mishra and C. Rath, *Dalton Transactions* 2014, 43, 5309.
26. Ph.D. thesis by Taneli Laamanen, "Defects in Persistent Luminescence Materials" Presented to the Laboratory of Materials Chemistry and Chemical Analysis,Department of Chemistry University of Turku, FINLAND and Graduate School of Materials Research, Turku, FINLAND,ISBN 978-951-29-4706-5 (PRINT), ISBN 978-951-29-4707-2 (PDF), ISSN 0082-7002.
27. J. Liu, Y. Zhao, Y. J. Jiang, C.M. Lee, Y.L. Liu and G.G. Siu, *Appl. Phys. Lett.* 2010, 97, 231907.
28. R.C. Roop, The Point Defect. Studies in Inorganic Chemistry, 21; Luminescence and the solid state, 2nd Edition, *Elsevier,* 138 Mountain Avenue, 2004, pp.39-112.
29. Ph.D. thesis C by Beauger, Universite de Nice, 1999, Nice, France.
30. Q. Wu, Z. Liu and H. Jiao, *Physica B*, 2009, 404, 2499.
31. J. Dong-dong, W. Bo-qun and Z. Jing, *Chin. Phys. Soc.,* 2000, 9, 0069.
32. E. Shafia, M. Bodaghi and M. Tahriri, *Current Applied Physics*, 10, 2010, 596.
33. E.A. Raja, B. Dhabekar, S. Menon, S.P. More, T.K. GunduRao and R.K. Kher, *Indian J. Pure & Appl. Phys.*2009, 47, 420.
34. A.J.J. Bos, *Radiation Measurements* 2007, 41, S45–S56.