Effect of NaF flux on microstructure and thermoluminescence properties of Sm^{3+} doped CdSiO_3 nanophosphor

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ABSTRACT

This work reports the preparation of $\text{CdSiO}_3:\text{Sm}^{3+}$ (1–7 mol%) nanophosphors by a low temperature solution combustion method. For the first time the effect of NaF flux on the crystallization behavior, morphology, and thermoluminescence property of 5 mol% Sm^{3+} doped CdSiO_3 has been investigated. The nanopowders are well characterized by powder X-ray diffraction (PXRD), Fourier Transform Infra-Red (FT-IR), and scanning electron microscopy (SEM). PXRD results indicate that the powder calcined at 800 °C for 2 h has monoclinic phase. SEM results show that the powder is highly porous and the pore size and shape can be modified by the addition of NaF flux. Addition of NaF could lead to formation of particle type morphology and the increase in wt% of NaF changes crystallinity and phase. The thermoluminescence glow curves for 2–6 wt% NaF in $\text{CdSiO}_3:\text{Sm}^{3+}$ show a single, well resolved glow peak at 126, 130 and 150 °C, respectively. But for the sample prepared with 8 wt% of NaF flux shows two glow peaks at 148 and 220 °C. With the addition of NaF flux, TL intensity can be effectively enhanced.

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1. Introduction

Over the last few years, rare earth ions doped inorganic nanomaterials have been particularly attractive because of their unique luminescent properties [1,2]. It has been proved by many researchers that the luminescent properties of nanoscale materials are completely different from their bulk materials [3,4]. Thermoluminescence (TL) is a well known phenomenon used for the dosimetry of ionizing radiations. The energy absorbed by a TL material during irradiation is released as visible and UV light on subsequent heating of the sample. Many research groups have showed that the luminescent nanomaterials have potential applications in dosimetry of ionizing radiations for the measurements of high doses using TL technique, where the conventional microcrystalline phosphors saturate [5–7]. The nanomaterials have also showed the linearity in their TL responses in wide ranges of exposures [8,9]. The increase in the number of surface states as well as recombination charge carriers in nanomaterials may be

the reason for their unique TL characteristics. Even though considerable amount of work has been done on TL of bulk materials, the TL properties of their nanocrystalline counterparts have often not been reported. Therefore, the effort towards improving the TL characteristics are still being continued for the same materials, either by synthesizing them at nano level by different methods or by varying the dopant impurities [10,11] or developing other new TL sensitive nanomaterials [12,13].

Silicate materials are useful in many applications of technological importance. Many metal silicates have been reported, and are being used in many areas: $\text{Mg}_2\text{SiO}_4:\text{Tb}$ in thermoluminescence dosimetry of the ionizing radiations [14], $\text{Gd}_2\text{SiO}_5:\text{Ce}$ in scintillation phosphors because of their relatively high-density, good light output, and fast decay time [15]. $\text{Zn}_2\text{SiO}_4:\text{Mn}$ was also used as the green component in the first tri-color lamp [16]. CdSiO_3 shows excellent phosphorescence property when doped with some transition metal and rare earth ions [17–19]. It is accepted that Sm^{3+} ions in CdSiO_3 host materials [18], can exhibit the dominant pink emission peaks under near-UV excitation. Compared with other rare earth ions, the color-rendering index on the proper host materials such as $\text{Ca}_3\text{Y}(\text{VO}_4)_3$, CaF_2 , etc. doped with Sm^{3+} ions is higher [20,21]. Further, the morphology of

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phosphors (shape and size of the powder particles) is one of the key parameters of their industrial application [22,23]. In order to obtain optimum emission characteristics for device applications, the characteristic features of host as well as concentration dependent studies of Sm^{3+} are essential.

In the present research work, we report Sm^{3+} doped CdSiO_3 nanophosphors prepared by combustion route using oxalyldihydrazide as a fuel followed by heat treatment at 800°C for 2 h. In general, the preparation of metal silicates is a difficult process, because most of the silicates melt at very high temperature and appear in glassy and crystalline form. Conventionally, solid state diffusion methods have been used for the synthesis of silicates. Another technique, sol–gel synthesis, has also been used which enables the preparation of fine, homogenous powders [24]. Solution combustion synthesis is a successful, low-cost, time saving method and has been effectively used for the preparation of a variety of industrially important materials [25]. The method is based on the vigorous, spontaneous exothermic reaction between fuel and metal nitrate. This method has been adopted to prepare many silicate materials, such as, CaSiO_3 , Zn_2SiO_4 , which were used for various applications in phosphor industry, electrical insulators, pigments, glass ceramics, molecular sieves, zeolites, hybrid optics, bio ceramics etc. Wollastonite (CaSiO_3) ceramics are generally used as a biomaterial in medical industry for artificial bone and dental root because they show good bioactivity and biocompatibility [26,27]. Therefore, we have also followed solution combustion method and it has been discussed in detail in our previous report [28]. In the process of phosphor production, many flux materials were used to improve the brightness of spherical shape phosphor particles of micrometer size [29]. It plays an important role in controlling size, distribution and shape of phosphor particles [30]. Duault et al. have studied the effect of Li_3PO_4 , Li_2CO_3 , Na_2CO_3 , K_2CO_3 flux on the morphology of $\text{LaPO}_4\text{:Ce,Tb}$ [23]. To the best of our knowledge, the effect of NaF flux addition on the crystallinity, microstructure and thermoluminescence properties of Sm^{3+} doped CdSiO_3 phosphor has not been reported so far. The thermoluminescent curves were analyzed by the glow peak shape method and the trap parameters such as activation energy (E), order of kinetics (b), and frequency factor (s) are estimated.

2. Experimental

2.1. Materials and synthesis

The chemicals, cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99.9%), samarium oxide (Sm_2O_3 , 99.9%), fumed silica (SiO_2 , 99.9%, surface area $200\text{ m}^2/\text{g}$), and sodium fluoride (NaF, 99.9%) were used as analytical reagents. Oxalyldihydrazide (ODH: $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$) is used as a fuel which was prepared in our laboratory; the detailed preparation is given elsewhere [25]. $\text{CdSiO}_3\text{:Sm}^{3+}$ (1–7 mol%) nanophosphors was synthesized by combustion method followed by heat treatment at 800°C for 2 h. Stoichiometric amount of Sm_2O_3 was taken in a 250 cm^3 glass beaker and dissolved in a solution of dilute HNO_3 (A.R.), and evaporated to dryness. The calculated amounts of cadmium nitrate, fumed silica and oxalyldihydrazide were added and dissolved in 50 cm^3 de-ionized water. The mixture was stirred until a uniform and transparent solution was obtained, and then gradually heated up in a pre-heated furnace at 500°C , until it became sticky with the vaporizing of water. Spontaneous ignition occurred, with the liberation of large volumes of gasses. The combustion was completed after a few seconds, and a foamy pale brown powder was obtained. Similar procedure was followed with different weights (2, 4, 6 and 8 wt%) of NaF flux for the preparation of only 5 mol% Sm^{3+} doped

CdSiO_3 . The as-prepared $\text{CdSiO}_3\text{:Sm}^{3+}$ samples were annealed at 800°C for 2 h. The molar ratio of fuel to oxidizer was maintained at 1 for all mixtures. No residual ODH and NO_3^- was detected by IR spectroscopy after this post heat-treatment.

2.2. Characterization

The Powder X-ray diffraction (PXRD) measurements were carried out on a Philips X'pert PRO PAnalytical X-ray diffractometer with graphite monochromatized $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.5418\text{ \AA}$) operated at 40 kV and 30 mA. The XRD patterns were collected in the range of $10^\circ \leq 2\theta \leq 70^\circ$. The morphologies of the phosphor powders were monitored by JEOL-JSM-6490 LV scanning electron microscope (SEM). The Fourier transform infrared (FT-IR) spectra of the samples were measured using Shimadzu FT-IR infra-red spectrophotometer and the KBr pellet technique in the range $4000\text{--}400\text{ cm}^{-1}$. UV–vis absorption of the samples was recorded on SL 159 ELICO UV–vis Spectrophotometer. The thermoluminescence (TL) measurements were measured on a model Nucleonix TL Reader, with a heating rate of 5°C/s in the temperature range of $40\text{--}400^\circ\text{C}$. Before measurement, 100 mg powder samples were pressed in to pellets (6 mm diameter and 1 mm thickness), and then exposed to a standard UV lamp peak at 254 nm with a power of 15 W. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Powder X-ray diffraction analysis (PXRD)

Fig. 1 shows the powder X-ray diffraction patterns of the $\text{CdSiO}_3\text{:Sm}^{3+}$ (1–7 mol%) phosphors calcined at 800°C for 2 h. All the diffraction peaks match very well with the standard values from the Joint Committee on Powder Diffraction Standards (JCPDS) data card No. 35–0810, which can be assigned to monoclinic structure. Since the ionic radii of Sm^{3+} ($r_{\text{Sm}^{3+}} = 0.096\text{ nm}$) is almost similar to that of Cd^{2+} ($r_{\text{Cd}^{2+}} = 0.097\text{ nm}$), it is expected that the Sm^{3+} ions can be easily occupied by the Cd^{2+} sites in CdSiO_3 host. Compared to solid-state reaction (1050°C) and sol–gel approach (900°C), it is obvious that the crystallinity temperature of the samples prepared by this method is significantly lower (800°C).

Fig. 1. Powder XRD patterns of solution combustion derived $\text{Cd}_{1-x}\text{Sm}_x\text{SiO}_3$ samples (a) $x=0.00$ (b) $x=0.01$ (c) $x=0.03$ (d) $x=0.05$ and (e) $x=0.07$ calcined at $800^\circ\text{C}/2\text{ h}$.

Fig. 2. Powder XRD patterns of NaF flux aided solution combustion derived $\text{CdSiO}_3:\text{Sm}^{3+}$ (only 5 mol%) samples calcined at $800^\circ\text{C}/2\text{ h}$ (a) no flux (b) 2 wt% NaF (c) 4 wt% NaF and (d) 6 wt% NaF (The vertical line pattern corresponds to standard PXRD pattern of monoclinic CdSiO_3).

In order to identify the effect of flux on the phase formation of the sample, the PXRD analysis of the $\text{CdSiO}_3:\text{Sm}^{3+}$ sample prepared with different wt% of NaF and the observed results are shown in Fig. 2. It is known that a flux in the process of preparation of phosphor contributes not only to the reaction of ceramic powders but also to the formation of a luminescent center in phosphors [31]. There is no effect on phase of $\text{CdSiO}_3:\text{Sm}^{3+}$ (5 mol%) when the NaF flux used is just 2.0 wt%. It is observed that the diffraction peak intensities slightly increase with the dosage of NaF from 0 wt% to 2.0 wt%, which illustrates that the flux can make the crystallinity of phosphor better.

We have also checked the effect of increase in the wt% of NaF on phase and crystallinity. It can be seen in the PXRD patterns obtained for 4.0 wt% and 6.0 wt% NaF (Fig. 2) that there is a decrease in the crystallinity and appearance of impurity peaks. The decrease in the crystallinity is due to appearance of highly crystalline impurity phases. The highly dominating impurity peaks at $2\theta=23.62, 32.21, 33.27$, and 49.50 can be ascribed to Cd_2SiO_4 (JCPDS No: 85–0595) and at $2\theta=34.84$ and 39.1 are due to appearance of small amounts Na_4SiO_4 (JCPDS No: 78–1432) phases along with CdSiO_3 peaks, which are very less intense. These results are also consistent with the FT-IR analysis (which will be dealt with in subsequent sections) in which the sharpness of peaks (639 and 680 cm^{-1}) corresponding to Si–O stretching frequency is decreased. This fact implies that addition of 2.0 wt% of NaF flux is sufficient to obtain better crystallization and particle morphology, further increase in its wt% leads to impurity phases.

3.2. Morphological analysis

The typical microstructure for $\text{CdSiO}_3:\text{Sm}^{3+}$ (5 mol%) nanophosphor particles prepared without and with NaF flux (2 wt% and 4 wt%) is shown in Fig. 3. The scanning electron micrograph shows that, the morphology of $\text{CdSiO}_3:\text{Sm}^{3+}$ powders prepared by combustion method without NaF flux is slightly different from those prepared with NaF flux. In general, the flux is used to act as a medium to incorporate the activators, reduce the firing temperature, and improve the crystallinity and morphology of the respective phosphors [32]. The pores and voids seen in Fig. 3A and B, are a result of large quantities of gases escaping during combustion reaction, which is a common feature of the materials produced by combustion synthesis. The effect of NaF flux on both morphology and particle size can be observed in the Fig. 3C and D. It is observed that the NaF flux plays a very important role in

changing the microstructure of the samples. The introduction of NaF can lead to the formation of a liquid phase at a relatively low temperature. The liquid phase can considerably promote the formation of the phosphor with different morphologies. Porous nature of the microstructure changes to particles-type morphology (Fig. 3C). The particles combine with each other to form a fused particle with increase in the quantity of NaF flux from 2 wt% to 4 wt% (Fig. 3D). The increase in wt% of NaF creates larger liquid phase, which suppresses the liberation of large quantity of gases during combustion. This causes the aggregation of particles in-to a larger one. Other parameters such as the melting and/or boiling points of this flux may also affect the formation and growth process of the particles [33]. These particles with the addition of NaF prove to be highly crystalline, which is highly suitable to fabricate solid-lighting devices.

3.3. FT-IR spectral analysis

The FT-IR spectra of $\text{CdSiO}_3:\text{Sm}^{3+}$ (1–7 mol%) samples calcined at 800°C for 2 h are shown in Fig. 4. It is observed that the broad band from 840 – 1240 cm^{-1} is due to asymmetric stretching vibration of Si–O–Si bond and stretching vibrations of terminal Si–O bonds. The peaks at 434 – 564 cm^{-1} , 639 cm^{-1} and 680 cm^{-1} are the characteristic stretching vibrations of Si–O–Si bridges [26]. The sharp peak corresponding to 680 cm^{-1} can be ascribed to Si–O bond, which exists in the form of SiO_3^{2-} . It can be noticed that there is no change in the position or intensity of absorption bands for the Sm^{3+} (1–7 mol%) doped CdSiO_3 (Fig. 4), which confirms that the dopant has not altered its phase and crystallinity. These results are consistent with those of PXRD results (Fig. 1). The small peak at 1655 cm^{-1} corresponding to C=O bond, may be due to adsorbed CO_2 in the sample during FT-IR measurements.

In order to understand the effect of NaF flux on the crystallinity and phase of the $\text{CdSiO}_3:\text{Sm}^{3+}$ (5 mol%) sample, FT-IR analysis was performed and is shown in Fig. 5. The intensity of the absorption band corresponding to 680 cm^{-1} decreases with increase in the amount of NaF flux and finally disappears for 6 wt%, which can be seen in the circled area of Fig. 5. It is also noted that the intensity of a strong absorption band at 639 cm^{-1} also decreases with increase in the NaF flux wt%. This may be due to formation of impurity phases in which the Si–O bond exists in SiO_4^{4-} . The above results are well supported by PXRD spectra (Fig. 2), which clearly tells the effect of flux on crystallinity and phase of the sample.

3.4. UV–vis absorption

Fig. 6 shows the UV–vis absorption spectra of Sm^{3+} doped (1–7 mol%) CdSiO_3 phosphor calcined at 800°C for 2 h. The absorption spectrum reveals a peak around 230 – 270 nm which corresponds to oxygen to silicon (O–Si) ligand-to-metal charge-transfer (LMCT) in the SiO_3^{2-} group [34]. The most commonly used method to estimate the energy gap (E_g) is the Tauc relation [35] i.e., $\alpha(h\nu)=K(h\nu-E_g)^{1/n}$, where ' $h\nu$ ' is the photon energy, ' α ' is the optical absorption coefficient, ' K ' is constant and ' n ' is independent of the optical transition with an assigned value of 2 and 1/2 for different allowed and indirect transitions respectively. The values of the optical band gaps of the un-doped and Sm^{3+} doped CdSiO_3 are obtained by plotting $(\alpha E)^2$ versus ' E ' in the high-absorption range followed by extrapolating the linear region of the plots to $(\alpha E)^2=0$ (Fig. 7). The analysis of the present data indicates that the plots provide the linear relations, which can be fitted with the above equation with $n=2$ for both the un-doped and Sm^{3+} doped samples. This indicates that the allowed direct transitions are responsible for the inter-band transitions in the

Fig. 3. SEM images of doped $\text{CdSiO}_3: \text{Sm}^{3+}$ (5 mol%) phosphors prepared with (A and B) no flux (C) 2.0 wt% NaF flux and (D) 4.0 wt% NaF flux.

Fig. 4. FT-IR spectra of $\text{Cd}_{1-x}\text{Sm}_x\text{SiO}_3$ samples calcined at $800^\circ\text{C}/2\text{ h}$ (a) $x=0.00$ (b) $x=0.01$ (c) $x=0.03$ (d) $x=0.05$ and (e) $x=0.07$.

un-doped and the doped samples. The optical energy band gap for the un-doped sample is found to be 5.33 eV and for the Sm^{3+} doped (1–7 mol%) phosphors it varies between 5.45 and 5.62 eV (Fig. 7). It is noticed that the optical band gap is found to be lower in the un-doped sample when compared to the Sm^{3+} doped

Fig. 5. FT-IR spectra of 5 mol% Sm^{3+} doped CdSiO_3 samples calcined at $800^\circ\text{C}/2\text{ h}$ (a) No flux (b) 2 wt% NaF (c) 4 wt% NaF and (d) 6 wt% NaF.

CdSiO_3 . To understand the effect of flux on the band gap, the UV–vis absorption spectra for Sm^{3+} (5 mol%) doped CdSiO_3 prepared with 2, 4, and 6 wt% NaF flux were measured and are shown in

Fig. 6. UV-vis absorption spectra of $\text{Cd}_{1-x}\text{Sm}_x\text{SiO}_3$ samples calcined at $800^\circ\text{C}/2\text{ h}$ (a) $x=0.00$ (b) $x=0.01$ (c) $x=0.03$ (d) $x=0.05$ and (e) $x=0.07$.

Fig. 7. Direct optical energy band gap of $\text{Cd}_{1-x}\text{Sm}_x\text{SiO}_3$ (a) $x=0.00$, (b) $x=0.01$, (c) $x=0.03$, (d) $x=0.05$, and (e) $x=0.07$.

Fig. 8. It is noticed that the intensity of the absorption peak has increased slightly and has shifted to a higher wavelength region for 2 wt% NaF flux, as compared to that of the sample prepared with no flux. With further increase in the wt% of NaF flux from 4 to 6, the peak is shifted to a lower wavelength region. This may be due to change in the phase and crystallinity of the samples. Fig. 9 shows the effect of different wt% of NaF on the direct band gap for 5 mol% Sm^{3+} doped CdSiO_3 sample. The direct band gap values for 2 wt% NaF flux used sample is slightly decreased due to change in the morphology. For 4 and 6 wt% the values are unusually decreased as compared to that of 2 wt%, which may be due to change in crystallinity and also due to mixed phase of the samples.

3.5. Thermoluminescence studies

The thermoluminescence (TL) glow curves were recorded for each sample having different Sm^{3+} concentrations (1–7 mol %) in CdSiO_3 host (without adding flux) irradiated by UV radiations for 5 min. It is observed that well resolved glow peak at $\sim 173^\circ\text{C}$ was recorded at a heating rate of 5°C s^{-1} . There is no appreciable shift in ' T_m ' with Sm^{3+} concentration, but there is slight decrease in the

Fig. 8. UV-vis absorption spectra of 5 mol% Sm^{3+} doped CdSiO_3 samples calcined at $800^\circ\text{C}/2\text{ h}$ (a) No flux (b) 2 wt% NaF (c) 4 wt% NaF and (d) 6 wt% NaF.

Fig. 9. Direct optical energy band gap of 5 mol% Sm^{3+} doped CdSiO_3 samples calcined at $800^\circ\text{C}/2\text{ h}$ (a) No flux (b) 2 wt% NaF (c) 4 wt% NaF and (d) 6 wt% NaF.

TL intensity on either sides of Sm^{3+} concentration. Fig. 10 shows the TL intensity variation with Sm^{3+} concentration and is found to be the highest for 5 mol% of Sm^{3+} in 5 min UV irradiation. In order to study the effect of UV dose on the TL intensity of 5 mol% of Sm^{3+} doped CdSiO_3 , we have recorded the TL spectra for the samples irradiated with UV for a prolonged time (3–20 min), and they are shown in Fig. 11. A well resolved glow peak at $\sim 173^\circ\text{C}$ was recorded in all the UV irradiated samples. It is observed that, initially the glow curves are well defined for low UV irradiated samples (up to 10 min). However, with further increase in UV irradiation time ($> 10\text{ min}$) the glow curves are flat indicating the existence of additional TL glow peaks.

The influence of different heating rates between $5\text{--}15^\circ\text{C s}^{-1}$ on TL response has been investigated on $\text{CdSiO}_3:\text{Sm}^{3+}$ (5 mol%: without flux) sample, irradiated with UV for 5 min and the observed results are shown in Fig. 12. It is found that with

Fig. 10. Variation of TL intensity with respect to Sm³⁺ concentration in CdSiO₃ samples.

Fig. 11. TL glow curves of CdSiO₃: Sm³⁺ (5 mol%) without NaF flux for different UV dose.

Fig. 12. TL glow curves of CdSiO₃: Sm³⁺ (5 mol%) without NaF flux for different heating rate for 10 min UV dose.

increase in heating rates the TL peak intensity and area under the peak are almost constant. However, peak temperature shifts towards the higher temperature side. The glow peak (T_m) is shifted from 173 °C to 189 °C with increase of heating rate from 5–15 °C s⁻¹. The shifting of peak with increase in heating rate is a phenomenon frequently observed in the practice of TL; it is attributed to thermal quenching [36].

The results presented in the current report clearly enlighten the influence of NaF flux addition on thermoluminescence property of CdSiO₃: Sm³⁺ phosphor. Effect of NaF flux (2–8 wt%) on TL intensity in CdSiO₃: Sm³⁺ (5 mol%) samples were studied for ~10 min UV irradiation and is shown in Fig. 13. A single well defined glow peak at 134 °C was recorded in 2 wt% NaF added CdSiO₃: Sm³⁺ (5 mol%). With increase of flux to 4 wt% the main glow peak was shifted to 137 °C. However, with further increase of flux (4–8 wt%), more shifting along with an extra shouldered peak at 216 °C was observed. The two glow peaks appearing in 8 wt% NaF doped CdSiO₃: Sm³⁺ indicate that there are possibly two kinds of trapping sites generated due to the formation of impurity phases. The shallow trapping center leads to the 148 °C glow peak at lower temperatures and 216 °C peak corresponds to deeper trapping centers at higher temperatures.

Figs. 14–17 show the TL glow curves of 2, 4, 6 and 8 wt% NaF flux added CdSiO₃: Sm³⁺ (5 mol%) phosphor, respectively under different UV exposures (3–30 min). A well resolved glow peak at ~126 °C was observed in all the UV irradiated samples with small shifting towards higher temperature side. However, a single well defined glow peak at 126 °C in 2 wt% NaF flux and 130 °C for 4 wt% and 150 °C for 6 wt% NaF flux aided samples is observed. In 8 wt% NaF aided sample, two glow peaks, one at ~148 °C and another at 220 °C (broad), was recorded in all the UV-irradiated samples. The maximum TL intensity was observed in 2 wt% NaF for 5 min UV exposure which then decreases. However in the case of 4 and 6 wt% NaF, maximum TL intensity was observed at 15 min and 5 min, respectively. Further in heavily added NaF flux TL intensity was found to be maximum at 10 min UV-dose. The variation of TL glow peak intensity as a function of UV exposure was studied and is shown in the insets of Figs. 14–17. The increase in TL intensity might be due to the increase in number of traps as a result of irradiation with different UV doses. The TL intensity also depends on the cross-section of the tracks and as well as the length of tracks in the matrix. These tracks represent the luminescence sites where the trapped electron-hole undergoes radiative or/and non-radiative transition upon excitation

Fig. 13. TL glow curves of CdSiO₃: Sm³⁺ (5 mol%) with different wt% of NaF flux for 5 min UV irradiation.

Fig. 14. TL glow curves of 2 wt% NaF in CdSiO₃: Sm³⁺ (5 mol%) with TL intensity for different UV irradiation (3–30 min). (Inset shows variation of TL intensity vs. UV dose).

Fig. 16. TL glow curves of 6 wt% NaF in CdSiO₃: Sm³⁺ (5 mol%) with TL intensity for different UV irradiation (3–25 min). (Inset shows variation of TL intensity vs. UV dose).

Fig. 15. TL glow curves of 4 wt% NaF in CdSiO₃: Sm³⁺ (5 mol%) with TL intensity for different UV irradiation (3–25 min). (Inset shows variation of TL intensity vs. UV dose).

Fig. 17. TL glow curves of 8 wt% NaF in CdSiO₃: Sm³⁺ (5 mol%) with TL intensity for different UV irradiation (3–25 min). (Inset shows variation of TL intensity vs. UV dose).

with a suitable source. In nanophosphor, since the surface to volume ratio increases significantly, it helps in the formation of different types of traps upon UV irradiation. The electrons and holes are expected to be trapped at tracks of different depth. Therefore, the trapped carriers at the surface states are released by heating the sample and they recombine with each other and give out luminescence which is known as thermoluminescence. In nanomaterials the length of such a track may be a few tens of nanometers, so the number of trap centers or luminescence centers will be less for lower doses. Similar observation was reported in various nanophosphors by different authors [37,38]. If the deep traps are present or formed at heavy dose irradiation inside the hosts of the nanomaterials, they may not be able to show TL emissions due to re-trapping within the deep trap. The emitted photons from the deep traps might get self-absorbed within the deep trap due to the presence of some meta stable energy levels within the track and photons may not reach to the TL detector. Therefore the saturation effects or decrease in the TL intensity is expected at higher UV doses.

In the present study it is observed that, if we increase the dose, more overlapped tracks are expected in the matrix, as a result of which saturation/decrease of TL intensity occurs. Thus on increasing the dose, a large number of surface defects are produced in the nanoparticles which ultimately keep on increasing with the dose till saturation is achieved [39]. The luminescent property of the phosphors arises from the complex interaction among host structure, activators, and defects. The charge unbalance and lattice distort could induce point defects in the structure, which would increase the non-radiative process that resulted in the reduction of luminescence intensity. As observed in Fig. 13, with the variation in the TL intensity of 5 mol% Sm³⁺ doped CdSiO₃ prepared with different wt% of NaF fluxes one can predict that it might be due to the formation of various types of traps and lattice defects. The ionic radius of Sm³⁺ ion (0.096 nm) is much closer to Cd²⁺ ions (0.097 nm) than to that of Si⁴⁺ ions (0.041 nm). In CdSiO₃:Sm³⁺ phosphors, the trivalent Sm³⁺ ions are substituted for Cd²⁺ ions, which induced the charge unbalance. The substitution of Sm³⁺ may lead to charge imbalance (2Sm³⁺–2Cd²⁺ → two holes) or

Table 1
Estimated trap parameters for addition of NaF flux (2–8 wt%) in CdSiO₃: Sm³⁺ (5 mol%).

NaF Flux (wt%)	Peak	T_m (°C)	Order of kinetics, b (μ_g)	Activation energy (eV)				Frequency factor, s (s^{-1})
				E_τ	E_δ	E_ω	E_{ave}	
Without flux	1	104	2(0.50)	0.69	0.73	0.71	0.71	6E+10
	2	142	2(0.51)	0.87	0.89	0.88	0.88	9E+11
	3	167	2(0.49)	0.81	0.86	0.84	0.83	5E+10
	4	196	2(0.48)	0.49	0.58	0.54	0.54	4E+06
2	1	091	2(0.50)	1.05	1.04	1.05	1.05	9E+15
	2	129	2(0.49)	0.82	0.86	0.84	0.84	6E+11
	3	143	2(0.50)	0.56	0.62	0.59	0.59	2E+08
	4	184	2(0.50)	0.41	0.50	0.45	0.45	6E+05
4	1	090	2(0.48)	1.09	1.09	1.09	1.09	4E+16
	2	127	2(0.49)	0.85	0.88	0.87	0.87	2E+12
	3	137	2(0.48)	0.59	0.66	0.63	0.63	6E+08
	4	190	2(0.48)	0.26	0.37	0.31	0.31	1E+04
6	1	098	2(0.50)	0.61	0.65	0.64	0.63	7E+09
	2	121	2(0.52)	1.56	1.39	1.47	1.48	3E+20
	3	140	2(0.50)	0.72	0.76	0.74	0.74	1E+10
	4	196	2(0.49)	0.43	0.52	0.47	0.47	8E+05
8	1	121	2(0.51)	0.51	0.56	0.54	0.54	8E+07
	2	137	2(0.51)	0.85	0.87	0.86	0.86	6E+11
	3	172	2(0.51)	0.82	0.86	0.84	0.84	5E+10
	4	210	2(0.50)	1.36	1.36	1.37	1.36	3E+15

point defect ($2\text{Sm}^{3+} - 3\text{Cd}^{2+} \rightarrow$ one vacant site of Cd^{2+}), which are playing a major role in luminescence process. The TL intensity and its position of UV irradiated CdSiO₃:Sm³⁺ sample are attributed to the defects corresponding to uneven dopant substitution. However, the TL glow curves of CdSiO₃:Sm³⁺ (5 mol%) sample prepared with different wt% of NaF flux (Fig. 13) appear to be same barring the variation in their intensities. The enhancement in the TL intensity might be due to the incorporation of Na⁺ and F⁻ ions which equalize the charge unbalance generated by Sm³⁺ substitution for Cd²⁺, and thus reduce the lattice distort and enhance the luminescent intensity. Further increase in the NaF content (> 2 wt%) could lead to decrease in the TL intensity, which might be due to the change in crystal structure and lattice parameters (Fig. 2). In contrast, the larger lattice distortion might be induced when 8 wt% of NaF was introduced to the host lattice, which would decrease the luminescent intensity of the phosphors. Therefore, 2 wt% NaF ions might be the optimal flux and charge compensator for the CdSiO₃:Sm³⁺ (5 mol%) phosphors. The variation in the TL intensity with the UV dose for the 2–8 wt% NaF flux aided 5 mol% Sm³⁺ doped CdSiO₃ (Figs. 14–17) is predicted to be due to competition/overlapping of electron–hole transition upon heating. This unevenness in TL response is due to various types of traps/defects formed due to the reduction in the particle size, non-equivalent ion substitution, different wt% of NaF content (charge compensator), destruction of actual crystal structure, and mixed/impurity phases.

4. Calculation of kinetic parameters

The glow curve is related to the trap levels that lie at different depths in the band gap between the conduction and the valence bands of CdSiO₃. These trap levels are characterized by different kinetic parameters. Kinetic parameters of trap levels are reported by various methods. Many of them are based on the observation of thermally stimulated relaxation spectra, i.e. TL spectra. We employed the Peak Shape (PS) method, which is generally called as Chen's [40] method, to determine the kinetic parameters of the glow peak of the NaF flux aided CdSiO₃:Sm³⁺ (5 mol%) sample. The peak shape method is mainly used to calculate the order of kinetics. Order of kinetics can be evaluated from the symmetry

factor (μ_g) of the glow peak and it is calculated using [41] Eq. (1).

$$\mu_g = (T_2 - T_m) / (T_2 - T_1) \quad (1)$$

where, T_1 , T_m and T_2 represent the temperature of half-intensity at low-temperature side, peak temperature and temperature of half-intensity at high-temperature side of TL peak, respectively. It is found that the geometrical factor (μ_g) ~ equal to 0.31, seems to be unrealistic because the values lie in between 0.42 and 0.52. The unexpected value of ' μ_g ' led us to speculate that this peak may be comprised of more than one peak having a close trap distribution, which is superimposed giving rise to a broad TL glow curve. This encouraged us to make use of the curve fitting technique to analyze the glow curve. The TL glow curve is first deconvoluted based on Gaussian function and then we studied the individual deconvoluted peak. Activation energy (E) was calculated by using the Chen's equations, which gives the trap depth in terms of τ , δ , ω . A general formula for ' E ' was given by Eq. (2).

$$E = C_\gamma (kT_m^2 / \gamma) - b_\gamma (2kT_m) \quad (2)$$

where γ is τ , δ , or ω . The values of τ , δ , and ω are respectively determined by low-temperature half-width ($\tau = T_m - T_1$), high-temperature half-width ($\delta = T_2 - T_m$) and full width ($\omega = T_2 - T_1$), and k is the Boltzmann constant. Therefore, according to Eq. (2), different values of ' E ' remarked as E_τ , E_δ and E_ω can be obtained when γ is τ , δ , or ω , respectively. For example, if γ stands for τ , then $C_\tau = 1.51 + 3.0(\mu_g - 0.42)$, $b_\tau = 1.58 + 4.2(\mu_g - 0.42)$, $E_\tau = 1.51(kT_m^2/\tau) - 1.58(2kT_m)$; if γ stands for δ , then $C_\delta = 0.976 + 7.3(\mu_g - 0.42)$, $b_\delta = 0$, $E_\delta = 0.976(kT_m^2/\delta) - 0(2kT_m)$; if γ stands for ω , then $C_\omega = 2.52 + 10.2(\mu_g - 0.42)$, $b_\omega = 1.0$, $E_\omega = 2.52(kT_m^2/\omega) - 1.0(2kT_m)$. The value of frequency factor (s) can be obtained with the following equation [15]

$$\frac{\beta E}{KT_m^2} = s \exp\left(\frac{-E}{KT_m}\right) [1 + (b-1)\Delta_m] \quad (3)$$

where β is the linear heating rate, b is the order of kinetics and $\Delta_m = \frac{2kT_m}{E}$.

Several authors have even reported similar studies for evaluation of kinetic parameters using Chen's peak shape method applied directly to the peaks which were deconvoluted using Origin 6.1 software without using any Glow curve de-convolution (GCD) functions [42]. The estimated peak parameters for CdSiO₃:Sm³⁺ (5 mol%) prepared without and with 2–8 wt% of NaF flux estimated are given in Table 1. The values of ' E ' were found to be in the range of 0.31–1.48 eV. This wide range might be due to the existence of both shallow traps and deep traps which have been observed in several nanomaterials [43]. The mean activation energy and the frequency factors for the 2 wt% NaF flux aided sample are found to be 1.05 eV, 9×10^{15} Hz and 0.45 eV, 6×10^{05} Hz pertaining to the glow curves with peaks at 91 °C and 184 °C respectively. The lower activation energy (0.45 eV) corresponding to higher temperature peak (184 °C) and higher activation energy (1.05 eV) corresponding to lower temperature peak (91 °C) is attributed to the complex nature of peaks. Sunta et al. discussed the limitation of peak shape method for the calculation of ' E ' of TL glow peaks. The limitation of the peak shape method is not because of the improper application of the methods, but is for reasons inherent in the shape of the peak itself. High values of δ , τ and ω together with low value of ' T_m ' lead to a lower value of ' E ' [44].

5. Conclusions

In summary, NaF flux aided solution combustion method has been followed to prepare CdSiO₃:Sm³⁺ nanocrystalline phosphors. The effect of NaF flux content on the crystal structure, morphology

and luminescent properties is investigated. PXRD and SEM studies reveal that 2 wt% NaF flux addition has significantly improved the crystallinity, reduced agglomeration of the particle without altering the monoclinic phase. With a further increase in NaF content (4–8 wt%), the crystallinity is decreased and formation of Cd_2SiO_4 phase was observed. The optical energy band gap for the un-doped and Sm^{3+} doped (1–7 mol%) phosphors was estimated and found to be 5.33 eV and for the Sm^{3+} doped (1–7 mol%) phosphors it varies between 5.45 and 5.62 eV. It is noticed that the optical band gap is found to be lower in the un-doped sample when compared to the Sm^{3+} doped CdSiO_3 . It is observed that, the absorption bands shifted in 8 wt% NaF flux, which might be attributed to phase change from CdSiO_3 to Cd_2SiO_4 . The thermoluminescence (TL) glow curves for 2–6 wt% NaF in CdSiO_3 show a single well resolved glow peak at 126, 130 and 150 °C respectively. However, in 8 wt% NaF added samples two glow peaks appear at ~ 148 °C and 220 °C respectively. With the addition of NaF flux, TL intensity can be enhanced effectively. The keen observation of our present work indicates that the addition of 2 wt% NaF flux during the preparation of Sm^{3+} doped CdSiO_3 is highly useful in enhancing its crystallinity, morphology and very importantly the thermoluminescence intensity.

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