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Studies on the Near White Light Emission of $SrSiO_3$ Doped with Dy^{3+} Phosphors

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Abstract

In present paper we prepared $SrSiO_3$ doped with different concentrations of Dy^{3+} ions (0.2, 0.5, 1.0, 1.5 and 2.0mol%) by modified high temperature solid state reaction technique. Sample with optimum Photoluminescence (PL) intensity was characterized by- X-ray diffraction (XRD) Technique. XRD spectrum observed for prepares sample matched quite significantly with Crystallographic open database (COD), card number 96-431-7121. This COD is for monoclinic $SrSiO_3$ with space group C 1 2/c 1 (15). Photoluminescence studies of all prepared samples were done. Emission spectra exhibited 2 prominent peaks at 473, 576 and 658 nm respectively. Here, Dy^{3+} acts as an activator. A peak centered at 473 nm is due to the transition $^4F_{9/2} \rightarrow ^6H_{15/2}$ (Blue Colour) of Dy^{3+} ions. Similarly, 576 and 658 nm peaks are originated due to transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ (Green Colour) of Dy^{3+}ions occupied at different sites. Emission at 660 nm is due to transition $^4F_{9/2} \rightarrow ^6H_{11/2}$ (Red Colour). CIE coordinates expressed that, the overall emission is near white light. In order to investigate the suitability of the samples for white colour light sources for industrial use, Correlated Colour Temperature (CCT). Values of CCT were found, well within the defined acceptable range and emission is considered to be cool in appearance.

Keywords

Luminescence, White LED, CCT, Dysprosium, Phosphor

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1. Introduction

It has been a challenge to prepare cost-effective white light emitting phosphor with good stability along with high quantum efficiency. Different borates, aluminates, and silicates doped with Dy^{3+} have been used extensively retrieving white light emission. Dy^{3+} can have its emission in the almost entire visible region which gives us the reason to choose Dy^{3+} as an activator. Rare earth Dysprosium ions have at least two dominant emission bands in the blue region (470–500 nm) due to $^4F_{9/2} \rightarrow ^6H_{15/2}$ transition and in the yellow region (560–600 nm) due to $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition [1-4].

Few silicates like $SrSiO_3$, $Sr_2MgSi_2O_7$, $Ca_2MgSi_2O_7$ and Sr_2SiO_4 doped with Dy^{3+} ions have already exhibited white light emissions [5-8].

In this paper we have prepared $SrSiO_3$: Dy^{3+} with changing concentration of Dy^{3+} (0.2, 0.5, 1.0, 1.5, 2.0 mol%). Conventional High-temperature solid-state reaction technique was employed for this. Detailed studies of photoluminescence process have been done. We got near white light emission when excited at 376 nm source. Correlated Colour Temperature and Thermoluminescence parameters were also calculated to check the suitability of prepared phosphors as a practical white light source.

2. Materials and Methods

The phosphor of $SrSiO_3$: Dy^{3+} powders with different concentration (0.2, 0.5, 1.0, 1.5, 2.0 mol%) of Dy^{3+} were

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prepared by solid-state reaction technique. The starting materials SiO_2, $SrCO_3$, and Dy_2O_3 with proper stoichiometric proportions were thoroughly ground for approximately 1 h in a mortar, pre-sintered at 900°C, then fired at 1300°C for approximately 2 h, with H_3BO_3 (1.6 mol%) used as a flux. [9-10]

Chemical reaction used for stoichiometric calculation is:-

$$SrCO_3 + SiO_2 + Dy_2O_3 \xrightarrow{1250^oC} SrSiO_3{:}Dy^{3+} + CO_2$$

The photoluminescence (PL) excitation and emission spectra were measured by a spectrofluorophotometer (SHIMADZU, RF-5301 PC, Kyoto, Japan) using a Xenon lamp of power 150 watts as an excitation source. To confirm the nature of phosphor, X-ray diffraction (XRD) characterization of the sample is done using PanalyticalXpert PRO MPD (Singapore) with copper k alpha anode of wavelength 1.5405 A°.

3. Results and Discussion

3.1. XRD Analysis

In order to obtain the crystallographic parameter of the sample, the powder X-ray diffraction spectra were analyzed by Rietveld fitting method [11].

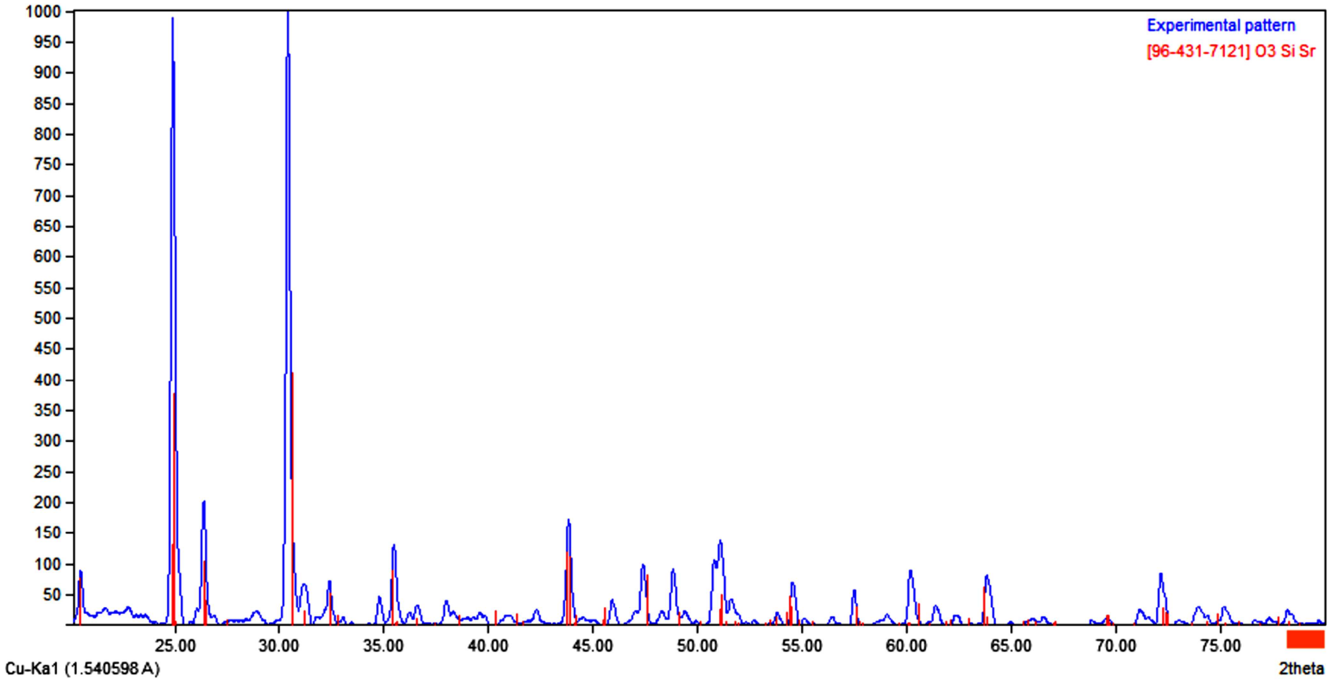

Figure 1. Observed and Standard XRD pattern of $SrSiO_3$: Dy^{3+}.

Figure 1 gives the comparison between observed, calculated and standard (COD card No. 96-431-7121) XRD pattern of $SrSiO_3$: Dy^{3+} phosphor. The Standard XRD pattern of $SrSiO_3$ (COD card No. 96-431-7121) seems to show quite a similar pattern as observed. The figure of merit while matching observed and standard XRD pattern was 0.7997 which illustrate that phase of prepared sample agrees with the standard pattern COD card No. 96-431-7121. The pattern is characterized by few prominent peaks found at different glancing angles.

The calculated spectra confirmed the presence of monoclinic $SrSiO_3$ with space group C 1 2/c 1 (15). The refinement of lattice parameters is done using software Celref Version 3. The refined values of monoclinic strontium meta-silicate were found as; a = 12.366 A°, b = 7.1538 A°, c= 10.9654 A°, α= 90°, β= 112.25°, γ= 90° and cell volume = 897.8 $(A°)^3$, which again signifies the proper preparation of the discussed sample and is shown in Table 1

Table 1. Refined lattice parameters of $SrSiO_3$: Dy^{3+}.

Initial values: (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	12.36	7.143	10.945	90	112.12	90	895.2
0	0	1	1	1	0	1	0	

Final values: (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.5418	12.366	7.1538	10.9654	90	112.25	90	897.8
0	0	0.1671	0.0091	0.1475	0	1.529	0	

h	k	l	2T (Obs)	2T-Zero	2Th (Cal)	Dif
-1	1	2	20.544	20.544	20.4393	0.1047
-3	1	1	24.958	24.958	24.9303	0.0277
0	2	1	26.437	26.437	26.4193	0.0177
0	2	2	30.458	30.458	30.5775	-0.1195
-1	1	4	35.531	35.531	35.505	0.026
-3	3	1	43.88	43.88	43.8608	0.0192
-3	3	3	47.44	47.44	47.5297	-0.0897
0	4	0	51.128	51.128	51.0673	0.0607
5	3	2	63.863	63.863	63.8662	-0.0032

There are few extra peaks in observed XRD pattern which could be due to a great number of stacking faults induced by the presence of the doping ions and also due to secondary phases and impurities formed during the elaboration process [9].

3.2. Photoluminescence Studies

Excitation spectra of $SrSiO_3$ doped with 0.5 mol% of Dy^{3+} are shown in Figure 2. Excitation spectrum was monitored at 575 nm. An intense peak is found at 362 nm. The emission spectrum is observed under an excitation of 362 nm source and, is shown in Figure 3.

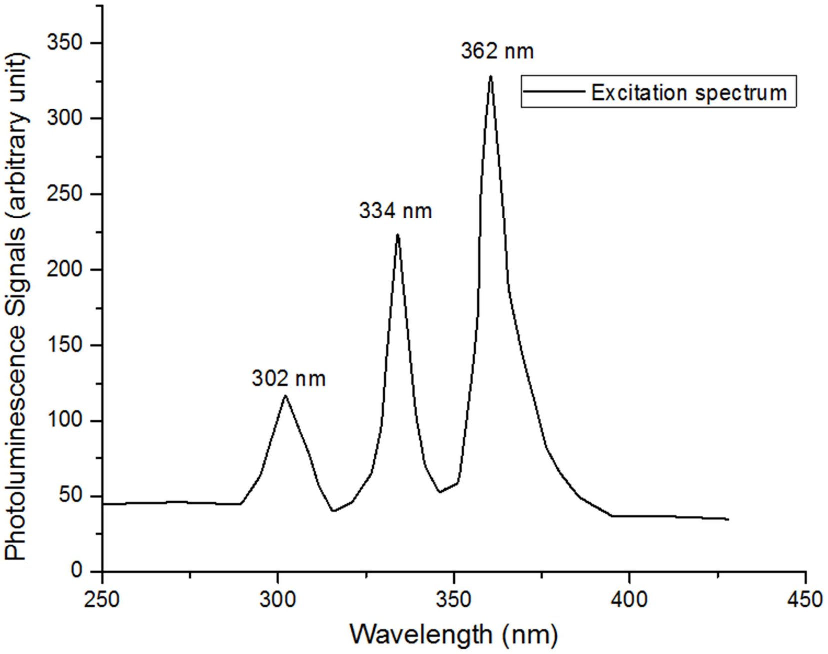

Figure 2. Excitation spectrum of $SrSiO_3$: Dy^{3+}.

There are three intense peaks in emission spectra at 476, 573, and 658 nm. The first peak centered at 476 nm (Blue region) is due to the transition $^4F_{9/2}\rightarrow{}^6H_{15/2}$ of Dy^{3+} ions located at different lattice sites. Similarly, transition $^4F_{9/2}\rightarrow{}^6H_{13/2}$ is responsible for the peaks centered at 573 (yellow-orange region). Another peak at 658 nm in red region is there because of the transition $^4F_{9/2}\rightarrow{}^6H_{11/2}$. Different transition possible in case of Dy^{3+}, are illustrated in Table 2 (Figure 4). The emission spectrum is monitored for different samples of $SrSiO_3$ doped with different concentrations of Dy^{3+}. It is readily observed that intensity of photoluminescence signals increases with increasing concentration of Dy^{3+} ions. It reaches optimum intensity when the concentration of Dy^{3+} was 1.5 mol% then photoluminescence intensity decrease due to concentration quenching of Dy^{3+} ions. CIE coordinate of the sample with 1.5 mol% of Dy was calculated to know exact colour emitted from the emission spectra and it was found that near white light emission is there which is illustrated in Figure 5.

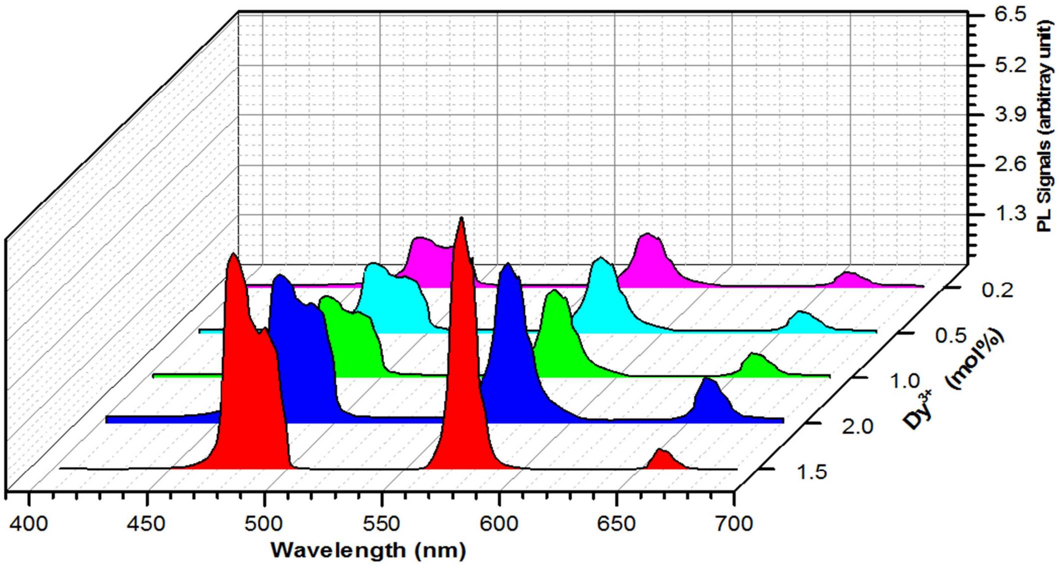

Figure 3. Emission Spectra of $SrSiO_3$: Dy^{3+}.

Table 2. Transition involved in process of emission.

S.No.	Emission Wavelength (Range)	Transition Involved (Dy^{3+})	Expected Colour
1	480 - 500 nm	$^4F_{9/2}\rightarrow{}^6H_{15/2}$	Blue
2	570 - 600 nm	$^4F_{9/2}\rightarrow{}^6H_{13/2}$	Green
3	650 - 670 nm	$^4F_{9/2}\rightarrow{}^6H_{11/2}$	Red

In order to investigate the prepared phosphors for suitability as a practical white light source, Correlated Color Temperature (CCT) and Colour Rendering Index (CRI) of the samples have been calculated.

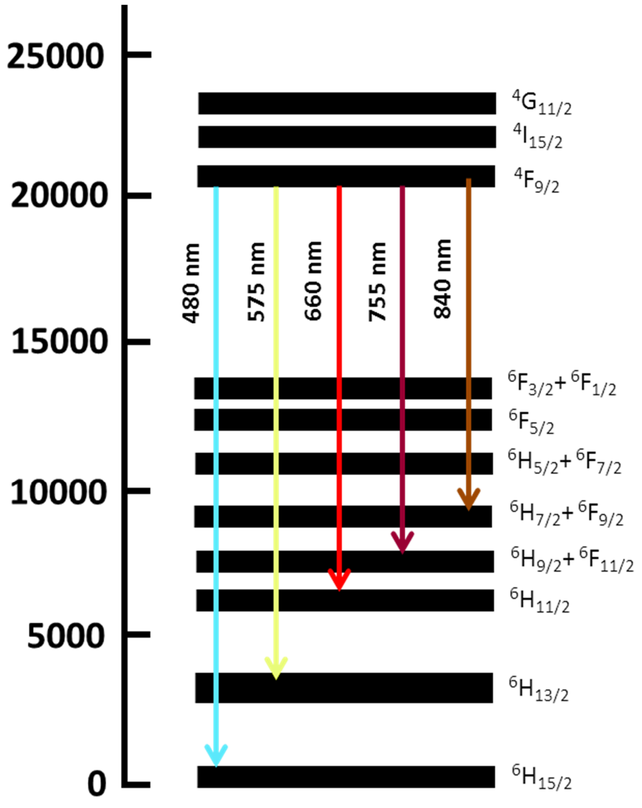

Figure 4. Energy level diagram of Dy^{3+} ions.

In our present case, from the viewpoint of ionic radii, it is reasonable to suggest that, the Dy^{3+} ions ($r_{Dy}{}^{3+}$= 0:091nm) are expected to occupy the Sr^{2+} (r_{Sr2+}=0.113 nm) sites in the $SrSiO_3$ host and no Dy^{3+} ion is expected to occupy the Si^{4+} sites (r_{Si4+}=0.041 nm). Due to these chemically non-equivalent substitutions, an excess of positive charge in the host lattice must be compensated. One possible way of charge compensation mechanism is that two Dy^{3+} ions replace three Sr^{2+} ions to balance the charge of these phosphors, which create two Dy^{o}_{Sr} positive defects and one V''_{Sr} negative defect [5-8],

$$2Dy^{3+}+3Sr^{2+}\longrightarrow 2Dy^{o}_{Sr}+V''_{Sr}$$

3.3. Correlated Colure Temperature (CCT)

The correlated color temperature (CCT) is a specification of the color appearance of the light emitted by a light source, relating its color to the color of light with respect to a reference light source when heated up to a specific temperature, in degrees Kelvin (K). The CCT rating for a lamp or a source is a general "warmth" or "coolness" measure of its appearance. However, opposite to the temperature scale, lamps with a CCT rating below 3200 K are usually considered "warm" sources, while those with a CCT above 4000 K are usually considered "cool" in appearance [12-15].

McCamy has proposed the analytical equation to calculate the CCT which is given [12-15] by

$$CCT = -449\,n^3 + 3525\,n^2 - 6823\,n + 5520.33;$$

Where $n=(x-x_e)/(y-y_e)$ is the inverse slope line and (x_e = 0.332, y_e=0.186) is the epicenter.

Generally, the preferred CCT values range from 3500 to 6500 K but the range from 3000 to 7800 K may also be accepted. Value of CCT calculated for sample with 1.5 mole% concentration of Dy^{3+} was found as 6312 K., which is well under the acceptable ranged and can be considered "cool" in appearance.

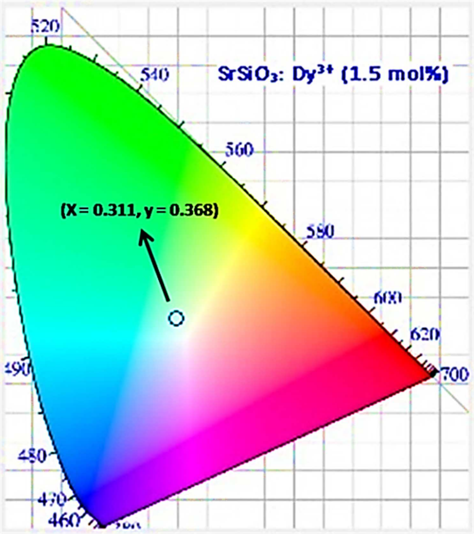

Figure 5. CIE coordinate of $SrSiO_3$: Dy^{3+} (1.5 mol%).

3.4. Thermoluminescence Studies

In order to discuss the formation of traps responsible for luminescence, we have studied thermoluminescence glow curve of Dy^{3+} doped in the $SrSiO_3$ host. Figure 6 shows the TL glow curves of $SrSiO_3$ doped with 1.5 mol% of Dy^{3+} samples. Two glow peaks, located at 105.83°C and 220.6°C in the Dy^{3+} doped $SrSiO_3$ phosphor, corresponding to two different traps formed due to the replacement of Dy^{3+} ions at the vacancies created by Sr^{2+} ions [6, 16-18]. We have used CGCD deconvolution technique (glow fit) to separate two different peaks (Figure 8). Trap depths using the deconvolved peaks were calculated using different techniques and the average value of the trap depth was found to be 0.51 and 0.57 eV for 105.83°C and 220.6°C peaks, respectively (Table 3). Peak centered at 105.83°C looks to be prominent and considered to be responsible for long-lasting properties of the sample, if materials show excellent long-lasting phosphorescence. Apart from this, we have studied the UV dose response of the sample. It was observed that TL intensity increases with increasing UV dose, and gets a maximum value when UV exposure is 20 minute, after which concentration quenching occurs results in the decrease of TL intensity. Figure 7 is indicating that the dose response is almost linear.

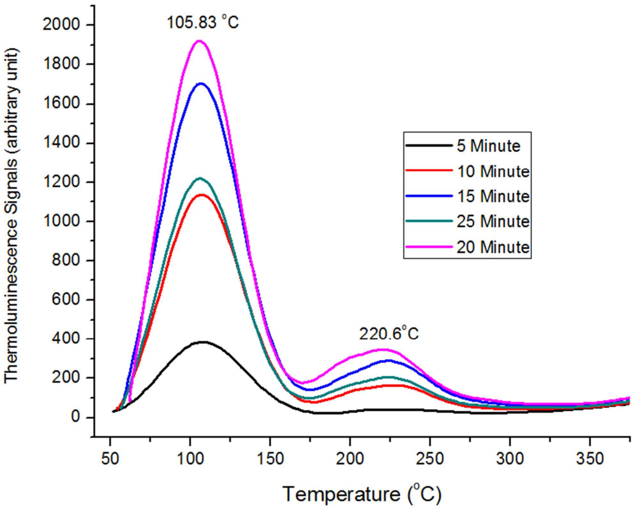

Figure 6. Thermoluminescence glow curve of $SrSiO_3$: Dy for different UV exposure.

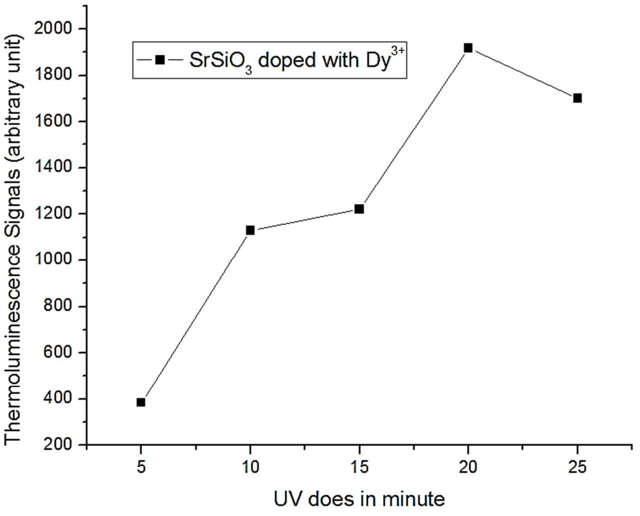

Figure 7. Dose-response curve of $SrSiO_3$: Dy^{3+}.

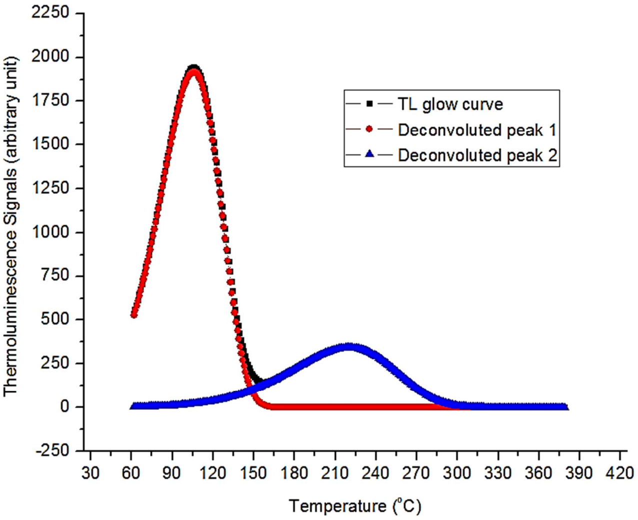

Figure 8. De-convoluted curve of $SrSiO_3$: Dy^{3+}.

Table 3. Trap depth calculation for de-convoluted peaks.

Peak#	**T_m**	**T_1**	**T_2**	**E_ω**	**E_δ**	**E_ζ**	**Shape Factor**
1	105.83	74.87	129.51	0.5111	0.5298	0.4939	0.42
2	220.60	168.87	260.78	0.5626	0.6109	0.5197	0.45

4. Conclusion

Samples of $SrSiO_3$ doped with different concentrations of Dy^{3+} were prepared using solid state reaction techniques. XRD patterns of these samples exhibited a fair agreement with the standard XRD patterns (COD card No. 96-431-7121) reported for $SrSiO_3$, with a figure of merit of 0.7997. Emission spectra expressed 3 emission peaks at 476, 573, and 658 nm arising due to transitions from the different energy levels of Dy^{3+} ions. CIE coordinates of each sample were near white light. CCT values calculated were found in the acceptable range and can be described as "cool" in appearance. In all, it can be concluded that $SrSiO_3$ doped with Dy^{3+} can be a suitable phosphor as a white light source and may be used in traffic signals, display devices etc.

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