TEMPERATURE DEPENDENT CHARACTERISTICS OF $SrAl_2O_4:Dy^{3+}$PHOSPHOR

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We report the detailed temperature-dependent characteristics of Dy^{3+} doped $SrAl_2O_4$ phosphor. The phosphor synthesised using precipitation method was annealed at three different temperatures, specifically 800ºC, 900ºC, and 1000ºC. The three samples were analyzed using XRD, SEM, TEM, RAMAN, and FTIR. The observed photoluminescence emissions were consisting of peaks arising from the host $SrAl_2O_4$ as well as the dopant Dy^{3+}. The crystallite sizes were found to be 27.22nm, 29.74nm, and 31.24nm, respectively, with the increase in annealing temperature. SEM, TEM images showed near-spherical, rod-like shapes of the crystals, and SAED confirmed the crystals were single-crystal. CIE analysis results showed that the colour coordinate was found to be very close to white colour in the three annealing temperatures, which is an advantage in the field of technology development.

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Keywords:Dy^{3+} doped phosphor; Precipitation method, Crystal characterizations, Photoluminescence

1. Introduction

As compared to traditional sulphide based phosphors, Eu^{2+}, Dy^{3+} ions doped $SrAl_2O_4$ phosphor have been luminescent materials with high brightness and persistence phosphorescence [1-3].The doped $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors give rise to an emission band at 520nm(green) which attributes to the $4f^6 5d^1 \rightarrow 4f^7$ transitions of $Eu^{2+}$and Dy^{3+} that induces the formation of hole trap levels and prolong the afterglow [1,4]. In recent years, researchers noticed that single Dy^{3+} doped $SrAl_2O_4$phosphor also possess valuable properties of high luminescence intensity, long-lasting time, chemical stability, emitting suitable colour and eco-friendliness [5,6]. Dy^{3+} ions have two prominent emission bands in the blue region (460-480nm) due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and in the yellow region (550-580nm) due to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition [7,8].Thus, Dy^{3+} doped $SrAl_2O_4$ phosphors have been extensively studied for various applications in the field of luminescence such as traffic signals, emergency signals, the dial plates of night-watch and interior decoration as well as in textile field [9,10]. Also, Dy^{3+} doped $SrAl_2O_4$ phosphor as potential single white light phosphor has become one significant achievement in the field of technology. Till now, most of the synthesis methods such as combustion method, solid-state reaction, sol-gel, reverse micro-emulsion, hydrothermal method and chemical precipitation were used to prepare this phosphor. Out of these, the chemical precipitation method is considered to be very safe; no harmful chemical reaction takes place and less time and energy-consuming. As reported in S.Tongbram *et al*.[11], Q. L. Ma*et al*. [12], the quenching concentration occurs at 3mol%Dy^{3+} when doped in the range of 1 mol% to 5mol% concentration of Dy^{3+} in $SrAl_2O_4$.So, there is a need to further investigate its temperature dependence on the 3mol%Dy^{3+} doped $SrAl_2O_4$ sample. In this

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paper, we report the synthesis of 3mol%Dy^{3+} doped $SrAl_2O_4$ phosphor using chemical precipitation method annealed at three different temperatures 800ºC, 900ºC and 1000ºC to study temperature dependent characteristics of $SrAl_2O_4$:Dy^{3+} phosphor. The phase formation, the particles size and its shapesof the $SrAl_2O_4$:Dy^{3+}samples were analysed using XRD pattern, and SEM, TEM images. The results of high resolution TEM and SAED were used to understand the microstructure of the material. EDS data were studied for determining the presence of the sample and any impurities. FTIR pattern was analysed to determine its functional groups. RAMAN spectroscopy studies were also carried out for providing a molecular fingerprint of the materials. The luminescent properties were studied using emission spectra of PL spectroscopy. The CIE coordinates were also used to calculate its colour of the phosphor.

2.Experimental

The3mol%Dy^{3+} doped $SrAl_2O_4$phosphor was prepared using a chemical precipitation method [13,14]. In this method, an appropriate stoichiometric amount of Strontium Nitrate [$Sr(NO_3)_2$],Aluminum Nitrate [$Al(NO_3)_3.9H_2O$] and Dysprosium Chloride [$DyCl_3.6H_2O$] were dissolved in distilled water and stirred for 1 hour using a magnetic stirrer.Ammonium Carbonate [$(NH_4)_2CO_3$] was used as a precipitant, and the solution was maintained at pH value 8-9.The resultant solution was centrifuged and washed several times using distilled water and acetone. The product obtained was dried in an oven at 100ºC for 48 hrs and grounded by mortar and pestle to make fine white powder. Finally, the powdered sample was annealed at 800ºC for 5hrs and thus obtained 3mol%Dy^{3+}doped $SrAl_2O_4$phosphor. The above synthesis process was repeated for 900ºC and 1000ºC, respectively.

Thus, the prepared samples were characterized for the determination of crystal structure and particle size using Bruker D8 (Germany)X-ray Diffractometer (XRD) with Cu Kα radiationof wavelength 1.5406Å.The morphology of the samples was characterized by Scanning Electron Microscopy (SEM) model JSM-7600F with accelerating voltage 0.1to 30kV and Transmission Electron Microscopy (TEM) model Tecnai G2,F30 with 300kV. The chemical composition of each sample was determined by Energy-Dispersive X-ray spectroscopy (EDX), and its FTIR measurement was carried out using Perkin Elmer FTIR Spectrometer. The Photoluminescence emissions were measured in the wavelength range of 200-850nmat room temperature using Ocean optics USB2000+UV-VIS spectrometer with an excitation wavelength of 325nm.The Raman spectrum of the samples was taken in the spectral range of 100-1350cm^{-1}using Raman spectrophotometer Horiba HR 800 model with excitation wavelength 514.5nm.

3. Results and discussion

3.1. X-ray Diffraction (XRD) structuralanalysis

Fig. 1 shows the XRD pattern of 3mol%Dy^{3+}doped $SrAl_2O_4$ annealed at three different temperatures 800ºC, 900ºC and 1000ºC. From the XRD pattern, the lattice parameter and the unit cell volume were calculated by using UNIT CELL software, and both the experimental and the standard values were nearly equal (as given in Table 1) which shows the formation of the monoclinic $SrAl_2O_4$ phosphor. All the three samples show the same monoclinic structure with space group $P2_1$and match well with JCPDS data file no. 01-074-0794.With the increase in thermal treatment, the intensity of diffraction peaks slightly increases and shifted toward slower 2Ɵ angles. One of the reasons may be due to a lattice expansion with an increase in annealing temperature as observed as an increase in unit cell volume[15].

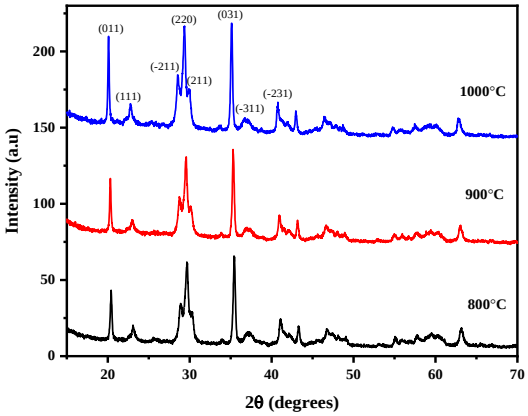

Fig. 1. XRD of 3mol%Dy^{3+}doped $SrAl_2O_4$ at three different temperatures.

Table 1. Lattice parameter and Volume calculation.

Sample:3mol%Dy^{3+}doped $SrAl_2O_4$	Theoretical: JCPDS data (file no.:01-074-0794)	Experimental (this work)		
		800ºC	900ºC	1000ºC
a (Å)	8.447	8.375	8.426	8.457
b (Å)	8.816	8.755	8.777	8.809
c (Å)	5.163	5.074	5.105	5.161
β (º)	93.420	93.171	93.248	93.115
Volume (10^6 pm^3)	383.800	371.479	376.947	383.941

In Table 3, among the structural data at three temperatures, the lattice parameter and the unit cell volume for 1000ºC was found very close to the standard values that indicate the formation of the single monoclinic phase. The result also supports that precipitation method used in the present work for the preparation of Dy^{3+}doped $SrAl_2O_4$ is justified.

The crystallite size of the material is calculated using the Scherrer's formula [14-16]

$$D = \frac{k\lambda}{\beta \cos(\theta)} \tag{1}$$

where D is the crystallite size, β is the full width at half maximum height of the diffraction peak, λ is the X-ray wavelength, θ(theta) is the Bragg's angle, k is Scherrer's constant (0.9). Table 2 shows the calculated crystallite size that corresponds to the maximum diffraction peak (0 3 1) of the Dy^{3+}doped $SrAl_2O_4$phosphor at the different temperatures 800ºC, 900ºC and 1000ºC as given in Fig.1.The crystallite size increases as 27.22nm, 29.74nm, 31.24nm with an increase in thermal treatment 800ºC, 900ºC, 1000ºC, respectively.

Table 2. Crystallite size at maximum diffraction peak (0 3 1).

Sample:3mol%Dy^{3+} doped $SrAl_2O_4$	Experimental (this work)		
	800ºC	900ºC	1000ºC
2Θ	35.44	35.32	35.12
FWHM	0.31	0.28	0.27
Crystallite size (nm)	27.22	29.74	31.24

3.2.Surface morphology and energy dispersiveX-ray (EDX) spectroscopy

Fig. 2 shows the SEM images of 3mol%Dy^{3+} doped $SrAl_2O_4$ at three different temperatures. It shows irregular shape in 800ºC and 900ºC with lots of agglomeration. At annealing temperature 1000ºC, a near-spherical shape with less agglomeration was observed, which represents a perfect crystal growth, and the crystallite sizes seem to be nearly equal. The Elemental compositions of the samples are determined by EDX. An EDX spectrum displays peaks corresponding to the energy level for which the most X-ray received. Fig. 3 gives the EDX spectrum that corresponds to the presence of Dy, Sr, Al, O in the 3mol%Dy^{3+}:$SrAl_2O_4$phosphor and its chemical composition at the three different temperatures are given in Table 3.

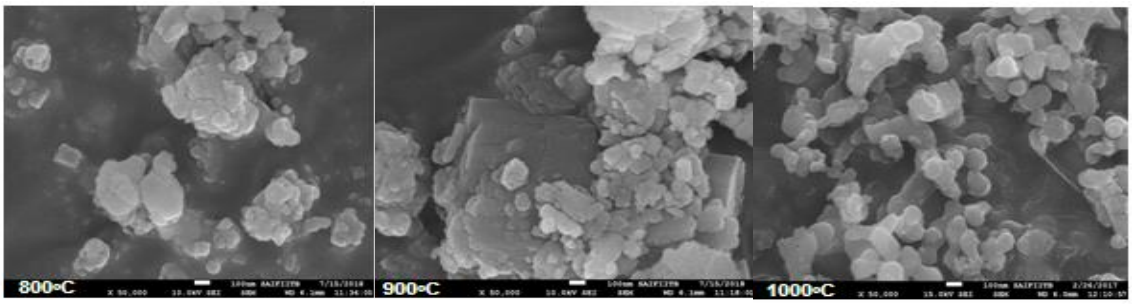

Fig. 2.SEM of 3mol%Dy^{3+}doped $SrAl_2O_4$at three different temperatures.

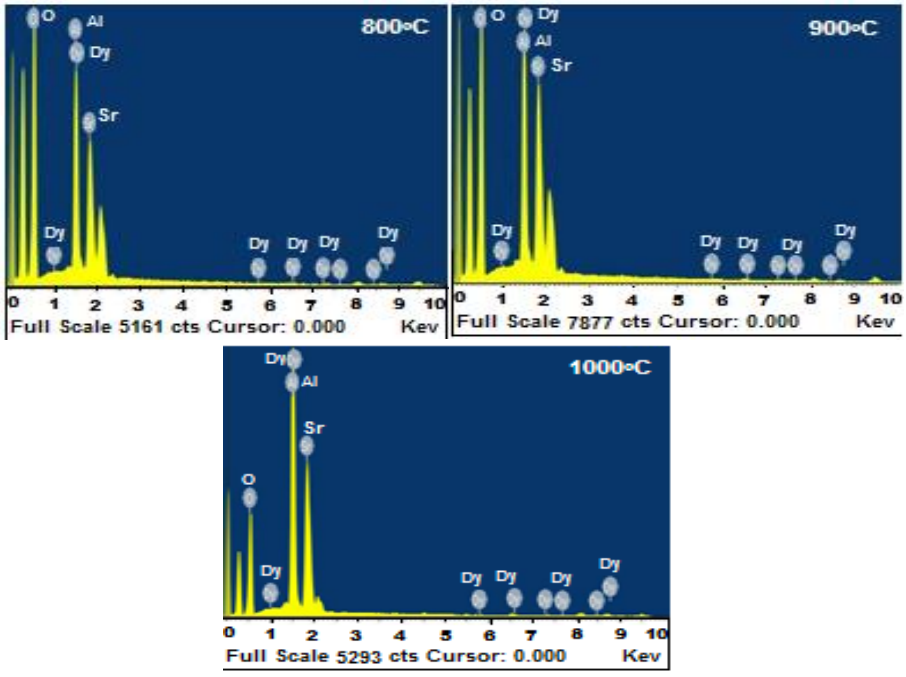

Fig. 3.EDS of3mol%Dy^{3+} doped $SrAl_2O_4$at three different temperatures.

Table3. Chemical composition of 3mol%Dy^{3+} doped $SrAl_2O_4$ at three different temperatures.

800°C			900°C			1000°C		
Element	Weight%	Atomic %	Element	Weight%	Atomic %	Element	Weight%	Atomic%
O K	55.18	79.87	O K	50.77	77.58	O K	42.03	68.79
Al K	14.25	12.23	Al K	14.20	12.86	Al K	21.07	20.44
Sr L	29.09	7.69	Sr L	33.31	9.30	Sr L	35.04	10.47
Dy L	1.47	0.21	Dy L	1.72	0.26	Dy L	1.87	0.30
Total	100			100			100	

3.3. Transmission electron microscopy(TEM) analysis

By considering its maximum intensity in XRD and perfect crystal growth, we present only the TEM images of the sample annealed at 1000ºC in Fig. 4. The TEM images show a near-spherical shape of the particles with rod-like shape and agglomeration is less seen. The rod-like shape benefits in LED devices as it enhances light extraction efficiency.

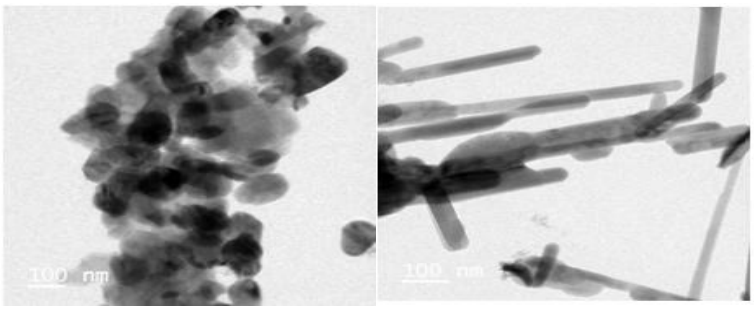

Fig. 4. TEM images of 3mol%Dy^{3+} doped $SrAl_2O_4$ at 1000ºC with the different selected area.

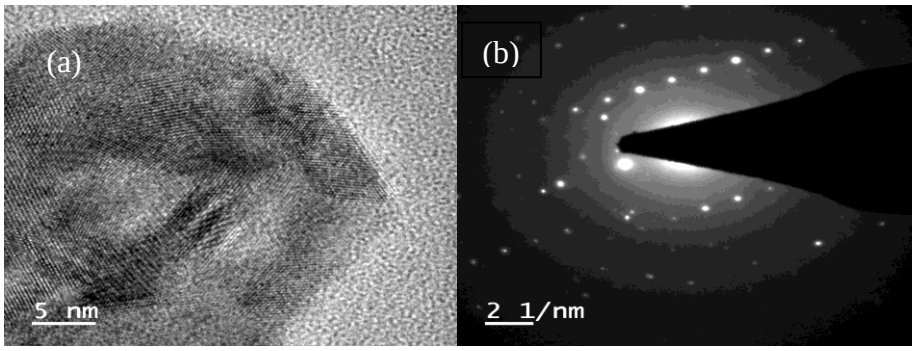

Fig. 5.(a) HRTEM and (b) SAED of 3mol%Dy^{3+} doped $SrAl_2O_4$at 1000ºC.

For further analysis, the high-resolution transmission electron microscopy(HRTEM) micrograph and selected area electron diffraction(SAED) images of 3mol%Dy^{3+} doped $SrAl_2O_4$ at 1000ºC are taken and shown in Fig. 5(a) and Fig.5(b) respectively. The clarity of the fringe patterns in high resolution micrograph shows the material crystallizes in single-phase and SAED image shows a single crystal. Also, the clear and strong diffraction spot in the SAED pattern indicates that the crystalline particles have sufficient sizes. From Fig 5(a),the experimental calculated the d-spacing value is found to be 2.44 Å which is very close to the standard value 2.43 Å (JCPDS file no.:01-074-0794). Thus, both the standard and experimental d-spacing values are approximately equal. It supports the XRD results of 3mol%Dy^{3+} doped $SrAl_2O_4$ at 1000ºCfor single monoclinic phase as discussed above.

3.4 Photoluminescence (PL) emission Spectra analysis

The emission spectra of 3mol%Dy^{3+} doped $SrAl_2O_4$ measured at three temperatures 800ºC, 900ºC and 1000ºCare shown in Fig. 6. All the spectra at the three different temperatures show a nearly same characteristic peak at 442nm, 477nm, 582nm and 648nm when excited at 325nm wavelength. The peak at 442nm corresponds to the host material, and the other three peaks correspond to $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, $^4F_{9/2} \rightarrow {}^6H_{11/2}$transitions of Dy^{3+} ions, respectively[17].These three characteristic emissions peak gives the information of Dy^{3+} ions acting as luminescence centres in the $SrAl_2O_4$ host. Also, we get maximum intensity at 1000ºC, which indicate a good annealing temperature for future analysis. In addition to it, the dominance of the broad blue emission spectrum at 477nm is due to crystal field insensitivity of the magnetic dipole $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition [18].

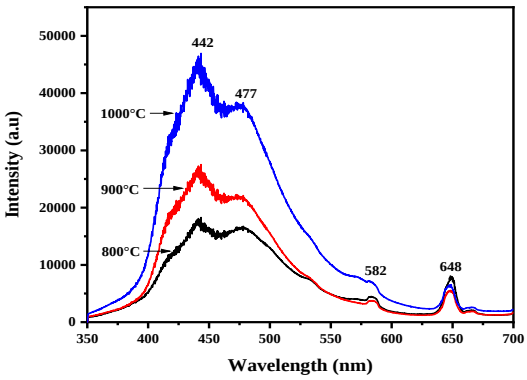

Fig. 6.Emission Spectra of 3mol%Dy^{3+} doped $SrAl_2O_4$at three different temperatures.

3.5.Fourier Transform Infrared Spectroscopy (FTIR) study

Fourier Transform Infrared Spectroscopy (FTIR) identifies the different chemical bonds in a molecule by producing an infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that is used to screen and scan for the functional groups and to characterize covalent bonding information. Fig. 7 shows the FTIR spectrum of 3mol%Dy^{3+} doped $SrAl_2O_4$ at the three different temperatures. The bands between 350 cm^{-1} and 1000 cm^{-1} correspond to the IR active vibration modes of $SrAl_2O_4$. The band at 1472cm^{-1} is attributed to the metal carbonates formed as intermediates during high-temperature synthesis [19]. The two bands positioned at 778cm^{-1} and 896 cm^{-1} originate from the aluminates groups (AlO_4). The band located at 643cm^{-1} and 844cm^{-1} attributes to Sr-O vibrations, and the band at 420cm^{-1} corresponds to O-Al-O vibrations [20].

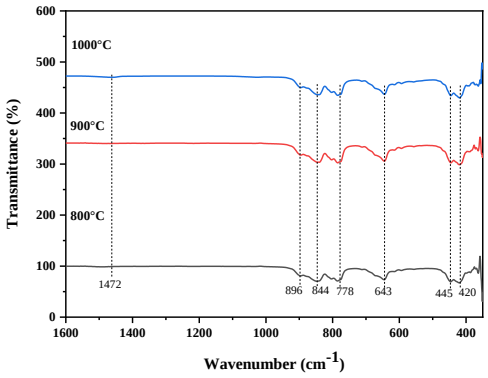

Fig. 7. FTIR of 3mol%Dy^{3+} doped $SrAl_2O_4$ at three different temperatures.

3.6.Raman spectroscopy study

Fig. 8 shows the Raman spectrum of 3mol%Dy^{3+} doped $SrAl_2O_4$ at three different temperatures. The similarity in the Raman spectra confirms the homogeneity of the prepared materials. The Raman spectra of 3mol%Dy^{3+} doped $SrAl_2O_4$ have less than 14 active modes which is partially due to the possible overlap of some symmetry vibrations of the weak features of Raman bands [21]. The mode at a frequency higher than 600 cm^{-1} attributes to Al-O stretching vibrations and the narrow low-frequency peaks below 250 cm^{-1} to tetrahedral vibrations or tilts (O-O-O angle between linked tetrahedral). The peak at 478 cm^{-1} contributes to the bending of O-Al-O bonds in corner-sharing tetrahedral, indicating that the polymorphs are present close to the monoclinic structure [22,23]. The Raman peak at 1073cm^{-1} also corresponds to C-O-H bending. Thus, confirmed the existence of the Dy^{3+} doped $SrAl_2O_4$ phosphor molecule in the prepared sample.

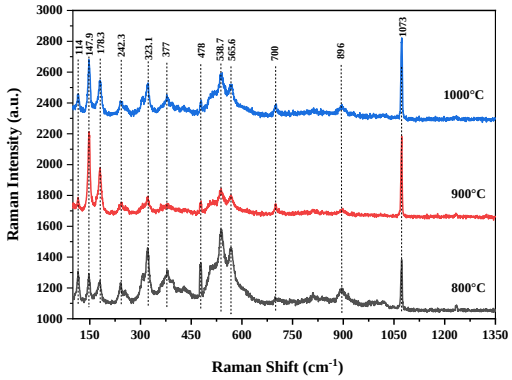

Fig. 8. Raman spectroscopy of 3mol%Dy^{3+} doped $SrAl_2O_4$ at three different temperatures.

3.7. CIE chromaticity study

The colour of any phosphor material is represented using colour coordinates. The colour coordinates of the sample were calculated from the PL emission spectrum wavelength data and the chromatic standard issued by the Commission International de l'Eclairage in 1931 (CIE 1931). The value (x, y) in Table 4 was calculated by the formula [24,25].

$$x = X/(X+Y+Z)$$

$$y = Y/(X+Y+Z) \qquad (2)$$

It was used to identify the colour of the sample in the CIE chromaticity diagram (as shown in Fig. 9). The last column in Table 5 represents the possible colour coordinates in CIE. Thus it shows that 3mol% Dy^{3+}doped $SrAl_2O_4$ gives white colour chromaticity at all the three annealing temperatures. From CIE diagram also, the coordinates were found very close to white light emission.

Table4. CIE colour chromaticity coordinates (x, y), Tristimulus values (X, Y, Z) of 3mol%Dy^{3+} doped $SrAl_2O_4$ sample at 800ºC, 900ºC, and 1000ºC.

Sample	Temperature	X(R)	Y(G)	Z(B)	*x*	*y*	CIE Colour
3mol%Dy^{3+} doped $SrAl_2O_4$	800ºC	16.9	16.96	16.9	0.333	0.334	white
	900ºC	22.54	22.78	25.06	0.320	0.324	white
	1000ºC	39.25	39.47	42.9	0.323	0.324	white

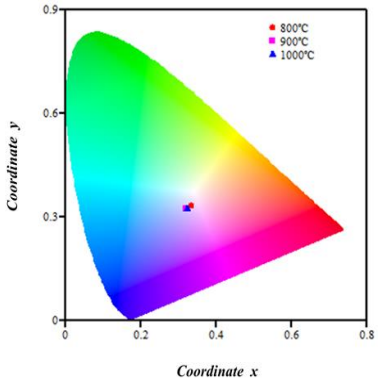

Fig. 9.CIE diagram of 3mol%Dy^{3+} doped $SrAl_2O_4$ at three different temperatures.

4. Conclusions

Dy^{3+} doped $SrAl_2O_4$ phosphor has been synthesized successfully using chemical precipitation method and annealed at the three different temperatures 800ºC, 900ºC and 1000ºC.The XRD analysis of the sample at the three different temperatures shows a monoclinic structure, and the crystallite sizes are estimated as 27.22nm, 29.74nm and 31.24nm, respectively. SEM and TEM images show near-spherical shape along with rod-like shape in some selected area of the sample. SAED analysis confirms to single-crystal, and CIE image coordinate is close to the white light emission. Thus, we conclude thatDy^{3+}doped $SrAl_2O_4$ phosphors can be a potential single white light phosphor despite intensity variation in different annealing temperature.

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