Solution Combustion Synthesis, Structural and Optical Properties of Dy$^{3+}$ Doped GdSrAl$_3$O$_7$ Nanophosphor

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ABSTRACT: Single phased dysprosium doped GdSrAl$_3$O$_7$ nanophosphor has been successfully obtained via low temperature solution combustion synthesis (SCS). The crystal structure and particle morphology of the nanophosphor were investigated by the X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FT-IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). All observations indicate that SCS yields pure-phased, well crystallized tetragonal GdSrAl$_3$O$_7$ phosphor with particle dimensions in the nano-regime at low sintering temperature (550°C). The photoluminescent excitation and emission spectra were studied to characterize the optical properties of the GdSrAl$_3$O$_7$: Dy$^{3+}$ nanophosphor. Several sharp excitation peaks attributed to intra-$4f$ transitions of the Dy$^{3+}$ ions in the near UV region were observed, as well as characteristic blue and yellow emission ascribed to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^4H_{13/2}$ transitions, respectively. The emission spectral features confirm that dysprosium occupies low symmetry site in GdSrAl$_3$O$_7$ lattice. In addition, the optimum Dy$^{3+}$ ions concentration and decay curves were also investigated. The optical features suggest that Dy$^{3+}$ doped GdSrAl$_3$O$_7$ nanophosphor may play a vital role in advanced lighting devices. © 2018 iGlobal Research and Publishing Foundation. All rights reserved.


Keywords: Combustion; Optical; GdSrAl$_3$O$_7$: Dy$^{3+}$; Nanophosphor.

INTRODUCTION

As important rare earth oxides, melilite complexes (ABC$_3$O$_7$) have been received considerable attention due to their stable structural features and high application potential in solid state laser materials, plasma display panels, mercury free- high discharge lamps (HID), high vision TV, plasma panel and scintillators [1-4]. The melilite ABC$_3$O$_7$ structure, where A is the rare earth elements, B is the alkaline earth elements and C is Al, Ga or In, is composed of eightfold coordinated alternating (A/B)$_2$ and corner–sharing tetrahedral anionic CO$_4^{2-}$ layers. The trivalent A and divalent B cations occupy C$_a$ symmetry sites while trivalent C cations are located at two non-equivalent tetragonal sites with S$_4$ and C$_s$ symmetries. It has been found that the two dimensionally connected tetrahedral layered oxide network stabilizes oxygen by local relaxation, leading to high conductivity of interstitial oxide anions in the melilite lattice [5-7]. Up to now, various synthetic routes have been adopted to synthesize different RE$^{3+}$ ions doped melilite oxide phosphors, including solid state method, sol-gel process and combustion approach [8-15]. As known, solid state process requires long sintering time (~24h) to increase diffusivity between precursor materials, resulting in agglomerated and coarse particles which adversely affect the efficiency of phosphor [8,16]. In sol-gel method, post sintering treatment at high temperature is needed to obtain the phosphor with single phase and high luminescence intensity [12]. In order to improve these drawbacks, solution combustion synthesis has been proved as an efficient, simple and self sustained process due to high reactivity of raw
materials at precursor level, which yields not only nano-sized oxide powders with large surface area but also allows homogenous doping of trace amounts of RE\textsuperscript{3+} ions in host lattice at low sintering temperature [17-19].

Among the melilite oxides, gadolinium strontium aluminate GdSrAl\textsubscript{2}O\textsubscript{7} having tetragonal crystal structure with space group P-42\textsubscript{1}m, could act as both efficient host lattice and sensitizer due to presence of Gd\textsuperscript{3+} as constituent ion, and offer excellent luminescent potentialities when doped with rare-earth ions (RE\textsuperscript{3+}) like other isostructural melilite oxides, GdCaAl\textsubscript{2}O\textsubscript{7} and GdSrGa\textsubscript{2}O\textsubscript{7} [8-11]. Recently, the doping of Tb\textsuperscript{3+} ions in GdSrAl\textsubscript{2}O\textsubscript{7} lattice has been investigating by Zhou et. al. [10] via EDTA sol-gel process, reporting the pure melilite phase formation at higher sintering temperature (900°C) for 5h but luminescent properties of dysprosium ions in this host has not been studied so far. This paper reports an effective and rapid solution combustion approach for the first time synthesis of Dy\textsuperscript{3+} doped GdSrAl\textsubscript{2}O\textsubscript{7} nanocrystalline phosphor at low temperature. The dopant Dy\textsuperscript{3+} ions has the well-known strong fluorescence in the visible spectral range around 480 nm and 570 nm ascribed to blue and yellow transitions from the \textsuperscript{7}F\textsubscript{02} state to \textsuperscript{2}H\textsubscript{15/2} and \textsuperscript{2}H\textsubscript{11/2} states, respectively. Dy\textsuperscript{3+} ions doped phosphor holds a great promise in white light emission by proper tuning of yellow to blue emission intensities on varying the composition of host [20-23]. Herein, the structural and photoluminescence features of Dy\textsuperscript{3+} doped GdSrAl\textsubscript{2}O\textsubscript{7} nanophosphor with energy transfer mechanism from Gd\textsuperscript{3+} to Dy\textsuperscript{3+} ions were investigated in details.

**MATERIALS AND METHODS**

Gd\textsubscript{1-x}Sr\textsubscript{x}Al\textsubscript{2}O\textsubscript{7}: xDy\textsuperscript{3+} nanopowders, where x = 1 to 15 mol\% were synthesized using urea assisted solution combustion process. The chemical equation for the reaction was:

\[
1-x\text{Gd(NO}_3\text{)}_3 + x\text{Dy(NO}_3\text{)}_3 + \text{Sr(NO}_3\text{)}_2 + 3\text{Al(NO}_3\text{)}_3 + 11.66\text{CH}_4\text{N}_2\text{O} \rightarrow \text{Gd}_{1-x}\text{Dy}_x\text{SrAl}_2\text{O}_7(s) + \text{gaseous products.}
\]

According to stoichiometric composition Gd\textsubscript{1-x}Dy\textsubscript{x}SrAl\textsubscript{2}O\textsubscript{7}, high purity raw materials Sr(NO\textsubscript{3})\textsubscript{2}, Gd(NO\textsubscript{3})\textsubscript{3},6H\textsubscript{2}O, Al(NO\textsubscript{3})\textsubscript{3}, Dy(NO\textsubscript{3})\textsubscript{3},6H\textsubscript{2}O and urea were dissolved in minimum quantity of deionized water. The amount of urea was calculated using total oxidizing and reducing values according to the concept used in propellant chemistry [24]. Finally the beaker containing the aqueous paste was placed in a preheated furnace maintained at 500°C. The mixture of metal nitrates (oxidizers) and fuel (urea) undergo rapid and self-sustaining combustion process and the chemical energy released during this exothermic redox reaction results in dehydration and foaming followed by decomposition. Consequently, the large amounts of volatile combustible gases generated along with flames, yields voluminous solid within 5-8 minutes. The foam thus obtained was again sintered at 550°C for 1h in order to eliminate unreacted nitrates, resulting in single phased dysprosium doped GdSrAl\textsubscript{2}O\textsubscript{7} nanophosphor.

To reveal the crystalline phase of Gd\textsubscript{1-x}Dy\textsubscript{x}SrAl\textsubscript{2}O\textsubscript{7} powders, X-ray diffraction (XRD) was carried out on Rigaku Ultima-IV X-ray powder diffractometer at 40 kV tube voltage and 40 mA tube current with CuK\textalpha\, radiation in the 2θ ranging from 15 to 70°. The functional groups in GdSrAl\textsubscript{2}O\textsubscript{7} lattice were identified by the Fourier transform infra-red spectroscopy (Perkin-Elmer spectrometer) in the spectral range 4000-4000 cm\textsuperscript{-1}. The morphology and particle size were evaluated using scanning electron microscopy (SEM) on Jeol JSM-6510 and transmission electron microscopy (TEM) on Hitachi F-7500. The photoluminescence excitation and emission spectra of the nanophosphor in the ultraviolet-visible region and decay curves under time scan-mode were analyzed by fluorescence spectrophotometer (Hitachi F-7000) equipped with Xe-lamp as the light source.

**RESULTS AND DISCUSSION**

**Structural studies**

GdSrAl\textsubscript{2}O\textsubscript{7} is one of the complex oxide of melilite family, consisting of tetragonal crystals with the space group P-42\textsubscript{1}m and lattice parameter a = 7.801 Å and c = 5.132 Å. The GdSrAl\textsubscript{2}O\textsubscript{7} lattice is built up of AlO\textsubscript{4}\textsuperscript{2-} tetrahedral layers and the Sr\textsuperscript{2+} and Gd\textsuperscript{3+} ions are randomly distributed in between the layers at Cs symmetry sites. The XRD patterns of Gd\textsubscript{0.90}Dy\textsubscript{0.10}SrAl\textsubscript{2}O\textsubscript{7} nanophosphor, as-synthesized (500°C) and sintered (550°C, 1h) along with standard data of melilite oxide, GdSrAl\textsubscript{2}O\textsubscript{7} (JCPDS No. 50-1817) are presented in Fig. 1. In the as-synthesized sample, diffraction peaks at 16.09 (001), 17.30 (111), 23.94 (111), 25.65 (210), 28.84 (201), 31.04 (211), 35.09 (002), 36.50 (310), 43.89 (212) and 51.46 (312) belonging to tetragonal phased GdSrAl\textsubscript{2}O\textsubscript{7} (JCPDS No. 50-1817) with a shoulder peak marked as ‘*’ at 19.8° due to unreacted nitrates were observed.

It is quite visible that the sintering of Gd\textsubscript{0.90}Dy\textsubscript{0.10}SrAl\textsubscript{2}O\textsubscript{7} powder at 550°C does not induce any significant phase change so far except the impurity peak gets disappeared completely. The XRD patterns indicate that well-crystallized melilite phased GdSrAl\textsubscript{2}O\textsubscript{7}: Dy\textsuperscript{3+} nanophosphor could be easily obtained under the low temperature synthetic conditions. Hence, it is very easy to conclude that SCS is an effective
approach which allows homogenous mixing of different oxidizers (i.e. metal nitrates) at molecular level during pre-sintering process due to self sustained combustion of metal nitrate and an organic fuel at low furnace temperature (500°C).

The XRD profiles of Gd$_{1-x}$Dy$_x$SrAl$_3$O$_7$ nanophosphors doped with different dysprosium contents, sintered at 550°C along with standard reference data (JCPDS No. 50-1817) are depicted in Fig. 2. The well defined diffraction peaks confirmed that, after sintering at 550°C, powder samples crystallize in a pure tetragonal GdSrAl$_3$O$_7$ phase (JCPDS No. 50-1817). It also implies that the incorporation of Dy$^{3+}$ ions does not cause any distortion in the melilite lattice as Dy$^{3+}$ ions ($R_{Dy^{3+}} = 0.97\,\text{Å}$) can easily enter into $C_s$ symmetry sites for substituting Gd$^{3+}$ ions ($R_{Gd^{3+}} = 1.00\,\text{Å}$) in GdSrAl$_3$O$_7$.

The average particle size, $D$ of Gd$_{1-x}$Dy$_x$SrAl$_3$O$_7$ powders, was determined from the XRD parameters according to Scherrer’s equation $D = 0.94\lambda /\beta \cos \theta$, where $\lambda$ is the wavelength of CuK$\alpha$ radiation (0.1548 nm), $\beta$ is the full width in radians at half-maximum (FWHM) and $\theta$ is the Bragg’s angle of an observed X-ray diffraction peak. From the FWHM value of the most intense peak (211), the calculated particle size corresponding to 1, 5, 10 and 15 mol% of Dy$^{3+}$ ions in Gd$_{1-x}$Dy$_x$SrAl$_3$O$_7$ powder, sintered at 550°C came out to be 49 nm, 48 nm, 45 nm and 42 nm, respectively. Within all samples, the average size standard deviation was 45 ± 4 nm, indicating that the amount of Dy$^{3+}$ ions has no remarkable influence on the particle size of Gd$_{1-x}$Dy$_x$SrAl$_3$O$_7$ nanophosphor.

The morphological features of Gd$_{0.90}$Dy$_{0.10}$SrAl$_3$O$_7$ nanophosphor, sintered at 550°C were investigated by scanning electron microscopy and transmission electron microscopy. SEM image of Gd$_{0.90}$Dy$_{0.10}$SrAl$_3$O$_7$ nanophosphor depicts smooth and densely packed tetragonal porous particles, as expected arise from the non-uniform distribution of temperature and mass flow in the combustion flame (Fig. 3).
The combustion derived products with high surface area and porous network are believed to be an outcome of large amount of escaping gaseous materials during the self-sustained combustion process [25-26]. TEM image of Gd$_{0.90}$Dy$_{0.10}$SrAl$_2$O$_7$ nanophosphor sintered at 550°C, shows monodispersed tetragonal shaped particles with sizes in 40-50 nm range (Fig. 4). The average particle size estimation of Gd$_{0.90}$Dy$_{0.10}$SrAl$_2$O$_7$ nanophosphor is consistent with that determined from the XRD patterns.

The FT-IR spectrum of Gd$_{0.90}$Dy$_{0.10}$SrAl$_2$O$_7$ nanophosphor, sintered at 550°C in the frequency region of 4000-400 cm$^{-1}$ is depicted in Fig. 5. Modes in the lower region (1000-400 cm$^{-1}$) are assigned to the aluminum-oxygen stretching and bending vibrations of AlO$_4^-$ tetrahedron and other metal-oxygen bonds present in the melilite structure. In addition, absorption bands related to characteristics H-O-H bending vibrations of absorbing free H$_2$O (1630 cm$^{-1}$) and O-H stretching vibration (3438 cm$^{-1}$) also appeared in the sample. It is significant to note that the fundamental residual NO$_x$ peak around 1384 cm$^{-1}$ was not detected in the spectrum, confirming the formation of impurity free pure melilite phased structure at low crystallization temperature.

**Optical studies**

The photoluminescence excitation (PLE) spectrum of Gd$_{0.90}$Dy$_{0.10}$SrAl$_2$O$_7$ nanophosphor, sintered at 550°C, monitored with $\lambda_{em} = 574$ nm.

The photoluminescence (PL) spectra of Gd$_{0.90}$Dy$_{0.10}$SrAl$_2$O$_7$ nanophosphor as-synthesized and sintered at 550°C, monitored with 350 nm ($^4$H$_{15/2} \rightarrow ^6$P$_{7/2}$) as excitation wavelength in 400-650 nm region is depicted in Fig. 7. The two main emission bands in the 450-500 nm (blue region) and 550-600 nm (yellow region) corresponding to transitions between well-defined 4$^f$ energy states of the Dy$^{3+}$ ions were observed. The blue emission containing multiple emission lines, centered at 478 nm and dominating yellow emission centered at 574 nm are assigned to $^4$F$_{9/2}$ $\rightarrow$ $^6$H$_{15/2}$ and $^4$F$_{9/2}$ $\rightarrow$ $^6$I$_{13/2}$ transitions of Dy$^{3+}$ ions, respectively. With respect to Dy$^{3+}$ ions, magnetic allowed dipole $^4$F$_{9/2}$ $\rightarrow$ $^4$H$_{15/2}$ transition gets hardly influenced by the crystal field symmetry of dysprosium ions while forced electric allowed transition $^4$F$_{9/2}$ $\rightarrow$ $^6$H$_{15/2}$ being hypersensitive appreciably affected by chemical surrounding of the luminescent center [30]. Both samples exhibits stronger forced electric transition (yellow emission) than magnetic dipole transition (blue emission) as there is a high probability of substitution of Dy$^{3+}$ ions into low inversion symmetric Gd sites (C$_3$) in this melilite oxide due to comparable size of Dy$^{3+}$ and Gd$^{3+}$ ions.
However, the PL spectrum of as-synthesized Gd₁₋ₓDyₓSrAl₂O₇ nanophosphor shows slightly weak emission with maintained shape and positions of peaks corresponding to both transitions as compared to that of sample, sintered at 550°C (1h). This indicates that Gd₁₋ₓDyₓSrAl₂O₇ nanophosphors are not well crystallized at 500°C due to presence of surface impurities in host lattice which may be omitted after sintering, leading to improvement in crystallinity as confirmed by the XRD measurements.

The PL spectra of Gd₁₋ₓDyₓSrAl₂O₇ nanophosphors, sintered at 550°C with dysprosium doping contents ranging from 1 to 15 mol%, monitored with 350 nm as excitation wavelength are shown in Fig. 8. For all Gd₁₋ₓDyₓSrAl₂O₇ samples, the hypersensitive yellow (⁴F₉/2→⁶H₁₃/₂) emission of Dy³⁺ ions is the prominent one as Dy³⁺ ions preferentially substitutes low symmetry Gd³⁺ sites (C₃v) with no inversion center in GdSrAl₂O₇ lattice. The relative PL intensities corresponding to both yellow and blue emission enhanced with the increasing concentration of Dy³⁺ ions, reaching the maximum at 10 mol% of dysprosium contents while decreased with the further increase of dopant concentration. Such behavior is due to cross-relaxation mechanism between luminescent centers, caused by quenching of the energy state ⁴F₉/2 at higher dysprosium contents via non-radiative energy transfer process such as;

\[
\text{Dy}^{3+}(\text{⁴F}_{9/2}) + \text{Dy}^{3+}(\text{⁶H}_{13/2}) \rightarrow \text{Dy}^{3+}(\text{⁴F}_{9/2}^{'}/\text{⁶H}_{7/2}) + \text{Dy}^{3+}(\text{⁴F}_{3/2})
\]

It has been noticed that value of yellow to blue emission ratio \(Y/B \sim 1.7\) does not show significant changes with the increasing Dy³⁺ contents in GdSrAl₂O₇ host, indicating hypersensitive electric forced transition (⁴F₁⁰₂→⁶H₁₃/₂) senses same crystal field environment at Dy³⁺ symmetry sites in GdSrAl₂O₇ lattice at different doping concentrations.

The luminescence decay curves corresponding to ⁴F₉/2 → ⁶H₁₃/₂ transition at 574 nm for Gd₁₋ₓDyₓSrAl₂O₇ nanophosphors in terms of Dy³⁺ ions concentrations, monitored with 350 nm excitation wavelength are shown in Fig. 9. In all samples, ⁴F₉/2→⁶H₁₃/₂ transitions show single exponential behavior, represented by the equation \(I = I₀ \exp (-t/\tau)\), where \(\tau\) is the radiative decay time, \(I\) and \(I₀\) are the luminescence intensities at time \(t\) and 0, respectively. The calculated lifetimes are 2.61, 2.43, 2.41, 2.39, 2.33 and 1.69 for 1, 3, 5, 10, 12 and 15 mol% of Dy³⁺ ions, respectively in Gd₁₋ₓSrAl₂O₇ nanophosphors. At higher concentration, the distance between the dysprosium ions shortens subsequently non-radiative energy transfer between optical active ions become more frequent, hence life time decreases with the increasing dopant concentration.
CONCLUSION
In Summary, highly crystalline melilite phased GdSrAl$_2$O$_7$: Dy$^{3+}$ nanophosphor has been successfully synthesized by low cost solution combustion approach at sintering temperature, 550°C as confirmed by the XRD patterns. Morphological studies reveal that uniform tetragonal particles with narrow size distribution could be obtained by this low temperature method. Optical studies of Dy$^{3+}$ doped GdSrAl$_2$O$_7$ nanophosphor were studied in details. The PL spectra exhibits stronger yellow emission (1$^4$F$_{9/2}$ → 2$^4$H$_{15/2}$) as compared to blue emission (1$^4$F$_{9/2}$ → 6$^4$I$_{15/2}$) under excitation at 350 nm, confirming that Dy$^{3+}$ preferably substituted low symmetry Gd$^{3+}$ sites in the melilite lattice. An efficient energy transfer from the Gd$^{3+}$ to Dy$^{3+}$ ions can be achieved. Luminescent analysis reveals that the optimum Dy$^{3+}$ concentration is around 10 mol% and non-radiative cross-relaxation process between neighboring Dy$^{3+}$ ions might be responsible for the concentration quenching phenomenon in this potential luminescent nanomaterial.

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