

Sol gel synthesis and optical characterization of the SrAlO:Dy nano phosphor

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Abstract

Dy doped SrAlO nano phosphors were synthesized by adopting a simple Sol-Gel Method. X-Ray Diffraction (XRD) profile confirms the monoclinic nature of Dy doped SrAlO nano phosphors. The results show that SrAlO:Dy with an average particle size of 80 nm is formed. In addition, Scanning electron microscopy (SEM), Photoluminescence (PL) and Fourier-Transform IR spectroscopy (FTIR) were also used to characterize the synthesized phosphor. The efficiency of the prepared phosphors was analyzed by means of its emission spectral profiles. We also observed a rich IR emission from the prepared phosphors under a Ultra-Violet (UV) source. Such luminescent powders are expected to be applied as IR sensor and MRI device applications.

Key words: Phosphors, optical properties, luminescence, XRD, SEM, Dysprosium.

Introduction

In recent years, the strontium aluminates have attracted intense research around the world, as they offer excellent properties such as high quantum efficiency, long persistence of the phosphorescence and good stability. Also, the importance of rare earth ions as efficient emitter in a variety of solid-state matrices is well known. Among rare earth ions, Eu/Dy is

often employed by researchers for making red emitting phosphors, where the prominent 612 nm emission band arises from electric dipole moment allowed transitions¹. The long lasting phosphors (LLP) oxide materials have been developed to replace the conventional sulfide afterglow materials because of their improved luminescent properties such as high initial brightness, long lasting time, suitable emission color and satisfactory chemical stability²⁻⁴,

which result in an unexpectedly large field of applications e.g. luminous paints in highways, airports, buildings and ceramic products⁵. With the development of newer technologies, several kinds of chemical synthesis techniques such as co-precipitation⁶, sol-gel⁷, reverse micro emulsion⁸ and combustion methods⁹⁻¹⁰ have been employed to prepare SrAl_2O_4 and its phosphors¹¹. Comparing these methods, sol-gel synthesis possesses some benefits, namely, relatively low preparation temperature, easy control of the stoichiometry, high levels of product homogeneity, and no need for the use of expensive equipment. In this article, we reported the synthesis of nanostructured SrAl_4O_7 doped with Dy via Sol Gel synthesis and effects on PL properties were investigated.

Experiment

The materials used for synthesis are strontium nitrate, aluminium nitrate and all other materials are 99.9% pure. The procedure of synthesizing nanoparticles is thoroughly described as follows: 98 wt.% of 2M Strontium acetate $[(\text{CH}_3\text{COO})_2\text{Sr} \cdot 2\text{H}_2\text{O}]$ was dissolved in 25ml of 2-methoxyethanol with vigorous stirring. 1 wt.% of 2M Dysprosium nitrate $[(\text{CH}_3\text{COO})_2\text{Dy} \cdot 2\text{H}_2\text{O}]$ was dissolved in 25ml of 2-methoxyethanol with vigorous stirring. Simultaneously, 1 wt.% of 2M Aluminum acetate $[\text{C}_4\text{H}_6\text{AlO}_4 \cdot 4\text{H}_2\text{O}]$ was dissolved in 25ml of 2-methoxyethanol with vigorous stirring and subsequently, it was added to the first solution to reach 50 ml in total. Then it was stirred for 30 min at room temperature for the second time. Ammonia was slowly

added to this solution with a constant stirring until a pH of 10.5 was achieved. After the stirring of the solution for 30min, acetic acid and ethylene glycol in the ratio 1:1 was added to the solution. The sol was heated at 80°C while being mechanically stirred with a magnetic stirrer. As the evaporation proceeded, the sol turned into a viscous gel. The gel was aged for 2h and then dried at 100°C for about 5h. The resulting materials were well grinded and annealed at 950°C for 5h to obtain Dy doped SrAl_4O_7 nanopowders. For the preparation of the gel precursors with different wt%, the same procedure was repeated with the wt% of Dysprosium nitrate being varied to 0.5, 2, 3, 4 and 5.

Characterization.

1. X-Ray Diffraction (XRD).

The structure and phase purity of the SrAl_4O_7 :Dy phosphor were investigated by XRD. The XRD patterns were obtained and are shown in Fig. 1 for SrAl_4O_7 :Dy. Diffraction patterns were obtained using CuK α radiation ($\lambda = 1.54051 \text{ \AA}$), at 30kV and 15mA. Measurements were made from $2\theta = 10^\circ$ to 80° with steps of 0.02° . The XRD patterns of the powders revealed that the structure of SrAl_4O_7 is Monoclinic, which matches with JCPDS data card No. 25-1289. The crystallites are less than approximately 50-90nm in size, appreciable broadening in the X-ray diffraction lines. SEM images of SrAl_4O_7 :Dy, which is non-uniform and may be due to the formation of fractal, attributed to sort of self organization. SEM image of SrAl_4O_7 sintered at 900°C for 3hrs appears to irregular shape.

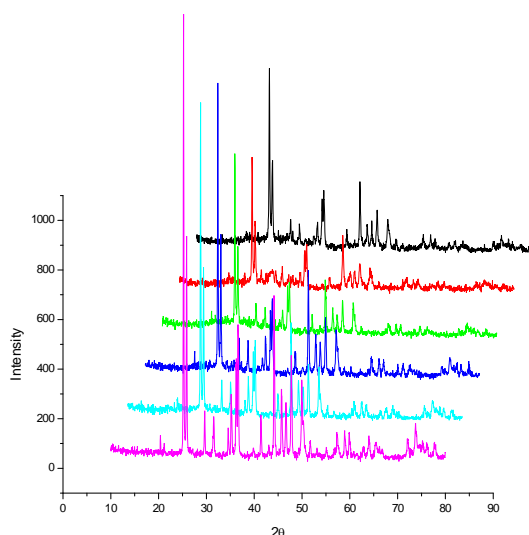


Fig. 1 XRD patterns of SrAl₄O₇:Dy

2. SEM Analysis :

The SEM study is carried out to investigate the surface morphology and the average crystallite size of the synthesized phosphors. Fig. 2 shows the representative SE Micrographs taken for SrAl₄O₇ : Dy phosphors at different Dy concentrations. Generally the particles are of irregular shape. SEM was used to study the surface morphology of the films. A representative micrograph of the film is shown in Fig. 2. The micrograph also showed that the particles were interlinked with each other, leading to the formation of big crystals. Also, it is found that some irregular aggregations formed in the sample. The particle sizes are 80, 77, 78, 75, 40, 49 respectively.

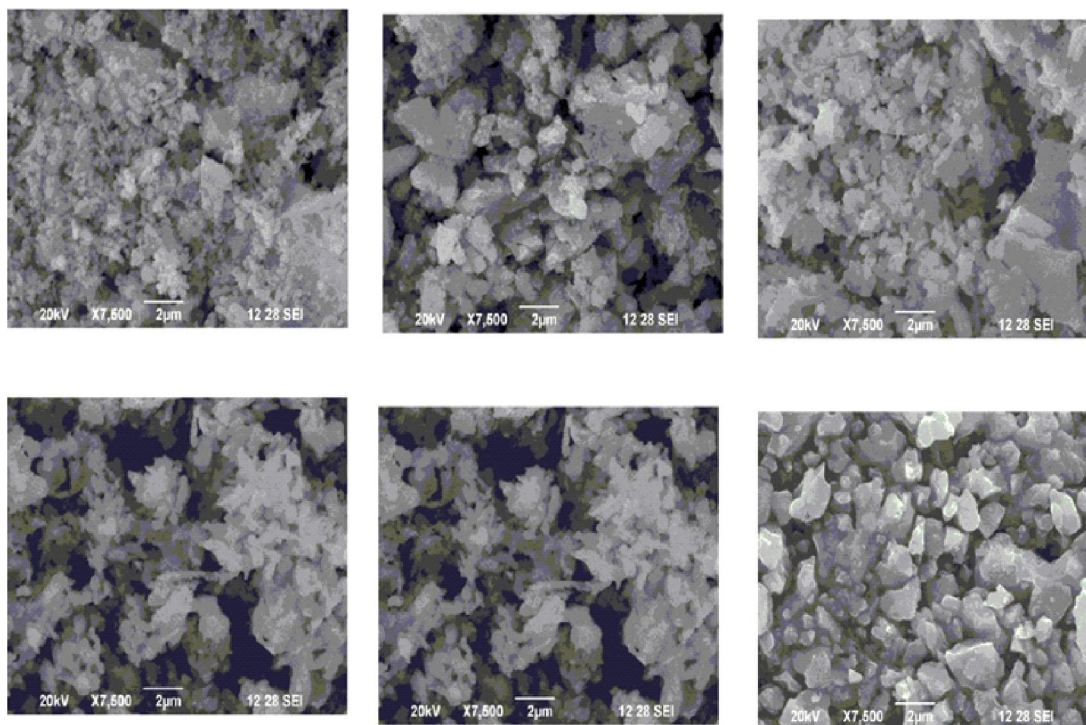


Fig. 2. SEM pictures of SrAl₄O₇:Dy

3. FTIR :

The FT-IR spectra of Dy doped SrAlO at 0.5%, 1%, 2%, 3%, 4%, and 5% of Dy are shown in Fig. 3. These shows typical metal-oxygen absorption peak at 857 cm^{-1} and 550 cm^{-1} . The strong IR absorption at 857 cm^{-1} indicates the stretching vibrations of Sr–O bonding and vibration peak at 550 cm^{-1} is attributed to Al–O bonding. The absorption peaks in the $550\text{--}850\text{ cm}^{-1}$ region are attributed to the SrAlO characteristic absorption corresponding to the Al–O stretching and bending modes in AlO_4 tetrahedral. There is a distinguishable and repeatable peak near 3540 cm^{-1} ; assigned to the stretching vibration of O–H on the films surface. As can be seen in figure, the six X-ray emission peaks at 0.53, 1.27, 1.50, 1.82, 6.52, 9.66 keV, 14.22 and 15.8 can be attributed to the characteristic X-ray emissions of O(K α 1), Dy(M α 1), Al(K α 1), Sr(L α 1), Dy(M α 1), Au(M α 1) & Au (L α 2) and Sr(L α 1) respectively. The Au element in the specimen was introduced in the process of Au sputtering for the SEM and elemental analyses. These data indicate that the Dy^{3+} ions have entered into the host SrAl_4O_7 .

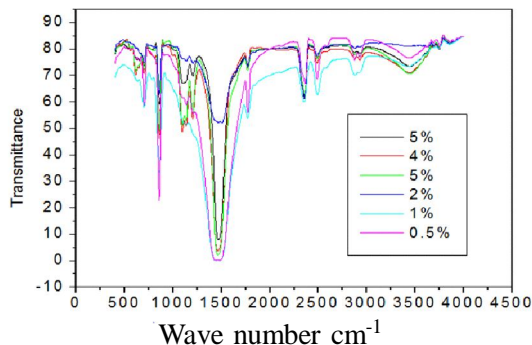


Figure. 3 FTIR spectra of Dy doped SrAl_4O_7 at different wt% of Dy.

4. DRS Spectrum :

The band gap energy (E_g) for the Dy doped Strontium Aluminate nanostructures were determined by the plot of the square of the modified Kubelka_Munk function vs. the photon energy ($h\nu$)⁸, shown in Fig. 4. The band gap can be obtained from a linear extrapolation of the absorbance edge to the wavelength axis. The band gap (E_g) of strontium aluminate samples are found to be in the range of 3.16 to 3.3 eV.

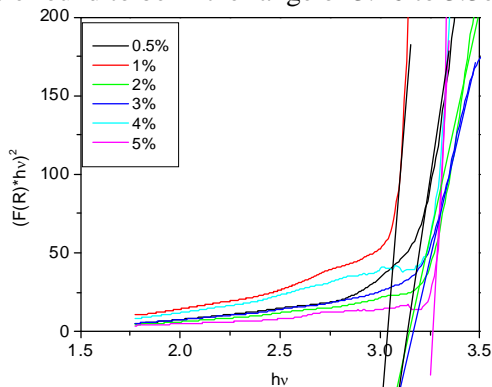


Figure 4. DRS spectra of Dy doped SrAl_4O_7 at different wt% of Dy.

5. Photoluminescence :

The photoluminescence spectra of SrAl_4O_7 :Dy nanoparticles under 360 nm excitation wavelength is shown in Fig. 5. The PL emission spectra of all samples exhibit three emission bands with corresponding peak wavelengths of 395 nm, 520 nm and 790 nm under excitation of 360 nm. The strong peak showing blue emission at 395 nm was due to the exciton emission, and weak green emission at 520 nm was due to oxygen interstitial. The strong UV emission corresponds to the exciton recombination related near-band edge emission of nanoparticles. The green emissions are possibly due to surface defects in the nanoparticles.

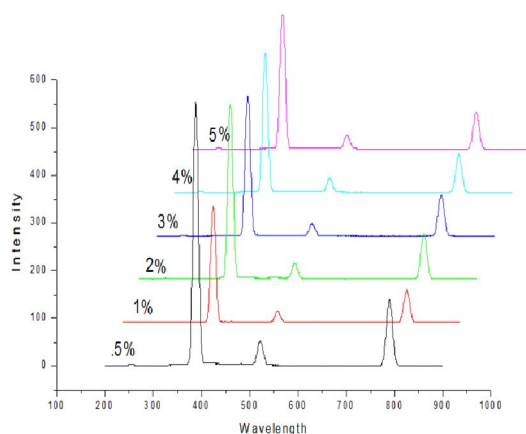


Fig. 5. Photoluminescence Spectra of Dy doped SrAl_4O_7 at different wt% of Dy.

The photoluminescence emission spectrum of SrAlO:Dy is shown in fig 5. which is obtained under the excitation wavelength 360nm. The spectra consist of three emission bands: a emission band at ~396 a week blue–green band at ~ 520 nm and a strong IR band at ~800 for SrAlO:Dy . The strong UV emission corresponds to the exciton recombination related near-band edge emission of nanoparticles. The weak blue and weak blue–green emissions are possibly due to surface defects in the nanoparticles. The week green band emission corresponds to the singly ionized oxygen vacancy in SrAlO:Dy . The low intensity of the green emission may be due to the low density of oxygen vacancies during the preparation of the nanoparticles, where as the strong room-temperature UV emission intensity should be attributed to the high purity with perfect crystallinity of the synthesized nanoparticles. It is well known that Dy doped strontium aluminates phosphors show long phosphorescence in green region. But in our case both samples doped or undoped give green emission peak at 520nm with 360nm excitation. The fact

that the emission characteristics are excitation dependent shows the emission mechanism is governed mainly by defect controlled processes. Further the emission does not arise from the activator ions (as seen in the undoped sample) suggesting that the defect centers act as trap levels in bringing out various emission features. To explain the decrease in photoluminescence intensity, we suggest that incorporation of Dy ions reduce the defects (exciton, oxygen vacancies), which act as sensitizers for energy transfer due to strong mixing of charge transfer.

Conclusion

The phosphors $\text{SrAl}_4\text{O}_7:\text{Dy}$ (at 0.5, 1, 2, 3, 4 and 5 wt% of Dy) with a monoclinic structure were successfully prepared by Sol-Gel method. The characteristic peaks of $\text{SrAl}_4\text{O}_7:\text{Dy}$ phosphors were observed and they are located at 395nm, 520nm and 800nm which are corresponding exciton emission and the oxygen interstitial. The luminescent intensity of Dy doped SrAl_4O_7 nanoparticles increases with increase in the Dy dopant concentration at first and then it decreases. The maximum intensity was achieved for about 1 mol% Dy^{3+} . The photoluminescence investigations reveals that the emission mechanism is governed mainly by defect controlled processes. The bandgap (E_g) of strontium aluminate samples are found to be in the range of 3.16 to 3.3 eV.

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