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SYNTHESIS AND OPTICAL PROPERTIES OF MN AND DY DOPED STRONTIUM ALUMINATE NANOPHOSPHORS

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Abstract: Luminescence investigations of Mn and Dy doped Strontium aluminate phosphors prepared through sol gel method. The prepared phosphors has been characterized by Powder X-ray diffraction, Scanning electron microscope, Optical properties were studied by photoluminescence analysis. Photoluminescence studies of the prepared phosphors showed prominent IR emission, green emission and UV emission.

INTRODUCTION

Rare-earth and non-rareearthdoped inorganic phosphors are widely used in a variety of applications, such as lamp industry, X-ray imaging, and colour display. Phosphors based on oxide matrices are attractive host materials for the development of advanced phosphors due to their ease of synthesis and stability. Rare earth doped aluminates serve as an important class of phosphors for fluorescent lamp and phosphorescence applications. Among the group Strontium aluminates are the most widely used members of the alkaline earth aluminates MAl_4O_7 (M = Ba, Ca or Sr) [1, 3]. They are commonly used as cements in a wide range of applications. Rare earth doped $SrAl_4O_7$ shows interesting luminescence properties [6–14] More specifically, $SrAl_4O_7$:Eu is one of the few materials exhibiting a long-lasting afterglow after excitation has ended, a phenomenon known as persistent luminescence [9,10,13]. Different kinds of techniques have been used to prepare $SrAl_4O_7$ such as solid state reaction, co-precipitation, microwave, and combustion and sol-gel synthesis. 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 $SrAl_4O_7$ and Mn and Dy doped $SrAl_4O_7$ via Sol Gel synthesis.

EXPERIMENTAL

Strontium aluminates phosphors were prepared by sol-gel synthesis method. All the reagents used in the experiments were in analytical grade and used without any further purification. Effects of the Mn and Dy on PL properties were investigated. The starting materials were Strontium acetate, Aluminum acetate and, Dysprosium nitrate, and 2methoxy ethanol as a solvent. 99% of 2M Strontium acetate [(CH3.COO)2 Ca.2H2O] with 1% of Aluminum acetate [C4H6AlO4.4H2O, and 1% of Manganese Nitrate for $SrAl_4O_7$:Mn and 1% of Dysprosium Nitrate for $SrAl_4O_7$:Dy were used as the precursors, the acetic acid and ethylene glycol were added 1:1 ratio to the precursor solution. The acetic acid used as the gelling agent and ethylene glycol act as reaction medium. The mixture was stirred 30 minuits magnetically at room temperature. The pH of the resulting solution was adjusted at 10.5 using ammonium hydroxide. After completion of the reaction, the solution was kept under constant stirring at 80˚C temperature using magnetic stirrer. After 2 hours white color viscous sols was occurred. The resultant sol gels were dried for 5 hours at 100˚C. The obtained powder was annealed at 950˚C for 2 hours to obtain $SrAl_4O_7$ nanopowders. The phase composition and phase structure were characterized by X-ray diffraction (XRD) pattern using Xpert PRO diffractometer with Cu Kα radiation ($\lambda = 1.5406\ A^0$) operating at 45kV, 40mA. The morphology and the composition of the products were examined by scanning electron microscopy (SEM, JSM-6390) equipped with an energy-dispersive spectrometry (EDS).

RESULTS AND DISCUSSION

Formation of these phosphors has been characterized by powder XRD. Fig.1(a-c) shows the representative powder XRD pattern for the $SrAl_4O_7$, $SrAl_4O_7$: Mn and $SrAl_4O_7$:Dy. It is reported that besides $SrAl_4O_7$ it was found that a pure monoclinic phase of parent $SrAl_4O_7$ is dominant in the XRD pattern (JCPDS.25-1289). The results proved that all phosphor samples prepared in this work are almost single $SrAl_4O_7$ phase, and the little amount of co-doped rare

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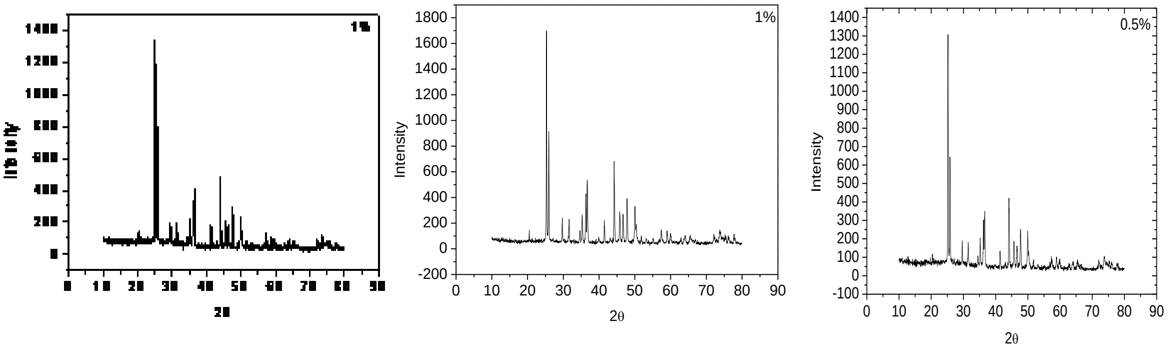
earth ions have almost no effect on the $SrAl_4O_7$ phase composition. The small amount of doped rare earth ions has virtually no effect on phase structures. The sharp peaks indicate that the $SrAl_4O_7$ nanoparticles (NP) were well crystallized.

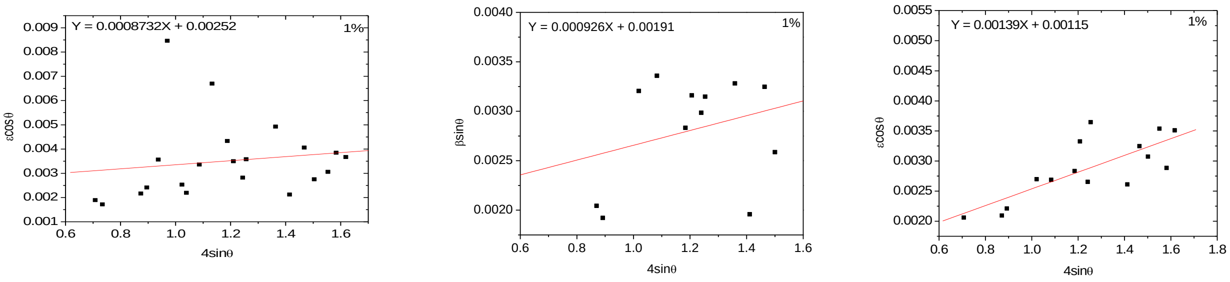


(a) (b) (c)

Fig.1(a-c):XRD patterns of (a) $SrAl_4O_7$ (b) $SrAl_4O_7$: Mn (c) $SrAl_4O_7$:Dy

The analysis of the crystallite size has been carried out using the broadening of the XRD peaks. Peak broadening comes from several sources, i.e. instrumental effect, finite crystallite size, and strain effect within the crystal lattice. Taking care of all the sources, crystallite size has been calculated using Williamson- Hall plot. Williamson and Hall plot is a classical method to obtain qualitative information of anisotropy in broadening. Williamson and Hall assumed that both size and strain. According to the Williamson-Hall method, the individual contributions to the broadening of reflections can be expressed as

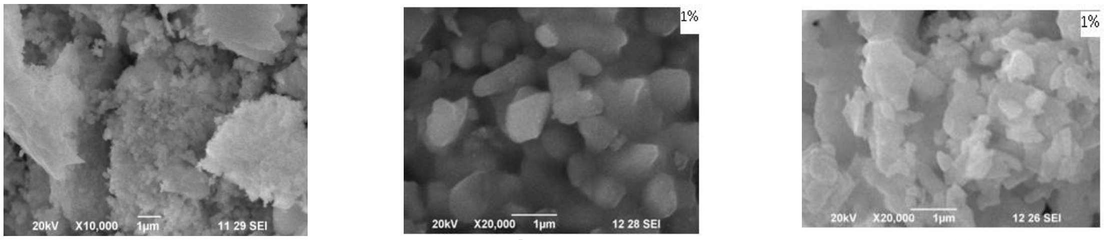
$$\beta_{hkl}\cos\theta_{hkl} = [K\lambda/D]+[4\square\sin\theta_{hkl}]$$



(a) (b) (c)

Fig.2(a-c): Williamson-Hall plots for (a) $SrAl_4O_7$ (b) $SrAl_4O_7$: Mn (c) $SrAl_4O_7$:Dy

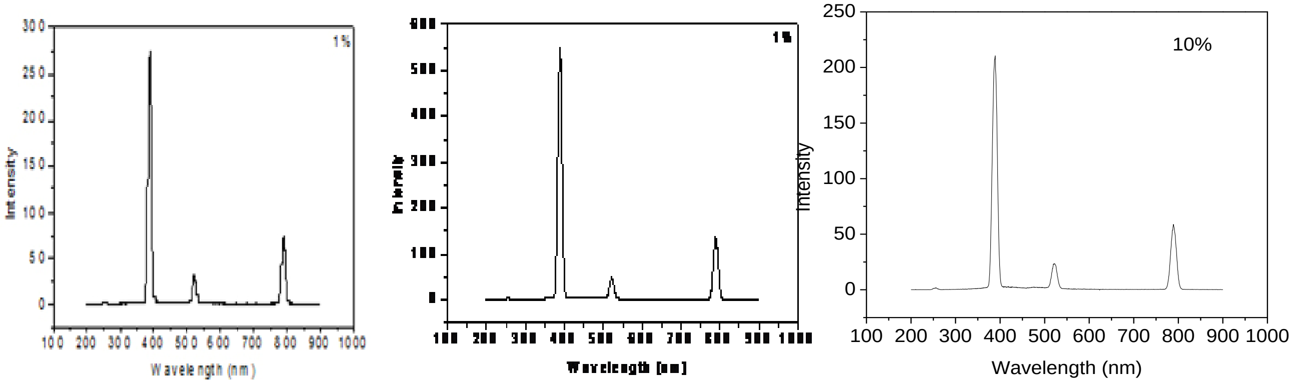
A plot is drawn with 4sinθ along the x-axis and βcosθ along the y-axis for as prepared $SrAl_4O_7$ and $SrAl_4O_7$: Mn, Dy nanoparticles as shown in Figure 2(a-c). From the linear fit to the data, the crystalline size was estimated from the y-intercept, and the strain ε, from the slope of the fit. Quantitative data obtained from the Williamson-Hall plot indicated that the average particle size attained for $SrAl_4O_7$, $SrAl_4O_7$: Mn and $SrAl_4O_7$: Dy was 72.5nm 55nm and 120nm respectively.



(a) (b) (c)

Fig.3(a-c) SEM images of (a) $SrAl_4O_7$ (b) $SrAl_4O_7$: Mn (c) $SrAl_4O_7$:Dy

The surface morphology of material in the form of granular structure with round morphology and agglomeration were investigated with a scanning electron microscope. Fig.3 (a-c) shows SEM of $SrAl_4O_7$, and Mn, Dy doped $SrAl_4O_7$. It shows uniform distribution of pores with clusters of crystallites over the entire material. The Mn and Dy doping significantly change the appearance of the particles and morphology.



(a) (b) (c)

Fig.4(a-c) Emission spectra of (a) $SrAl_4O_7$ *(b)* $SrAl_4O_7$*: Mn (c)* $SrAl_4O_7$*:Dy*

The photoluminescence spectra of $SrAl_4O_7$, Mn doped $SrAl_4O_7$ and Dy doped $SrAl_4O_7$ nanoparticles under 360 nm excitation wavelength is shown in Fig.4 (a-c) respectively. The PL emission spectra of all samples exhibit three emission bands with corresponding peak wavelengths of 395 nm for exiton emission, 520 for green emission attributed to oxygen interstitial and 790 under excitation of 360nm. $SrAl_4O_7$: Mn nanocrystals are found to have increased photoluminescence efficiency associated with the magnetic impurity Mn^{2+}. For small particles like the $SrAl_4O_7$: Mn nanocrystals, majority of the Mn^{2+} ions are at the near-surface sites and occupy axial or lower symmetry sites.

CONCLUSIONS

$SrAl_4O_7$, $SrAl_4O_7$: Mn and Dy phosphor has been synthesized by the Sol Gel method. XRD patterns show the phase formation of pure $SrAl_4O_7$ phases. XRD analysis shows that the prepared compositions retain the monoclinic phase of $SrAl_4O_7$. The SEM images confirm the irregular particle shape that was produced from the sol gel method. The main peaks of emission spectra of the luminescent nanoparticles are at 395 nm, 520nm and 790 nm. This fundamental work might be important in developing new IR imaging devices.

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