SYNTHESIS AND CHARACTERIZATION OF $SrAl_2O_4$: Sm PHOSPHOR BY LOW TEMPERATURE SYNTHESIS

Ahalya H. G[1], B.H. Doreswamy[2], B.M. Nagabhushana[3]

[1]*Department of Physics, SJB Institute of Technology, Bangalore, Karnataka State, India*
[2]*Professor, Department of Physics, SJB Institute of Technology, Bangalore, Karnataka State, India*
[3]*Professor, Department of Chemistry, M.S. Ramaiah Institute of Technology, Bangalore, Karnataka State, India*

Abstract

The alkaline earth aluminate phosphor $SrAl_2O_4$: Sm synthesized by solution combustion method at low temperature (550˚C) using metal nitrates with oxalyne dihydrazine as fuel. This process results in large production of phosphor with low density, can be achieved within 5 minutes when compared to other conventional methods. The synthesized product was characterized by X-Ray Diffraction studies, Scanning Electron Microscope, Thermal studies, FTIR, Atomic Force Microscopy and UV-VISIBLE. XRD confirms monoclinic phase, Scanning Eectron Microscope prove that the nano phosphor is highly voluminous and porus. Thermal behaviour shows that loss of weight is less when compared to other methods. Atomic force microscopy shows that the particle size varies with calcination temperature. The average particle size without calcination is found to be 50 to 100nm. The band gap of nano phosphor found to be 5.18ev.

Keywords: *$SrAl_2O_4$: Sm, Alkaline Earth Aluminates, X-Ray Diffraction, Atomic Force Microscopy, TG-DTA*

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1. INTRODUCTION

Phosphor is a solid which converts certain type of incident energy into electromagnetic energy. The incident energy may be ultraviolet, ϒ radiation etc., which serves as the excitation source [1]. Certain nano powders are depending on the point defects hence small amount of dopant brings drastic change in color emission. Sm^{3+} activated $SrAl_2O_4$ is one of the best material to study phosphorescence due to high quantum efficiency in the visible region, long persistence, high brightness, best chemical stability when compared to sulphide materials [1-5]. In addition for the next generation display and lighting purpose these materials are under investigation [2, 3]. Generally rare earth doped aluminates have greater impact on defect centers within the band gap. The emission of light from ultra violet, visible and Infra red depends on the host material properties [3]. Many reports available on $SrAl_2O_4$: Eu^{2+}, Dy^{3+} and other rare earths can be used for cold lighting purposes. This is explained on the basis of trapping mechanism between ground state and excited state. Now a day's one dimensional inorganic nano structures attracts people because of their high end applications in electronics and optics [4]. Since the aluminate phosphors are very sensitive to humidity hence many research going on the strontium aluminate to improve water resistant properties [5,6]. The photo luminescence properties depend on phase of the material [7].

The alkaline earth aluminates [AEA] general formula is AB_2O_4. Where A is Sr^{2+} divalent atom. B is Al^{3+} trivalent cation. Which have corner sharing tetrahedral from six member ring [9].These materials can be synthesized by various conventional methods. The disadvantages of other than solution combustion Synthesis are they (i) requires high temperature, (ii) more time, (iii) obtained nano particle is of the order of micrometer, (iv) asymmetric distribution of the particles, (v) crushing of phosphor is very risky job, (vi)sample should be prepared in reductive atmosphere, (vii) poor homogeneity of the particles, (viii) requires high calcinations temperature [8,9]. When compared to other conventional methods Solution combustion synthesis (SCS) is one of the best method to improve luminescent properties to produce almost homogeneous nano crystallized fine powder. Due to endothermic reaction gases liberated by decomposition and depending on ratio of oxidizer to fuel ratio, requires very less synthesis time and low temperature [11,12]. In the present study we have synthesized $SrAl_2O_4$:Sm by Solution Combustion Synthesis and effect of calcinations temperature was studied along with different characterization. The detailed discussion is as follows.

2. EXPERIMENTAL PROCEDURE

2.1 Materials Used

All chemicals are from sigma Aldrich. Analytical grade aluminium nitrate $[Al(NO_3)_2.9H_2O]$, strontium nitrate $[Sr(NO_3)_2.4H_2O]$, $Sm(NO_3)$ and fuel oxalynie dihydrazine (ODH prepared in lab) were used as staring materials.

2.2 Preparation of Oxalyne Di Hydrazine Fuel

The ODH fuel can be obtained by mixing Diethyl Oxalate with Hydrazine Hydrate with double distilled water processing it in quartz container with ice cubes stirr it well. Put it aside for a day filter it then place it in hot air oven at 150˚ C for 24 hours.

2.3 Preparation of $SrAl_2O_4$: Sm

The redox mixtures taken in Stoichiometric ratio by calculating total oxidizing and fuel valency ratios that is $Ø_e$ = 1.The precursors are mixed in a dish with double distilled water. Stir the precursor well. Then the mixture introduced into 550 ^{0}C preheated muffle furnace. During the first step mixture melts, undergoes dehydration then the gases like oxides of nitrogen, carbon and ammonia were released. Because of exothermic process large amount of energy released during the reaction. The redox mixture catch up fire and burn with more brightness. During burning the foam further swells to the rim of container. The entire combustion process completes within 5 to 6 minutes. The flame temperature is as high as 1400˚C to 1600˚C, converts the vapour phase of oxides into mixed aluminates. The flame persists for nearly 40 seconds. The product is milled a fine nano low density powder can be obtained.

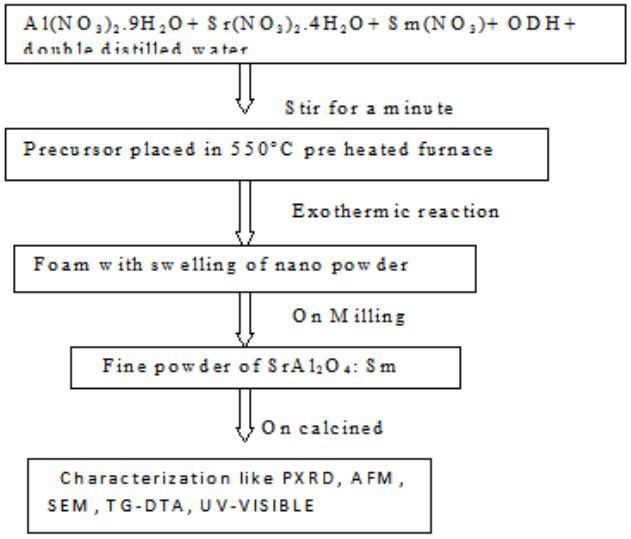

Fig 1 $SrAl_2O_4$: Sm preparation flow chart

2.3 Instrument Description

Powder XRD data of the phosphor was collected from Rigaku- D X-ray diffractor (40kV, 35mA) using Cu/Kα radiation (λ = 1.5418Å) continuous scan at the rate of 10˚/min. The particle size and morphological investigations of phosphor prepared in the process carried out with a scanning electron microscope (SEM, LEO 440 System). TG /DTA measurements with TG209F3 Tarsus. AFM studies carried out with non contact mode AF60, FTIR spectroscopy recorded with an IR spectrometer Model EQUINOX55, Bruker Co. Germany using KBr discs. the UV-Visible instrument was DU 640 spectrometer.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction Studies with Calcination Effects

To know the crystalline structures of $SrAl_2O_4$:Sm calcined for 3 hours at different temperatures (500°C, 700°C, 900°C). X-Ray Diffraction studies were carried out at room temperature. Fig 2 shows the XRD patterns of $SrAl_2O_4$:Sm. The reflections can be indexed to $SrAl_2O_4$: Sm monoclinic phase. The XRD peaks matched with JCPDS 34-0379 with lattice parameters a = 8.442 Å, b = 8.822 Å, c = 5.160 Å and β = 93.415 ^{0} [13]. The structure of low temperature phase has three dimensional network of corner sharing AlO_4[14]. Average size of the particle found to be 65nm which is calculated from Debye - Schrieffer formula D= β Cosθ / 4Sinθ. Where β is the full width at half maximum.The impurity peaks at 25° might be due to $Sr_3Al_2O_6$ [17]. This is due to evolution of heat during combustion reaction. This shows the fuel is not enough to form the pure monoclinic phase due to low adiabatic temperature[18]. Another impurity peak at 32° is due to phase existence of precipitate of Aluminium hydrate in precursor solution. Due to increase of Amidic group (NH_2-). This group is effective on complex formation between metallic ions and fuel [19]. The as formed $SrAl_2O_4$:Sm was calcined for different temperatures 3 hours. It can be noted that there is no much difference between as formed and calcined. Hence it can be concluded that the compound has formed at the first step itself.

3.2 Scanning Electron Micrograph (SEM)

Fig 3 (a-d) shows SEM of strontium aluminate doped with Samarium prepared by solution combustion synthesis at different calcination temperatures for 3 hours. In case of combustion synthesis release of large volume of gases from mixed solution result in the production of fluffy form nano particles. The grain boundaries with complete morphology can be seen [15].The wide particle size distribution as well as irregular shapes of the particles probably due to non uniform distribution of temperature and mass flow in the combustion wave [16]. The nano structured materials usually have large surface area hence they possess the properties which differ from bulk materials due to quantum confinement effects [11]. More voids were observed that is due to evolution of gases during combustion reaction. SEM images have taken for different calcination temperatures. The particles are almost spherical. As the calcination temperature increases bigger size particles observed due to agglomeration effect.

3.3 Thermal Studies of $SrAl_2O_4$: Sm

The thermal behaviour of solution combustion synthesised solid nano powder was studied. The plot of Thermo Gravimetric Analysis and Differential Thermal Analysis is as shown in Fig 4. Thermo gravimetric Analysis (TGA) gives the information about amount of weight loss and Differential Thermal Analysis (DTA) rate of change in the weight of a material as a function of temperature or under a controlled atmosphere..In case of $SrAl_2O_4$:Sm TG curve shows 3 distinct weight loss steps. The first step weight loss observed to be 2.4% from 30 ^{0}C to 200 ^{0}C this is due to dehydration. In sol gel method weight loss is 5% due to dehydration [8]. First step weight loss is less in combustion when compared to other methods like solution gel and solid state methods. The second step weight loss is from 200 ^{0}C to 700^{0}C that corresponds to the decomposition. The sharp and intense exothermic peak was observed at 295^{0}C in

Differential Thermal Analysis curve. The weight loss associated from 200 ^{0}C to 700 ^{0}C is 7.7% that is due to decomposition. The loss of is due to oxidation. In this steps more amount of gases such as nitrogen dioxide released.7.7% .No other peak observed in DTA it shows no residue organics in ashes hence the prepared sample is pure enough. From the graph we can deduce that during combustion process of the compound decomposition and auto combustion of sample takes place.

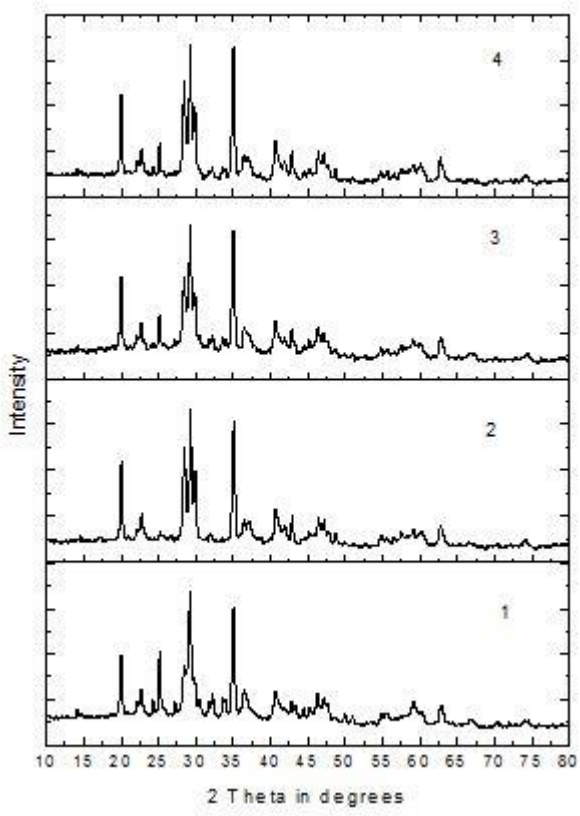

Fig 2 XRD of as formed and at different calcination temperatures.

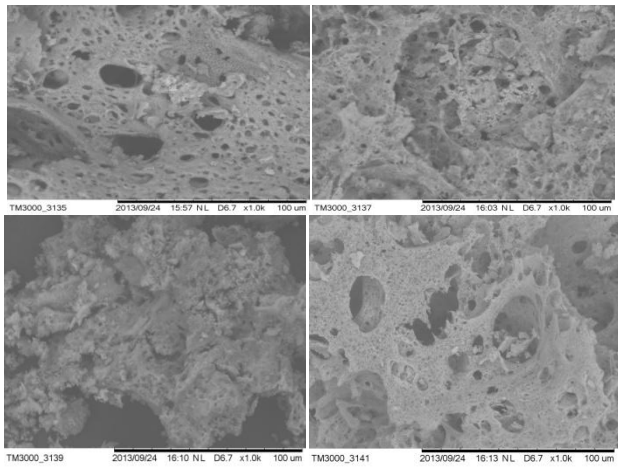

Fig 3 SEM of as formed and calcined images

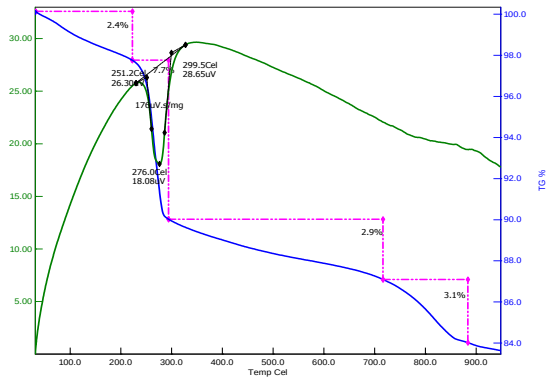

Fig 4 TG and DTA of $SrAl_2O_4$: Sm

3.4 AFM Studies

Atomic Force Microscopy with non contact mode results of as formed reveal that strontium aluminates doped with Samarium have an average particle size observed to be from 50 nm to 100 nm. The calcined phosphor shows agglomeration of nano particles whose size comes out to be 100nm to 300nm Fig 5 (a and b) shows 2 d and 3 d images of nano phosphor.

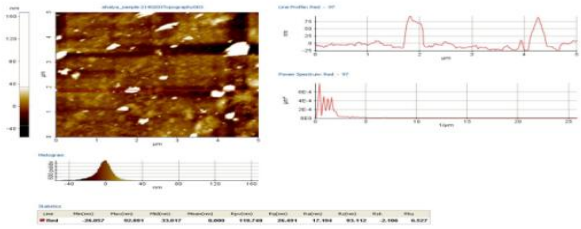

Fig 5 (a) 2 d AFM of $SrAl_2O_4$: Sm

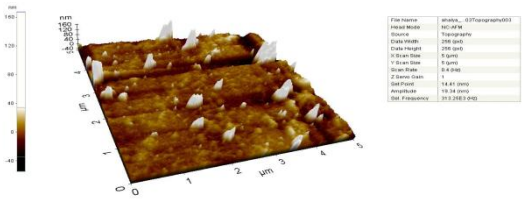

Fig 5 (b) 3 d AFM of $SrAl_2O_4$: Sm

3.5 FTIR of 500˚C Calcined $SrAl_2O_4$: Sm

The FT-IR spectrum of $SrAl_2O_4$:Sm calcined for 3 hours 500˚C powder sample is shown in Fig 6. The bands between 350 and 1000 cm^{-1} can all be assigned to Infra Red active vibration modes of $SrAl_2O_4$:Sm 500^{0}C calcined phosphor. Symmetric bonding of O-Al-O appears below 500 cm^{-1} the anti symmetric stretching bands range from 588-845 cm^{-1} is due to the Sr-O vibrations. The bands at 782 and 900 cm^{-1} is from aluminates group (AlO_4). The band at 1471 cm^{-1} is C-O vibration band. The band located at 3744 cm^{-1} is –OH group symmetric vibration.

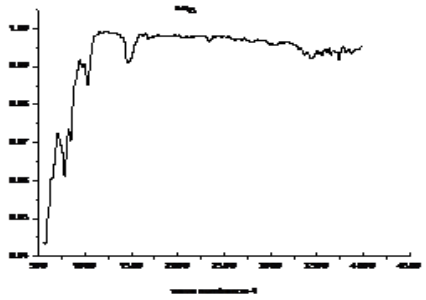

Fig 6 FTIR of 500˚C calcined $SrAl_2O_4$: Sm

3.6 UV-Visible Absorption Spectra of 500˚C Calcined $SrAl_2O_4$: Sm

One of the important characterization to know the behaviour of nano powder is optical absorption spectra (90nm to 500nm). This is as shown in Fig 6. It is a measure of band gap between filled valance band and empty conduction band. An abrupt increase in absorption can be observed at 240nm. This is due to the energy gap. No absorption observed when wave length $\lambda > 400$nm. Hence band gap was calculated corresponding to 240nm using Beer Lamberts law which comes out to be 5.18ev.

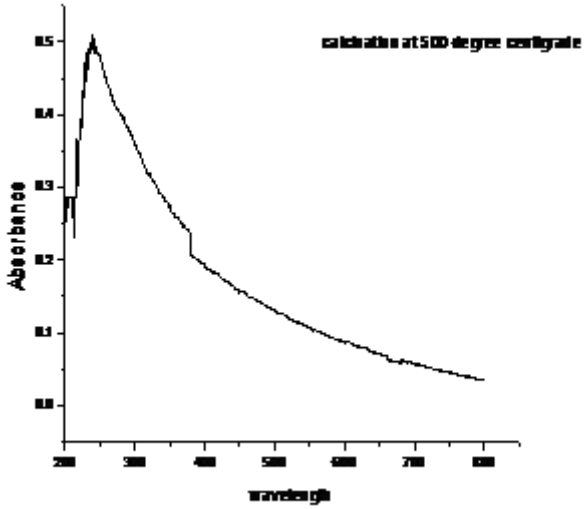

Fig 7 UV-Visible of $SrAl_2O_4$: Sm

4. CONCLUSIONS

$SrAl_2O_4$: Sm was successfully synthesized via Solution combustion synthesis from respective metal nitrates and fuel oxalyne dihydrazine. Well crystallized nano powders were obtained at 550˚C with in 5 minutes. The flame temperature is about 1400˚C to 1600˚C. The process of synthesis is very fast and energy efficient. XRD pattern verifies monoclinic phase with average size 65nm without calcination and 100 to 300nm with calcination verified by AFM. Thermal analysis proves the combustion technique has less loss of weight when compared to other methods. From TG/ DTA we can conclude combustion is better method when compared to other methods.UV-visible proves that the material is semiconductor with band gap 5.18ev.

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BIOGRAPHIES

Ahalya H.G, Research Scholar, VTU, Belgum having experience of 5 years in research field. Very much interested on metal oxide luminescent materials. Synthesizing new materials using solution combustion synthesis and other wet chemical methods. Testing Rare earth dopants for luminescence

Dr. B H Doreswamy obtained his Ph.D. Degree in Physics from University of Mysore. He is an active researcher and has published more than 40 research papers in reputed national and international journals. His fields of research are X-ray crystallography, Crystal

structure studies of materials of medical and biological interest. He is guiding 05 students for their Ph.D. Degree and presently heading the Department of Physics, SJB Institute of Technology, Bangalore.

Dr. B M Nagabhushana obtained his Ph.D. Degree in Chemistry from University of Bangalore. He is an active researcher and has published more than 140 research papers in reputed national and international journals. His fields of research in Material and nano science. He is guiding nearly 15 student. He is the secretary of Karnataka chapter Luminescence society of India. He has a research group of nearly 150 members.