International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.05 pp 926-931, 2016

Solution Combustion Synthesis of Single Phase Blue-White Phosphor Sr_2CeO_4

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Abstract : Sr_2CeO_4 is a blue white phosphor which has been recently identified by combinatorial technique and is proposed to be one of the potential candidates as a phosphor for use in lamps and field emission displays. There have been many reports on the preparation of Sr_2CeO_4 by various chemical methods in recent past. Here we report the synthesis and characterization of this blue white phosphor Sr_2CeO_4 using glycine- nitrate solution combustion method. X-ray powder diffraction confirms the formation of pure Sr_2CeO_4 phase crystallizing in orthorhombic structure after annealing at 1000°C for 12 hrs without any trace of impurities. The crystallite size calculated by using Scherrer formula revealed the presence of formation of nano crystallites. The SEM study revealed the presence of distributed particle sizes in the range of 0.4 to 2.0 micron with an average particle size of around 0.8μ. The photo luminescence spectra confirmed the formation of Sr_2CeO_4 phase with maximum emission intensity for sample prepared at 1000 at 470 nm. The present work shows that the phosphor can be prepared at relatively lower temperatures and can be used for many display applications.
Keywords: Combustion Synthesis, Photoluminescence, X-Ray Diffraction, Scanning Electron Microscopy.

Introduction

Luminescent materials have been explored for a long time and are still one of the major fields of materials research leading to different applications such as displays and luminescent devices [1]. A comprehensive summary of the progress in the field of phosphor materials has been reported by Chen et al [1]. Since oxide based phosphors are probably the best fitted materials under electron excitation, the development of Sr_2CeO_4 blue phosphor has opened a new frontier in this field. This blue white phosphor was first identified by Danielson et al. using combinatorial technique in the year 2000 [2].With an emission maximum at ~ 470 nm and long excited state lifetime, it is expected to be a potential candidate for field emission displays and lamps. The structure of Sr_2CeO_4 is an anisotropic structure which consists of one dimensional chains. These one dimensional chains are composed of edge sharing CeO_6octahedra separated by Sr atoms. These octahedras run parallel to the [001] crystallographic direction. The distance between two adjacent octahedras is 3.597 Å. The origin of luminescence in Sr_2CeO_4 has been assigned to the ligand to metal Ce^{4+} charge transfer [2]. The synthesis of Sr_2CeO_4 has been tried in past by different chemical routes. These methods involve conventional solid-state method [3- 6], Pechini method [7], chemical co-precipitation technique [8-9], microwave calcinations and pulsed laser deposition [10], ultrasonic spray pyrolysis [11], carbonate-gel composite technique [12], and citrate-gel method [13].The effect of particle size [9,13] and substitution of rare earth ions such as Eu^{3+}, Yb^{3+}, Sm^{3+}etc has also been studied from the view point of increasing the emission intensity without affecting the excitation wavelength [14-15]. One of the advantages of low particle size is that it can enhance the packing density. Enhancement in the packing density then can lead to high flux density. Synthesis using the

conventional solid-state route does not give control over phase purity, particle size, crystallinity and morphology. The preparation of Sr_2CeO_4 using the conventional solid-state method involves a heat treatment at temperature above 1100^oC which is higher than low temperature methods [6].

Combustion synthesis has been used recently for the preparation of various nano materials because it is one the simple, versatile and rapid process for preparing nano materials. Apart from yielding nano materials, combustion synthesis also ensures formation of homogeneous powders with controlled doping in single step [16]. Chick et al. reported the synthesis of metal oxides such as ferrites, manganites and chromites by developing glycine-nitrate combustion synthesis [17]. This method of synthesis offers distinct advantages over other synthesis methods. Few advantages are homogeneous mixing of metal ions at the molecular level, thereby leading to homogeneous powders; less reaction time leading to synthesis of fine particles. In this method, fuels like glycine, citric acid, urea, glycerol etc. are used along with oxidizing agents like metal nitrates. Glycine has a zwitterionc character which allows effective complexation with metal ions of varying ionic sizes. In this method the amino acid glycine plays two major roles. One is a complex formation with the metal ions involved. Here glycine acting as a bidentate ligand. Secondly it increases solubility of metal ions and thus avoids selective precipitation. The two different end groups i.e., the carboxylic group and the amino group can be utilized for complex formation. The combustion process is a self-sustainable process and the high temperatures are achieved due to the exothermic nature of the reaction ensuring the formation and crystallization of oxides. This method has been effectively used for synthesis of semiconducting and magnetic oxides [18-19]. Here we report the synthesis of blue white phosphor Sr_2CeO_4 using glycine-nitrate combustion method. Characterization of the obtained powder was carried out using X-ray diffraction, SEM and Photoluminescence spectroscopy.

Experimental

The starting materials Strontium nitrate $Sr(NO_3)_2$ and Cerium nitrate $Ce(NO_3)_3.6H_2O$were dissolved in distilled water in order to keep the Sr:Ce ratio 2:1 and glycine solution was then added to this mixture. The concentration of glycine was kept as 2 moles of glycine per mole of metal ion. This aqueous solution containing of metal nitrates and glycine was then evaporated on a hot plate at around 200 °C till it formed a thick mass, which subsequently burned by auto-combustion process to give a fine powder. The fine powder thus obtained after combustion process was further annealed at 800°C, 900°C, 1000°C and 1110°C for 12hrs in order to study the phase formation. X-ray powder diffraction data were collected using Philips PW-1830 diffractometer. Scanning electron micrographs were observed using a Leica Cambridge 440 microscope. Photoluminescence spectra were recorded atroom temperature with an excitation wavelength of 350 nm.

Results and Discussion

Figure 1 shows the comparison of simulated powder diffraction of Sr_2CeO_4 with the powder diffraction pattern of the samples annealed at different temperatures for 12 hrs. The sample annealed at 900°C exhibited the Sr_2CeO_4 phase along with minor reflections for $SrCeO_3$ and CeO_2. It was observed that complete phase formation takes place only after heating the powder at 1000 °C and all other samples annealed at lower temperatures showed the presence of minor secondary phases such as CeO_2 or $SrCeO_3$ perovskite phase along with the reflections for Sr_2CeO_4 which is in agreement with previous reports [3, 9]. The x- ray powder diffraction pattern for sample annealed at 1000 °C for 12 hrs confirms the formation of single phase Sr_2CeO_4. In this case no secondary phases such as $SrCeO_3$, CeO_2, and SrO were detected. All the reflections were found to be corresponding to the pure Sr_2CeO_4 which can be indexed on an orthorhombic pattern with lattice constants a = 6.1190, b = 10.3490, c = 3.5960, which are in agreement with the values reported by Danielson *et al.* [3]. Thus formation of single phase Sr_2CeO_4 at 1000 °C with a reduction in heating time as compared to conventional solid-state route is one of the advantages of glycine nitrate combustion method used for synthesis here. This is one major advantage in comparison to other synthesis methods reported in literature. For example by using co-precipitation method to obtain single phase of Sr_2CeO_4, the temperature as high as 1300°C was required with dwell time of 24 hrs [9]. Whereas the other methods like spray pyrolysis [11] and citrate gel method [13] have been reported to be un successful for synthesis of pure phase Sr_2CeO_4.

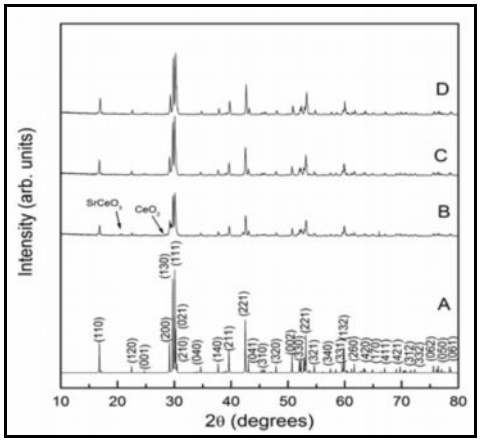

Figure 1. X-ray diffraction pattern of Sr_2CeO_4 Simulated B) Annealed at 900 °C for 12 hours, C) Annealed at 1000°C for 12 hours and D) Annealed at 1100 °C for 12 hours

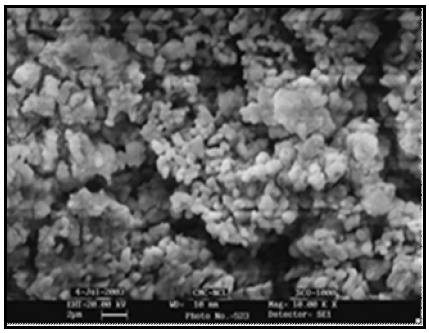

Figure 2. SEM image of Sr_2CeO_4 particles annealed at 1000 °C

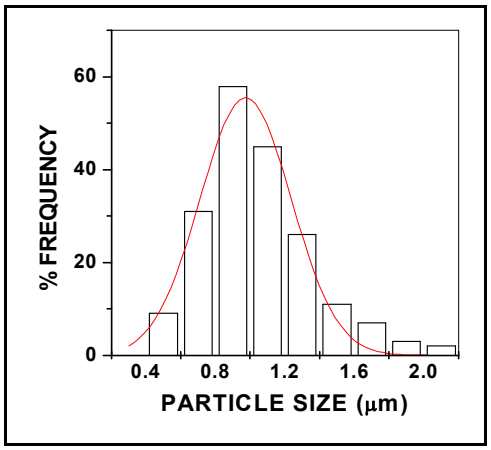

Figure 3. Grain size histogram of the Sr_2CeO_4 particles fired at 1000 ^oC

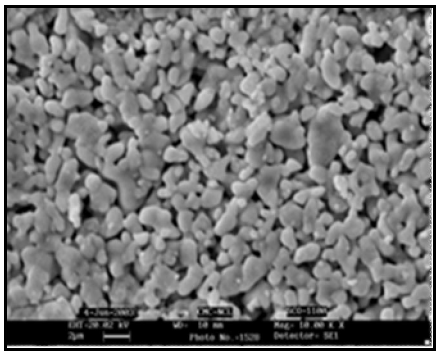

Figure 4. SEM image of Sr_2CeO_4 particles fired at 1100 ^oC

The average crystallite size for the powders annealed at different temperatures were calculated using Sherrer's formula $D = 0.9\lambda/\beta\cos\theta$ where D is the crystallite size, λ is the wavelength, β is the FWHM and θ is the diffraction angle. Using this crystallite size obtained for different samples is shown in table 1. As evident from the data presented, the crystallite size increases with increase in annealing temperature.

Table1. Crystallite size of Sr_2CeO_4 powders annealed at different temperatures

Annealing Temp (°C)	Crystallite Size (nm)
800	49
900	72
1000	86

The SEM image of the Sr_2CeO_4 particles annealed at 1000 °C and 1100 °C is shown in figure 2 and figure 4. The particles synthesized by solution combustion method were granular and the diameters were less than 1 μm. The sample annealed at 1000 °C showed that many particles exist individually and a few are agglomerated. The particles annealed at 1100°C clearly showed that the agglomerations have reduced with almost individual particles existing. Also the density has increased as compared to the sample annealed at 1000°C. The reduction in the particle could assist in providing efficient packing density.

Figure 3 shows the size distribution histogram of the Sr_2CeO_4 particles annealed at 1000 °C. The particles obtained by solution combustion method are fine and are having a narrow size distribution. The average particle size of 0.8 μm was observed. The narrow size distribution and a particle size in the sub-micrometer range can give higher packing density as compared to the particles prepared by conventional method.

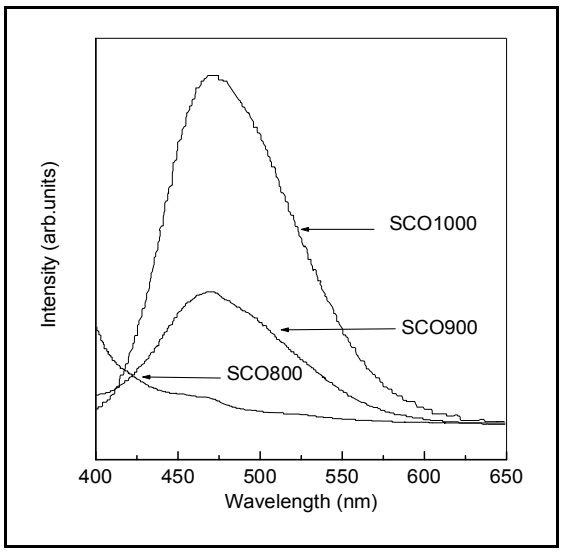

Figure 5. Room temperature Photoluminescence spectra of the samples annealed at 800°C, 900 °C and 1000 °C

Figure 5 shows the room temperature Photoluminescence spectra of the samples annealed at 800 °C, 900 °C and 1000 °C respectively recorded with an excitation wavelength of 350 nm. It is quite clear from the above spectra that, a broad emission is observed at 470 nm in the blue region which is characteristic of Sr_2CeO_4. It is in agreement with the previously reported values [14]. The emission intensity goes on increasing with the increase in the annealing temperature. For the sample annealed at 800 °C only a small hump is observed around 470 nm indicating the presence of other impurity phases seen from XRD. In the case of the sample annealed at 900°C a broad emission peak corresponding to Sr_2CeO_4 is observed at 470 nm indicating that the major phase is Sr_2CeO_4. The sudden rise in the emission intensity for the sample annealed at 1000°C as compared with the other two samples could be attributed to enhanced crystallinity of the sample as compared to powder prepared

at lower temperature. It also confirms the pure phase formation after annealing at 1000°C. In order to check the single phase nature of the sample annealed at 1000°C, we varied the excitation wavelength. The emission wavelength was found to remain the same around 470 nm irrespective of the excitation wavelength again indicating the phase purity of our sample.

Conclusions

Synthesis of blue white phosphor Sr_2CeO_4 has been successfully carried out using glycine-nitrate solution combustion method. The obtained powder showed complete phase purity. Pure phase Sr_2CeO_4 with significant decrease in heating time can be obtained at a lower temperature of 1000 °C as compared to previous reports. The particles obtained are of fine nature and agglomerated with an average particle size of 0.8 μm. Increasing the calcination temperature of the powders led to increased particle size. Small particles with uniform distribution are advantageous from the point of view if better packing density is required for application purpose.

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