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Role of rpm on the synthesis of Sol-Gel Derivate BSO Thin Films

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Abstract - *In this work, we reported the synthesis of Bismuth Silicate ($Bi_4Si_3O_{12}$)(BSO) thin films on glass substrates by the sol-gel technique at different rpm 1500, 2000, 2500 and 3000 rpm for the 30s and annealed at 700ºC. The structural, optical, luminescence and morphological properties of the prepared thin films have been studied by X-ray Diffraction, UV-Vis spectroscopy, photoluminescence (PL) spectroscopy and SEM. XRD pattern of the films showed polycrystalline body centred cubic structure with (310) (321) plane growth orientation[1]. The absorbance of the film decreases with increasing wavelength and the transmittance was generally high in UV region. The energy band gap was found to be in the range of 3.54-3.75eV[2]. The thickness of the films decreases with increase in rpm. PL spectra of all the films are shown yellow emission at 575 nm under the excitation of 405 nm[3]. Surface morphology of the coated films was noticed by means of Scanning Electron Microscopic (SEM) technique.*

***Key Words*: Ferroelectric thin film, Bismuth silicate, Alkali earth metals**

1.INTRODUCTION

Bismuth silicon $Bi_{12}SiO_{20}$(BSO), belong to the selenite family, with the general formula $Bi_{12}MO_{20}$ where (M=Si, Ge, Ti, Pb, Mn, $B_{1/2}$,$P_{1/2}$). BSO is a stoichiometric selenite with a fully occupied oxygen sub lattice that meets all the major criteria for application as a low sintering temperature (Ts=850ºC)[1]. Among these, Bismuth silicate, $Bi_4Si_3O_{12}$(BSO) has attracted a great deal of interest due to its excellent properties such as high hardness, large specific heat, small thermal expansion, high optical damage threshold, and high optical transmittance[2-5], good mechanical, thermal, electrical and electro-optical properties, it also exhibits good photoconductivity in the near ultraviolet spectral range[6]. The nonlinear optical characteristics of BSO have been used in a variety of applications, i.e., spatial light modulators, hologram recording devices and photorefractive incoherent-to-coherent optical converters [7-8]. $Bi_4Si_3O_{12}$(BSO) scintillation crystal has potential use in medical imaging, high-energy nuclear physics experiments [9-11]. Recently, rare earth ion-doped bismuth silicate has been studied due to its excellent luminescent properties and potential application in white LEDs [12-15]. It has excellent prospects as a luminescent substrate because of its special features and great chemical and physical stability [16-18].

$Bi_4Si_3O_{12}$(BSO) thin films have already been successfully synthesized by chemical vapour deposition[19], pulsed laser deposition[20], dip coating method[21] and sol-gel process[22-24]. Among these, the sol-gel technique has many advantages over other synthesis techniques; such as excellent control over chemistry, homogeneity, purity and crystalline phase[25]. In this work, we report on the preparation of $Bi_4Si_3O_{12}$(BSO) thin films using sol-gel spin coating technique and the effect of spin speed on structural, optical, luminescent and surface morphology of the prepared BSO thin films.

2.MATERIALS AND METHODS

Synthesis of BSO ($Bi_4Si_3O_{12}$) thin film by sol gel method deposited on glass substrates from a solution of bismuth nitrate using spin coating method. An appropriate amount of Bismuth nitrate was firstly dissolved in the 5 ml of acetic acid with a magnetic stirrer for 30mins, which was followed by the addition of 0.25 ml of Tetraethyl orthosilicate and 5 ml of 2-Methoxyethanol under constant stirring for 1h. The sol was then deposited onto glass substrates using the spin coating system. The spin speed has been varied in steps of 1500 rpm, 2000 rpm, 2500 rpm and 3000 rpm. Each layer was heated on pre-sintered for 30 mins at 250ºC for drying process in the closed furnace. These deposition and drying process was repeated 10 times to get the appropriate film thickness. Finally, all the deposited BSO thin films were subjected to annealing process at 700ºC for 2h to change amorphous to a crystalline structure.

The prepared $Bi_4Si_3O_{12}$ (BSO) thin films were subjected to XRD, UV-Visible, Photoluminescence and SEM analyses. The crystallites of the BSO thin films obtained by increasing spin speed were characterized by X-Ray Diffraction (XRD) using X'PERT PROX-ray diffractometer which was operated at 40 KV and 30 mA with CuKα_1 radiation of wavelength 1.5407Aº. The thickness of the film has been measured using Stylus profilometer. Optical properties of the films were examined by UV-Visible and Photoluminescence Spectrophotometer. UV-Visible spectra were recorded in the range of 280-1100 nm by using Ocean optics HR 2000 spectrophotometer. The photoluminescence (PL) spectra were recorded using Varian

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Cary Eclipse with a xenon lamp as the light source at room temperature at an excitation wavelength of 200-900 nm. The surface morphology analysis was done by Vega 3 Tescan respectively.

3. RESULTS AND DISCUSSION

3.1 Structural properties

The XRD patterns of $Bi_4Si_3O_{12}$(BSO) thin films at a different spin speed such as 1500, 2000, 2500 and 3000 rpm and annealed at 700ºC were shown in fig.1. All the samples deposited on glass substrate were polycrystalline with orthorhombic structure and highly oriented preferentially along (321) and (310) planes in nature [26]. The diffraction peaks were indexed based on the body centred cubic BSO structure ICDD card n0:36-0287[27]. No other peaks were observed. The intensity of preferential orientation decreased with increasing spin speed, but its orientation did not change. It is happening since the large part of the solution of the BSO is throwing away from the substrate where it cannot avoid the centrifugal force of the rotational motion. And if the BSO thin film deposited on the substrate is increased then the probability to form a crystal orientation is large[28]. Shortly, if the spin speed is too high, the solution will not stay on the surface and will spread out of the films, the film will be very thin. Similarly, if the spin speed is very short, the solution will not reach to the boundaries of the substrate, the fill will be very thin. However, if the spin time is very high it will also have a negative impact on film morphology. Therefore, there must be a balance between spin speed, acceleration and spin time[29].

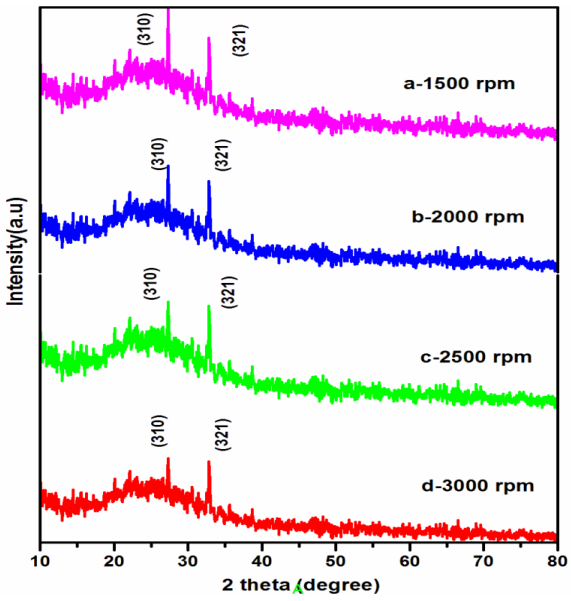

Fig -1 XRD patterns of the BSO thin films annealed at 700ºC(a-1500, b-2000, c-2500, d-2500 rpm) respectively.

The average thickness of the films was measured using stylus profilometer are 172.74nm, 143.7nm, 98.62 nm, 78.42nm, for spinning speed rate of 1500, 2000, 2500 and 3000 rpm., respectively. Fig 2. Plotted the film thickness versus spinning speed. As appeared in figure 2, the higher the spinning speed, the thinner the film. This shows that increasing spin speed decreased the thickness of the film. The relation between film thickness h, and spin rate ώ, obeys the power law relation of the form $h \alpha \omega^{-3/2}$[30].

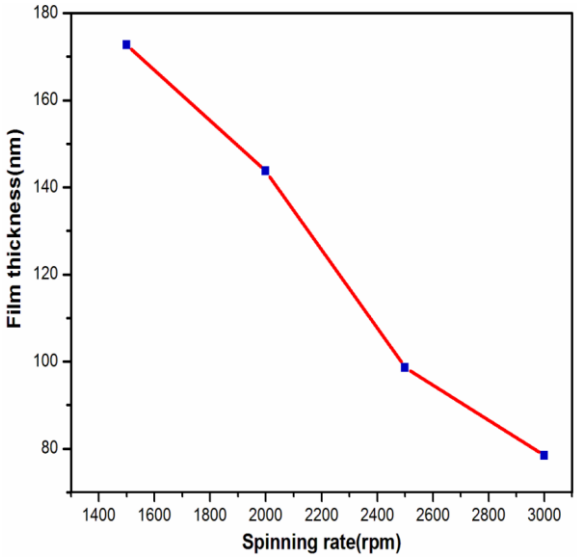

Fig -2 Film thickness as a function of a spinning rate

The average particle size, dislocation density and strain were calculated for as prepared samples with increasing spinning speed shown in table 1. The full width at half maximum (FWHM) of the intense diffraction peaks was used to calculate the crystalline size of the prepared film using the Debye-Scherrer formula

$$D=0.9\lambda/\beta \cos\theta \quad [1]$$

Where,

λ = 1.5407 Å
β = Full width Half maximum
θ =Diffracting angle

The dislocation densities and strain of the prepared films are calculated by the below equation(2) and (3)

$$\delta = 1/D^2 \text{ (lines/m}^2\text{)} \quad [2]$$
$$\varepsilon = \beta/4 \tan\theta \text{ (lines/ m}^2\text{)} \quad [3]$$

The intensity of the plane get decreases as the spinning rate increased from 1500-3000 rpm, might be to the increase of the particle size, decrease in dislocation density and decrease in strain. This is clearly observed from Table.1. The intensity of the plane get decreases as the spinning speed increased from 1500 rpm-300rpm, might be to the

decrease of the particle size, increase in dislocation density and increase in strain. This is clearly observed from Table.1

Table -1: Structural parameters of the prepared BSO thin films with different spinning speed

Sample Name	Particle size D (nm)	Dislocation density ($\times 10^{14}$) (lines/m^2)	Strain ($\times 10^{-3}$) (lines.m^{-4})
a	46.25	0.4670	3.01
b	43.95	0.517	3.15
c	42.11	0.5640	3.34
d	33.86	0.8974	4.143

3.2 UV-Visible spectroscopy

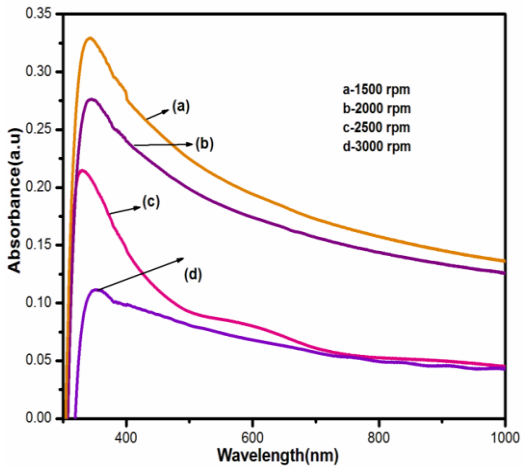

Fig -3: Absorbance spectra of the BSO thin films annealed at 700ºC(a-1500, b-2000, c-2500, d-2500 rpm) respectively.

The spectral distribution of absorbance and transmittance was measured in the wavelength range 300-1100 nm for the BSO films deposited on a glass substrate with increasing spin rate such as 1500, 2000, 2500 and 3000 rpm are shown in fig(3.3,3.4). From fig 3.3, it is found that in the visible region, the films have shown good absorbance. In the IR region, the absorbance decreases and the films became transparent. From the optical transmittance spectra (fig 3.4) the percentage of transmittance is found to increase from 70% to 82% with increasing spin rate. The highest transmittance was obtained by 3000 rpm about 82% in the visible wavelength region. The increase of transmittance can be explained by the reduction of light scattering in the film which was caused by the lower thickness[31].

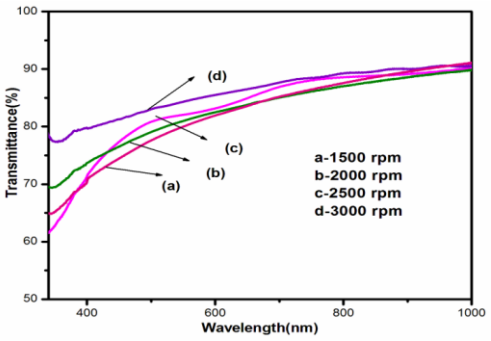

Fig -4: Transmittance spectra of the BSO thin films annealed at 700ºC(a-1500, b-2000, c-2500, d-2500 rpm) respectively.

The optical band gap for the prepared films has been calculated from the relation between absorption co-efficient and the incident photon energy. The optical absorption edge was estimated by the tauc law,

$$\alpha h\nu = A(h\nu - E_g)^n$$

where E_g is the band gap, α is the absorption co-efficient, δ is the frequency, A is the constant and n can take values n=1/2, 3/2 depending on the mode transition. Where E_g is the energy gap between the bottom of the conduction band top of the valance band at the same values of the wave vector. The optical bandgap is determined from the graph of $(\alpha h\nu)^2$ versus $h\nu$ which is plotted in fig.3.5. the intercept (extrapolation) of the straight line to $(\alpha h\nu)^2=0$ gives the direct energy band gap of the prepared sample. The energy gap varied from 3.5 to 3.8 eV it corresponds to previously reported in[32]. The band gap value shows an increased from (3.54-3.75eV) with increasing spin speed. In general, the value of optical energy gap increases as film thickness decreases, may be due to the fact that the values of band gap depend on many factors like coating speed(rpm), the granular structure, the nature and concentration of the precursors, the structural defects and the crystal structure of the films[33].

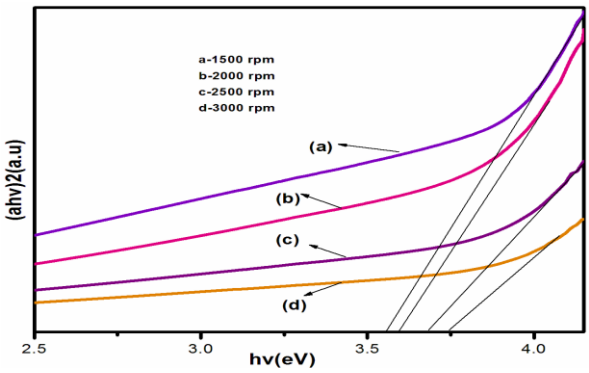

Fig -5: Band gap of the BSO thin films annealed at 700ºC (a-1500, b-2000, c-2500, d-2500 rpm) respectively.

3.5 SEM Analysis

Scanning electron microscopy is a promising technique for the analysis of surface texture and topography of the thin films, as it explores valuable information regarding the growth mechanism, shape and size of the particles and grains in the thin film. In the present study, Fig 3.6 (a-d). a) Quite uniform and dense, and well-defined pyramidal particles, with upturned, could be observed. b) Uniform distribution of porous with the aperture. c) Most of the particles on the substrate transformed into a face-up cubes. d) Well, adherent and porous cauliflower structure.

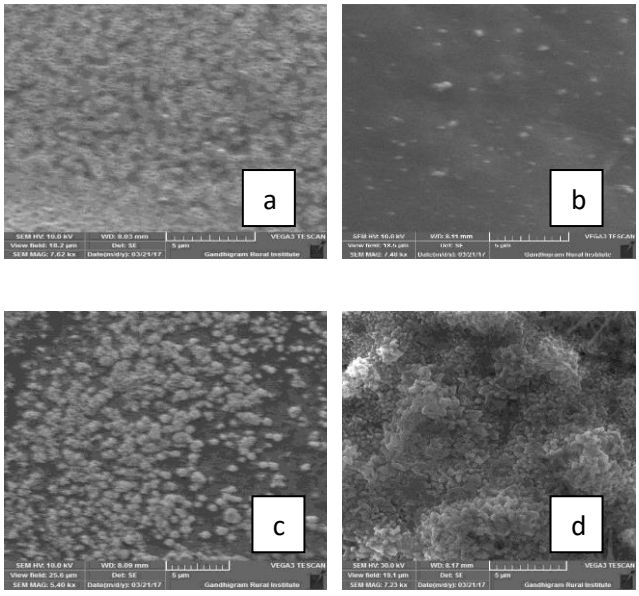

Fig -6 :SEM images of the BSO thin films annealed at 700ºC (a)1500 rpm, (b) 2000 rpm, (c) 2500 rpm, (d) 2500 rpm respectively

3.5 Photoluminescence studies(PL)

Photoluminescence spectroscopy is a non-destructive and high sensitivity tool, which is widely used to study photochemistry and photophysics and semiconductor materials in the photocatalysis field. In addition, PL can supply information such as lattice defects, grain boundary and surface oxygen vacancies as well as the separation and recombination of photo induced charge carriers. Fig 3.4 showed that PL spectra with range 400-700nm of the thin films prepared at different spin speed 1500, 2000, 2500 and 3000 rpm were carried out at an excitation wavelength of 405nm at room temperature. PL spectra showed a strong emission peak at 575nm is ascribed to the electron hole recombination of localized excitons which associated with oxygen vacancies can be a possible reason for this emission. The emission intensities for the BSO films increase with increasing spin speed indicates a higher recombination rate of photo-generated electrons and holes in the former case under UV radiation(34).

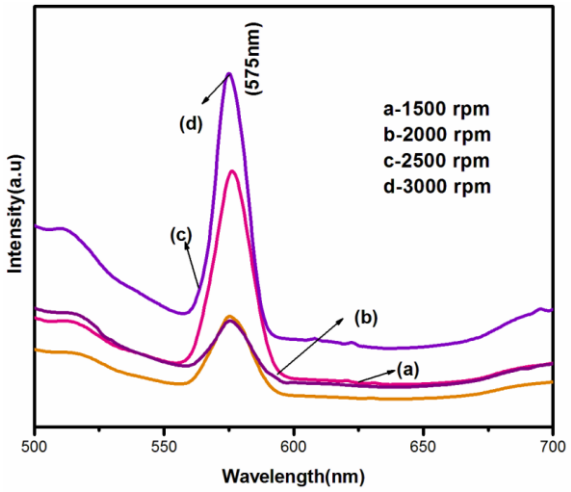

Fig -7: Photoluminescence spectra of the BSO thin films with different spin speed(a-1500rm, b-2000 rpm, c-2500 rpm, d-3000 rpm.

3. CONCLUSIONS

BSO thin films have been successfully deposited on a glass substrate using sol-gel spin coating method with the different spin rate at 1500, 2000, 2500 and 3000 rpm. The optical study revealed that the transmittance and the optical band gap increased. From the X-ray diffraction analysis the as prepared thin films are found to be a body centre cubic structure it was also observed that the crystalline size decreases but dislocation density, micro strain and the number of crystallites increased with increasing spin speed due to decrease in film thickness Photoluminescence spectra of BSO thin films revealed that strong emission observed at 575 nm. UV visible spectra exhibited that the transmittance increased from 70% to 82% and optical band gap of BSO thin films was also varied from 3.54 to 3.75 eV due to the increasing spin speed. Surface morphology of the coated films was noticed by means of Scanning Electron Microscopic (SEM) technique. These results confirmed that the spin speed clearly influences on the thickness structural and optical properties of BSO thin films. The higher spin speed rate shows the formation of the thinnest film. Lowest spin speed rate produces the thickest film.

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