Comparative Study of XRD Analysis of Bi_2S_3 Synthesized by Solid State Solvothermal Route and Precipitation Route

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Abstract **- Bismuth sulfide preparation and its X-ray diffraction studies are reported in this paper. In this study, we have synthesized Bi_2S_x (x = 3.15, 3.45) compound material with different Sulfur content by conventional high temperature solid state solvothermal reaction of Bismuth and Sulfur which confirms that the (121) preferred orientation. This paper also describes the synthesis and X-ray diffraction studies of Bismuth sulfide powder via versatile precipitation technique. Synthesized powder was characterized by X-ray diffraction technique which indicates that surfactants play major role in synthesis of Bismuth sulfide. The employed solid state solvothermal route played an important role to progress the homogeneous reaction and preparation of pure and fine Bi_2S_3 powder. The possible application of this material in photovoltaic devices is suggested.**

Keywords - Bismuth sulfide, Solid State Solvothermal Route, Precipitation route, XRD, Crystallite size.

I. INTRODUCTION

Bismuth sulfide (Bi_2S_3) is a typical lamellar structured semiconductor with a bulk direct band gap of 1.3 eV [1]. It has been the focus of attention, because of its unique physical and chemical properties and various technological applications such as in electrochemical hydrogen storage, hydrogen sensors, x-ray computed tomography imaging, optical switches, biomolecular detection, nanodevices and as photo-responsive materials [2-5].

The solid state solvothermal route is a well established approach for fabricating inorganic materials with desired micro/nano structures and controlled crystalline orientation. The advantage of this approach is it allows materials to be prepared at temperature substantially below those required by traditional solid state reaction route. In this paper we have synthesized Bi_2S_3 with different sulfur content as 5% and 15% in ampoule by conventional high temperature solid state solvothermal route [6-8]. It may be predicted that up scaling of this method will lead to large quantities of Bismuth sulfide with high purity and novel morphologies.

Chemical precipitation of nano-sized powder from salt solution is among the simplest techniques for rapid synthesis of large amount of material in a controlled manner [17]. This technique was used to precipitate metal sulfide powder. In the recent years, nano-sized particles gained importance in many field and can be produced bottom-up in liquids by means of precipitation [17, 18]. In the present work, Bi_2S_3 powder was synthesized using using Cetyl trimethyl ammonium bromide and Sodium dodecyl sulfate (SDS) or in the absence of any surfactant.

II. EXPERIMENTAL DETAILS

A. Solid state solvothermal route

The Bi_2S_x (x = 3.15, 3.45) compound with x = 3.15, 3.45 was synthesized by mixing analytical grade individual elements in quartz ampoules in which pressure of 10^{-2} mbar was achieved. The melting of elements mixed in ampoule was then carried out in an indigenous electric furnace at heating rate of 3K/min up to 1150 K. To ensure homogeneity of the melt holding at 1150 K is carried out for twelve hours. The melt was then cooled down to room temperature inside the furnace at a cooling rate of 4K/min. The solid ingot was then powdered to a mean particle size of ~100 µm using the process of grinding and then sieving.

B. Precipitation route

The prepared solution of 0.2 M Bismuth nitrate (Bi (NO_3) $5H_2O$) as cationic precursor and 0.2 M Sodium sulfide (Na_2S) as anionic precursor appropriately mixed to obtain proportion of 2:3. In a typical synthesis, 4.22 g ($Bi(NO_3)$ $5H_2O$) was dissolved in 25 ml (2N) nitric acid with 0.93 g Ethylene diamine tetra acetate (EDTA). Here, EDTA as a complexing agent plays important in controlled supply of the free metal ions for reduction and may be considered as a metal ion buffer. After the starting materials dissolves completely, the 50 ml 2.40 g Na_2S solution was added drop wise into Bismuth nitrate solution under vigorous stirring and 25 ml 1.82 g using Cetyl trimethyl ammonium bromide solution as a surfactant introduced into the homogeneous solution. The stir bath was maintained at 80° C for 12 h keeping pH of solution constant at 1.4 and settle down the sample for a day, then decant the sample. After that keep inside the fume-hood to remove volatile compounds until intermediate state is occur. The black product was holding at 60°C for 6-8 hr inside the

oven for complete drying. Then made its fine powder by mortar & pestle for further process. The experimental condition was same for another sample except SDS as a surfactant and in absence of any surfactant.

III. RESULTS AND DISCUSSION

The X-ray powder diffraction (XRD) performed with a Philips Xpert MPD, Range (2θ): 3° to 130°; at a scan speed 2°/min. using Cu-K_α radiation of 0.15406 nm wavelength. The analysis of XRD data shows that synthesized Bi_2S_3 powder having different sulfur content as shown in Fig.1 confirms the phase formation of the material in orthorhombic bismuthinite crystal structure.

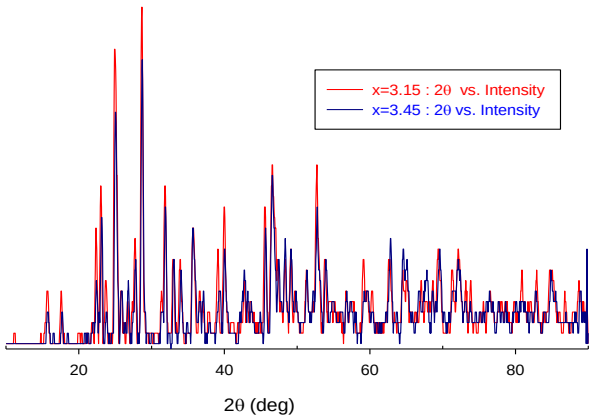

Fig. 1 Powder XRD pattern of the as-synthesized Bi_2S_x (x = 3.05, 3.15)

The absence of XRD peaks due to any alloy except Bi_2S_3 in the XRD spectra confirm that the single phase material was formed. The (121) preferred orientation and splitting of peaks due to orthorhombic structure matches well with the standard JCPDS data (File no.-84-0279) that demonstrate good crystalline quality and structural homogeneity of synthesized powders.

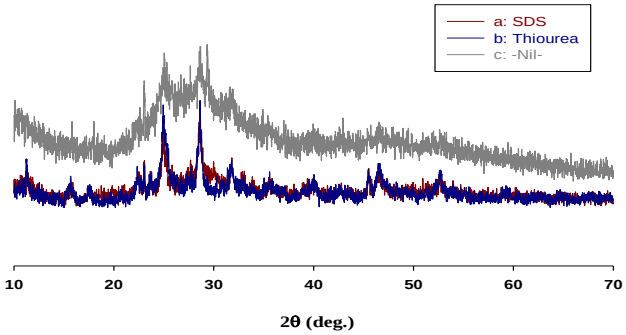

Fig. 2 Powder XRD patterns of the as-synthesized Bi_2S_3 nanoparticles

As show in Fig. 2 XRD patterns indicates that surfactants play major role in synthesis of Bismuth sulfide via precipitation. Both Thiourea and Sodium dodecyl sulfate as the surfactants (Fig.2a, 2b) results in bismuth sulfide with orthorhombic phase having major peak at (121) that matches well with the standard JCPDS data (File no.-84-0279).

For the orthorhombic lattice parameters evaluation, we have used the quadratic relation:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Where, (*h k l*) are the Miller indices of reflecting planes appearing on the diffraction spectrum and *'d'* is the spacing between adjacent planes. The calculated lattice parameters (orthorhombic unit cell parameters *a*, *b*, *c*) and unit cell volume (V = *abc*) are shown in Table 1, 2. The crystallite size of the samples is determined from x-ray data using Scherer's formula [19]:

$$L = \frac{k\lambda}{\beta \cos\theta}$$

Where, 'L' is the crystallite size, k = 0.9 is the shape factor, the wavelength of the x-rays λ= 0.15406 nm, β is the line broadening in radians and θ is the Bragg's angle.

The calculated values of lattice parameters and crystallite size of as synthesized Bismuth sulfide material is as shown in Table. 1,2.

TABLE 1

Calculated Values of Lattice Parameters and Crystallite Size of Bi_2S_3 by Solid State Solvothermal Route

Sulfur Content	lattice parameters			Unit cell volume $V(nm^3)$	Crystallite size *(nm)*
	a (nm)	*b (nm)*	*c (nm)*		
3.15	0.398	1.112	1.132	0.501	24.34
3.45	0.398	1.113	1.12	0.496	25.17

TABLE 2

Calculated Values of Lattice Parameters and Crystallite Size of Bi_2S_3 by Precipitation Route

Used Surfactant	lattice parameters			unit cell volume $V(nm)^3$	crystallite size *(nm)*
	a (nm)	*b (nm)*	*c (nm)*		
SDS	0.398	1.101	1.135	0.497	31.26
CTAB	0.400	1.197	1.129	0.540	35.40
Absence of Surfactant	0.394	1.113	1.150	0.504	35.96

IV. CONCLUSIONS

The Bi_2S_3 powders of orthorhombic phase were prepared by two different methods where the particle size were 30-40 nm studied with preferred orientation (121) with a little amount of impurities. Result indicates that XRD pattern and lattice parameters calculated are in good agreement with standard data. Crystallite size with solid state solvothermal route was lesser than the crystallite size with precipitation technique. Synthesized material can be useful for preparation of Bi_2S_3 thin films using various techniques for its application in optoelectronic devices.

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REFERENCES

[1] Wang Y., Chen J, Wang P, Chen L, Chen Y B & Wu L-M, *J Phys Chem*,113(2009) 16009.
[2] Oled R., et al; *Nat mater*, 5(2006) 1571.
[3] Yi X., et al; *Solid State Commun*, 149(2009)1894.
[4] Kun Y., et al; *Proceeding of 1st IEEE Int Conf on Nano/Micro Engg and Mol* Syst, (2006)1509.
[5] Yao K., et al; *J Phy Chem*, C112(2008) 8721.
[6] Chen X., et al; W., *J Cryst Growth*, 256(2006) 368.
[7] JI T., et al; *Chinese Sci Bull*, 51(2006) 655.
[8] Lou W., et al., J *Chem. Mate., 19*(2007) 872.
[9] Rehani B. R., et al., *Indian J Pure & Appl Phys*, 44(2006)157.
[10] Cullity B. D., et al., *Elements of X-ray diffraction*, (2001), 3rd ed. Prentice Hall Publication, India,
[11] Suryanarayana C., et al., *X-ray Diffraction*, (1998), A Practical Approach Springer, New York.
[12] Gang Xie, Zheng-Ping Qiao, et. al., *J Cryst Growth & Design*, 4-3 (2004)513.
[13] Mingwang S, Wu Z, et. al.; *J Cryst Growth*, 265(2004)318.
[14] Shi Huaqiang, Zhou Xiaodong, et. al., *Mater latt*, 60(2006)1793.
[15] X S Peng, G W Meng; J. Phys. D; *Appl Phys*, 34(2001)3224.
[16] Li-Dong Zhao, Bo-Ping Zhang, et.al., *J Sol St Chem*, 181(2008)3278.
[17] A. Binnaz, Yeliz Koca; *Digest J nanomaterials and Biostructures*, 4-1(2009) 73.
[18] Alison Emslie Lewis; *Hydrometallurgy*; 104(2010)222.
[19] P. Singh, A. Kumar, et.al.; *J Cryst Growth*, 306(2007)303.
[20] Solanki S I, Patel I B, Shah N M, *Multi Disciplinary Edu global Quest*, 2-3#7 (2013)37.
[21] Solanki S I, Patel I B, Shah N M, 58th DAE- *Solid State Physics Symposium, AIP Conf. Proc.*, 1591(2014)1473.
[22] Solanki S I, Patel I B, *Tech Lett*, 1-10 (2014)9.