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Research Paper

Characterization of Structural, Morphological studies of Nano Crystal

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Abstract

In present study, we were able to successfully synthesize single-crystalline $BaSnO_3$ nano crystal using a straightforward Chemical precipitation technique. $BaSnO_3$ have a length of up to several micrometers and a diameter of 25-50 nm and are single-crystalline, structure obtained from XRD and the functional group analysis FT-Raman and a scanning electron microscope (FE-SEM) used to study about the morphological structure of nanocrystal.

Keywords: XRD, Raman study, FESEM, Chemical precipitation techniques etc.,

INTRODUCTION

The architecture of electronic devices demands the multifunctionality of the basic materials used in it. TCOs are such class of materials that can be insulating, semiconducting and metal depending on its chemical constituents and these materials displays various properties like superconductivity, magnetism and ferroelectricity etc. Perovskites are the materials that falls in the category of Transparent Conducting oxide (TCO) or Transparent oxide Semiconductors(TOS) due to their richness in multifunctional properties. But mobilities in TCOs are strongly dependent on the temperatures, phase purity and electron effective mass. One of the key issues in mobility driven devices is that it is temperature dependent (μ is proportional to $T^{-3/2}$)due to lattice

scattering. It is very efficient to address both factor simultaneously, however in very interesting Perovskites material such manoeuvring is possible. Thus research advancements in Perovskites .materials are carried extensively to explore materials whichhave higher carrier mobilities. Alkaline earth stannates with chemical formula $ASnO_3$ (A= Ca,Sr and Ba) are the class of materials that has high mobility (up to ~ 350 $cm^2V^{-1}s^{-1}$) reported at room temperature (RT). Generally at room temperature, the binary oxides TCOs show very low mobility ~ 1 to 3 $cm^2V^{-1}s^{-1}$ but ternary oxides like alkaline earth stannates having dispersed conduction has high RT mobilities. La doped Barium stannates ($Ba_{1-x}SnLa_xO_3$) has shown the highest mobility of 320 $cm^2V^{-1}s^{-1}$ in degenerate semiconducting TCOs [1-3]. Thus these features motivate us to explore $BaSnO_3$ system. In this chapter detailed study of $BaSnO_3$ system is extensively studied from synthesis to structural, optical, composition,electrical studies and annealing studies. Also, Al doped $BaSnO_3$ system is studied structurally,morphologically and optically.

IMPORTANT FEATURES OF $BaSnO_3$ CRYSTAL

In the cubic packing of large Oxygen O^{2-} anion and Ba^{2+} having ionic radii of 1.40Å and 1.34Å respectively , Sn^{4+} having the smallest ionic radii of 0.71Å occupies the one fourth of octahedral voids in that packing. In the cubic unit cell Ba sits at the corner, oxygen at the centre of the faces and Sn at the centre. Ba^{2+} has coordination number 12 with O^{2-} while Sn forms the octahedral which is SnO_6 . The 3-D expanse of this octahedral is shown in figure 1. When there is change in coordination number then there is deviation from the cubic

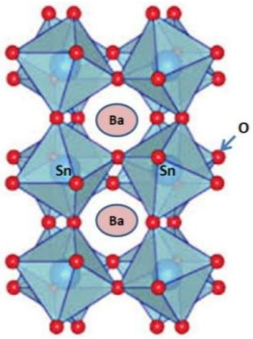

Fig.1 Crystal structure of $BaSnO_3$ in 3-D expanse of SnO_6 octahedra

The tolerance factor 't' given $t = (R_{Ba} + R_O)/\sqrt{2}(R_{Sn} + R_O)$ the ratio of ionic radii plays

important role in deciding the cubic structure of $BaSnO_3$ .For $BaSnO_3$ the value of 't'comes out to be 1 (perfect cubic structure). With increase in ionic radii in Ca^{2+} -1Å pm, Sr^{2+}- 1.18 Å and Ba^{2+}-1.35 Å there is increase in cubic nature from distorted orthorhombic structure. Also Goldschmidt tolerance factor increases from 0.93(Ca) to 0.96(Sr) to 1.0 (Ba) [3,4]. $BaSnO_3$ is an insulating cubic perovskite having lattice parameter a= 4.12Å, having band gap of 3.3eV, good quality crystals can have more band gap. $BaSnO_3$is thermally stable upto 1000℃ and is widely used as capacitors, gas sensors, humidity sensors etc. In the 3-D view the corner sharing of SnO_6 octahedra , Sn-O-Sn makes an angleof 180º, Thus there is electron hopping between two Sn sites, also through DFT (density Functional Theory) calculations it is seen that the conduction and of $BaSnO_3$ consists of Sn 5s state [4]. The highly dispersive (i.e. having high band width) conduction band of Bariumstannate with 5s state resembles with the Indium oxide conduction band in dispersivenes which is the cause of low effective mass of electron in the conduction band and hence causes high mobility [5,6].

Experimental

Materials and Methods

SnCl2.2H2O and BaCO3, the precursor for NH3.H2O , NaOH the oxide source, Ethanol, Deionized Water were purchased from Merck. Because the chemicals were of analytical regent grade with 99 percent purity, they were utilized exactly as received. Simple chemical route was used to synthesize $BaSnO_3$ nano crystal materials. X-ray powder diffraction method PL and CV were used to characterize structural and optical with Electrical studies respectively

SYNTHESIS PROCEDURES

The synthesis was done through facile chemical route keeping the focus on the concern of phase purity. In the synthesis of $BaSnO_3$ by chemical co precipitation method the optimization of pH for phase purity was done by using two different routes as is described below:

Route 1: Precursors $SnCl_4.5H_2O$ and $BaCO_3$; NH_3 as base

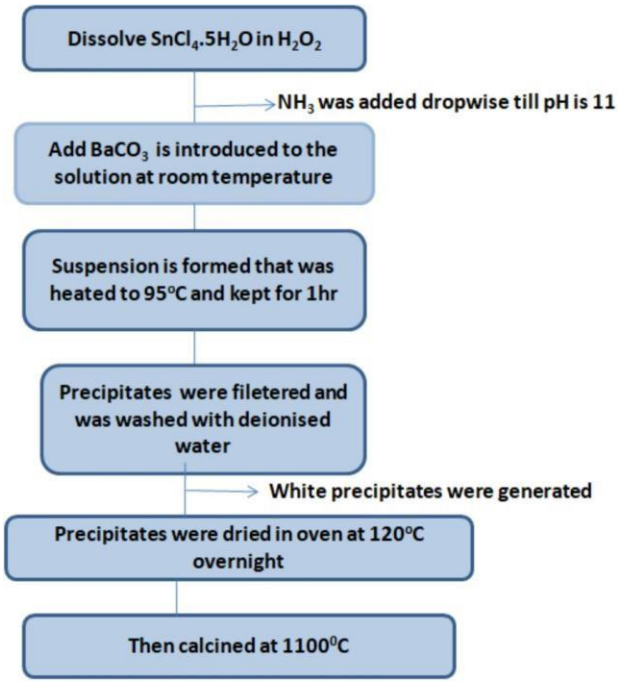

Figure 1.1: Schematic diagram of Sample preparation by Route 1

In this $SnCl_4.5H_2O$ was dissolved in H_2O_2 and NH_3 was added drop-wise till it reaches pH 11.Many experiments were performed on different pH in range 8, 9 and 10. When the desired pHis reached then $BaCO_3$ was added precipitates were formed. Then those suspensions of mixed solutions were heated to 95℃ for 1 hr. The precipitates were washed with deionized waterand were dried in the oven for 24 hrs. Then the dried white colored precipitates werecalcined at temperature 1100℃. The steps followed are shown below in the form of flowchartin figure 1.1.

RESULTS AND DISCUSSION:

X-RAY DIFFRACTION STUDIES

X-ray diffraction (XRD) pattern of all five samples is plotted in figure 1.2. The XRD pattern of BSO-8, BSO-9, BSO-10 matches well with (JCPDS file no.77-0451) with cell parameters as a=4.750, c=3.196 and the peaks are related to tetragonal structure of SnO_2.While BSO-11 has cubic Perovskites $BaSnO_3$ phase (JCPDS file no.15-0780) with small amount of SnO_2 phase (Figure 1.2). The sample prepared with route 2 is found with pure $BaSnO_3$ phase and

named as BSO-11*. In XRD pattern, the first three planes corresponding to (110), (200) and (211) gives the fingerprints of $BaSnO_3$ crystal structure. Lesser impurity peaks were observed in this method.

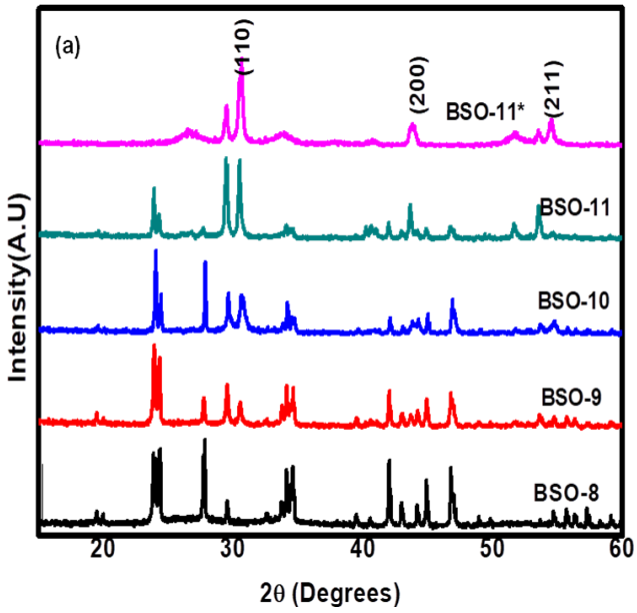

Figure 1.3: XRD pattern of BSO samples prepared at different pH

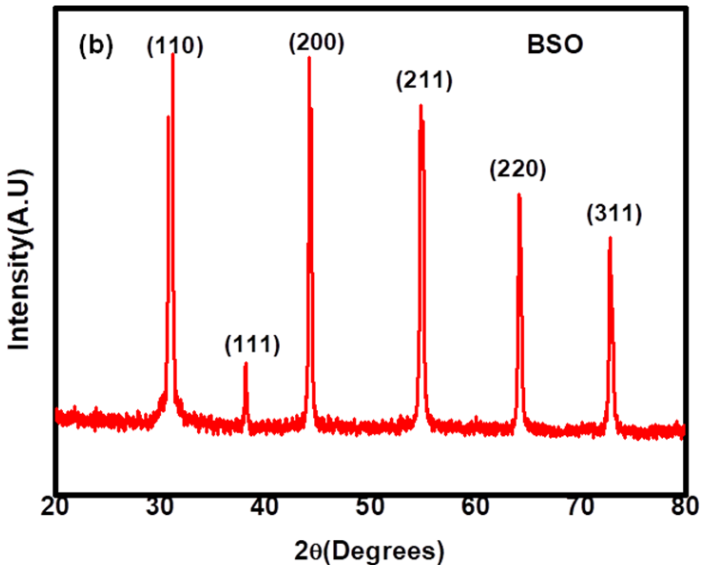

Figure 1.4: XRD pattern of BSO obtained at pH 11.5

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XRD studies reveal that, phase formation of $BaSnO_3$ dependence strongly on the choice of precursors and pH. It is found that with $BaCO_3$ as precursor, $BaSnO_3$ phase doesn't get formed at pH less than 11. Also, at high pH of 11 the impurity phase of SnO_2 also appears with $BaSnO_3$ phase. While with $BaCl_2$, impurity phase is completely suppressed and pure phase of $BaSnO_3$ is obtained. At low pH simple ions are formed while at higher pH complex ions are formed, thus $BaSnO_3$ phase is formed at higher pH. It can be concluded that at low pH with weak base NH_3 stable $BaCO_3$ was not able to disassociate. Thus, our further studies are on BSO sample.

RAMAN ANALYSIS

Structural studies of BSO samples were also investigated with the help of room temperature Raman spectroscopy. The Raman spectra of BSO is shown in figure 1.5. As such cubic Perovskites don't have first order Raman modes but due to the distortion from the cubic symmetry we observe characteristic Raman modes. Various longitudinal (LO) as well as transverse (TO) optical phonon modes were observed. Raman peak at 413cm^{-1} and 691 cm^{-1} originates due to O-Sn-O stretching mode, peak at 230 cm^{-1} corresponds to the SnO_6 octahedron while the peak at 519 cm^{-1} is associated with Sn-O torsional mode. Peaks at 570 cm^{-1} and831 cm^{-1} corresponds to the scattering due to the surface disorder [8-10].

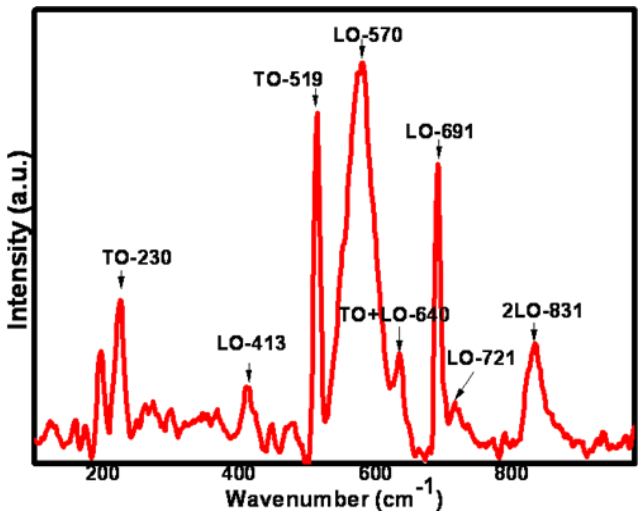

Figure 1.6: Raman spectra of BSO

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MORPHOLOGICAL STUDIES (FESEM)

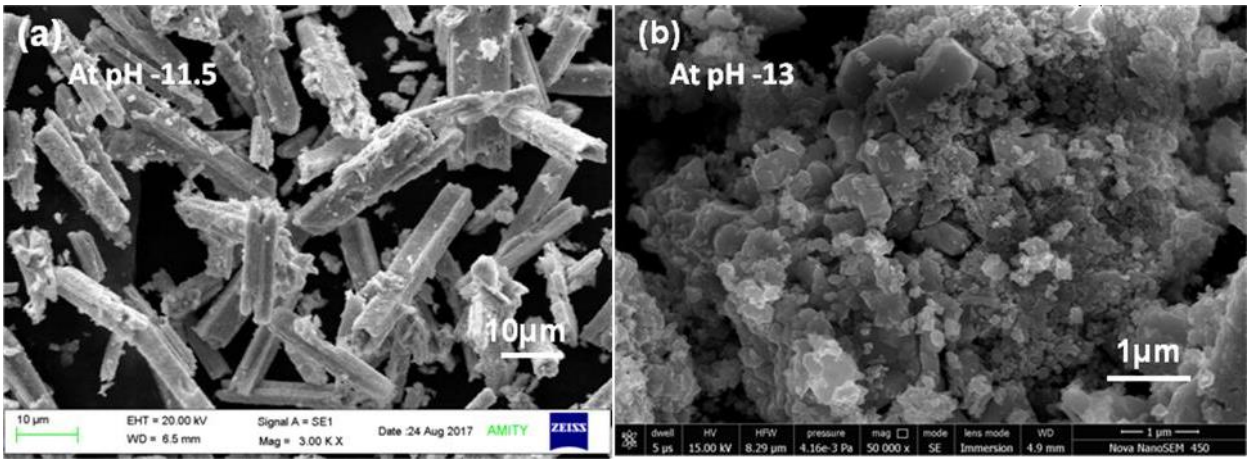

Figure 1.7: FESEM images of (a) micro rods of BSO (b) BSO-13

The morphological studies of BSO sample using FESEM has been carried out in detail and is summarized in figure 1.7. The SEM micrographs for BSO sample has rod like structure. It is observed from these FESEM images that, these microrods of $BaSnO_3$ are having average length of 10-15µm and diameters 0.5-1 µm. The higher magnification FESEM image in figure 1.7 depicts the open ends of micro rods of BSO. Thus, these open ends make the sample BSO good candidate for dye adsorption in DSSC studies which is explained in chapter 6 respectively. To investigate further the role of pH in deciding the morphology we, synthesizedthe BSO sample at pH 13. The figure 1.7 shows the drastic change in morphology.The changein morphology with pH clearly depicts the dominance of pH in desired morphology.[11-12].We can conclude that with pH above 11.5, the solubility of the precursor solution changes. As pH hastendency to shift the chemical equilibrium of solution. Thus, with high pH the solubility decreases due to which supersaturation, nucleation gets affected.[13-15]. Now more ions have tendency to agglomerate which results in formation of 3-D morphology i.e. flakes of average width 1µm as shown in figure 1..7 (a) & (b).

CONCLUSION

The pH plays the crucial role in deciding the purity of phase and affects the morphology of $BaSnO_3$ synthesized via chemical precipitation route. The BSO microrods synthesized were porous and are transparent in the visible range having direct band gap of 3.1 eV. Al doping of BSO significantly affects the structural, compositional and optical properties.

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