Influence of Sulphur Doping in SnSe Nanoflakes Preparedby Microwave Assisted Solvothermal Synthesis

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Abstract: Nanostructured SnSe studied for their high Seebeck coefficient with low thermal conductivity is reported to be a potential material for thermoelectric applications. Recently, nano-structuring of SnSe withsulphurdoping has been estimated theoretically to enhance the figure of merit and hence ispredicted to be favourable for thermoelectric applications.Thestructural, optical and morphological properties of SnSe nanoflakessynthesized via scalable and facile microwave assisted solvothermal synthesis isreported in this work. X-ray diffraction reveals a single phase orthorhombic structure with a crystallite size of ~38nm.Morphology studies from FESEM reveals that the edge to edge length of single flake is ~1.3µm. Topography studies from AFM indicate square-like two dimensional nanoflakeswith length of 1.6µm,breadth of 800nm, thickness of ~250nmand roughness 36rms.Optical properties indicate a direct band gap of ~1.03eV.Energy dispersive spectroscopy (EDS) demonstrates the presence of 9% sulphur along with the expected 1:1 ratio of Sn and Se that is attributed to the presence of monolayer of Thioglycolic acid (TGA) which is used as the shape directing agent. A fine tuning of morphology as well as optimization of sulphur content is possible by TGA which would be promising for thermoelectric application.

1.INTRODUCTION

SnSe,SnTe,PbTe are some of the IV-VI th group compounds that are investigated for their thermoelectric properties. Thermoelectric materials have the property to change the waste heat into electricity and vice-versa on the basis of Seebeck effect [1].Apart from thermoelectric properties,SnSe is also investigated and reported in literature [2] as Topological crystalline insulator where the dissipation less high conduction of charge carriers found in the surface are protected by crystalline mirror symmetry.SnSe is a narrow band gap semiconductor that was initially studied as a good thermoelectric material and for the application of thin film solar cells [2]. Ultra-lowthermal conductivity of SnSe is reported to enhance the thermoelectric figure of merit [3]. The thermoelectric properties like ZT of SnSe increase higher and higher on nanostructuring with respect to single crystal SnSe [4].Recent theoretical investigation has predicted out that sulphur doping in nanostructured SnSe is a potential candidate for thermoelectrics [5]. Microwave assisted solvothermal synthesis is emerging as an efficient method to fabricate nanostructures in a short duration which is scalable and reproducible for large scale applications[6]. In this present work structural,morphological and optical properties of nanostructured SnSe prepared through fast facile and scalable microwave assisted solvothermal synthesis is investigated and presented.

2.SAMPLE PREPARATION AND CHARACTERIZATION

2.1 Microwave Assisted Synthesis of SnSe Nanoflakes

$SnCl_2.2H_2O$ (0.5mmol), Se powder(0.5mmol), 3ml TOP, 10ml Pentane-di-ol and 1ml TGA were used as starting materials without further purification.Microwave assisted synthesis was carried out in the CEM research based single mode microwave owen as mentioned in literature for a different type of chalcogenides [7]. $SnCl_2.2H_2O$ mixed with Pentane-di-ol (PD), Sellenium shots mixed with Tri-octyl phospine (TOP) andTGA, the obtain mixture was taken in quartz ampule and subjected to microwave at 180□ for 30 minutes with vigorous magnetic stirring. The obtained black precipitate was centrifuged and cleaned with ethyl alcohol and acetone. Finally, the black powder was dried and used for structural, morphological, and optical studies. The microwave synthesis of SnSe nanoflakes were carried out using CEM Discover SP research based microwave apparatus which has inbuilt temperature and pressure controlling system.

2.2 Characterization

Powder diffraction pattern of XRD indicates the single phase nature of the SnSe nanoflakes.From the observation of X-ray diffraction, the assembly of SnSe nanoflakes are polycrystalline in nature. As shown in figure 1(a), all the diffraction peaks could be indexed to the orthorhombic SnSe (space group Pnma) with the cell parameters a=11.46Å, b=4.11 Å, c=4.39 Å. The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The Xrd pattern of SnSe nanoflakes match with the theoretical data as shown by the Rietveld refinement in figure 1(a). The crystallite size of prepared SnSe nanoflakes is estimated to be ~38nm corresponding to the main peak as determined by Debye Scherrer formula ($\tau=K\lambda/\beta\cos\theta$). Where τ is the crystallite size, K is a constant taken to be 1, wavelength of X-ray (1.54Å), β is the full width at half maximum (FWHM) obtained from the main peak and θ is the diffraction angle. The energy dispersive spectroscopy (EDS) spectrum of the SnSe nanoflakes as shown in figure 1(b) shows the presence of small but significant amount of sulphur along with Sn and Se while the inset shows the EDS compositional analysis made using "Bruker made XFlash X130" in a single flake. The molar ratio of Sn/Se is found to be 0.92 which is nearer to stoichiometric ratio of SnSe like 1:1.

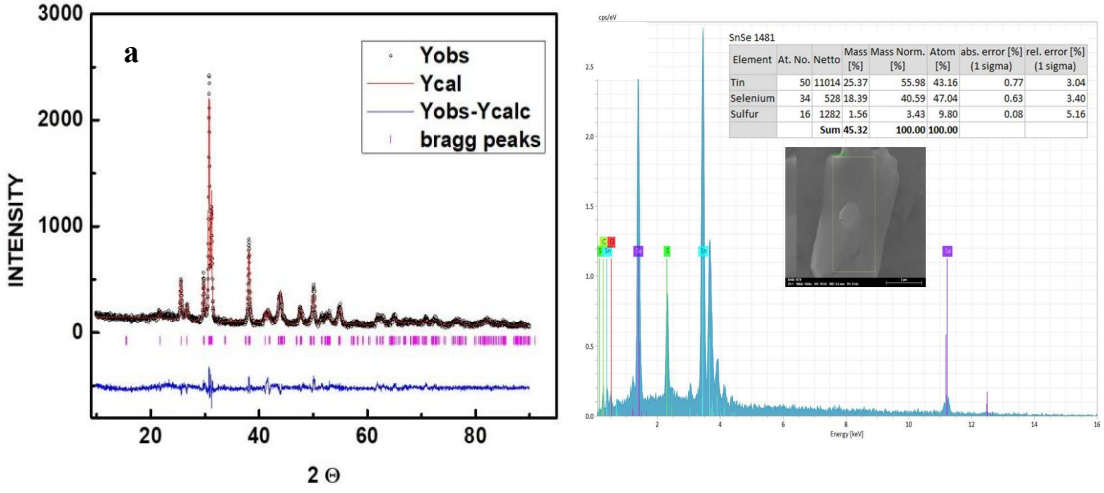

FIGURE 1. (a) Rietveld Refinement of SnSe nanoflakes (b) EDS spectrum (Inset) EDS composition of single SnSe.

2.3 Morphology Studies

The morphology of SnSe nanoflakes were studied using FEI made "NOVA NANOSEM 450" as shown in figure 2a) and 2b). Figure 2a) shows the lower magnification image of SnSe nanoflakes while figure 2b) shows the higher magnification image of single nanoflakes with cross sectional edge to edge length of ~1.3µm. The white coloured structure above the single phase is the C-axis growth which is restricted by shape directing agent TGA. TGA is also acting as a reducing agent as well as to control the morphology of the SnSe nanoflakesin the preparation of sample.

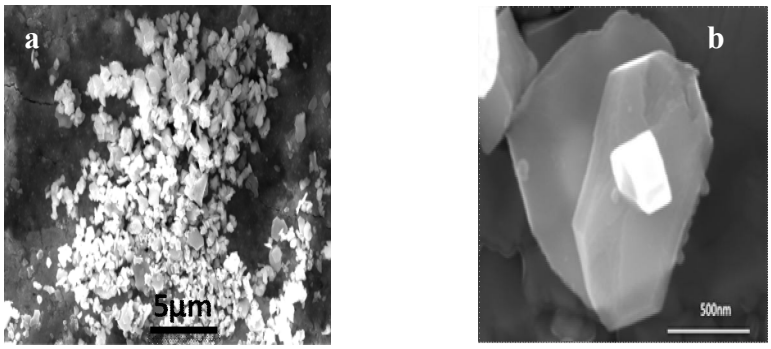

Figure 2. FESEM images of nanocrystalline SnSe:(a) Lower magnification and (b) higher magnification

2.4 Topography and Optical Properties of Nanocrystalline SnSe

AFM images of nanocrystalline SnSe shown in fig 3. In fig 3(a) the distance measurents were made along the X, Y, and Z direction of single nanoflakes of SnSe which is shown in figures 3(b), 3(c), and 3(d) respectively. Figure 3 shows the topography of single flake SnSe with the edge to edge length of 1.3µm along the X direction. Breadth of the single flake is found to be 800nm as measured along Y direction which is shown in figure 3C. Thickness of nanocrystal is found to be 250nm which is observed from the void taken as the reference to the maximum peak of the flake. The band gap of SnSe is determined by UV-visible spectroscopy and $BaSO_4$ powder is used for complete reflectance.Inset of figure 4i.e; 4(a) shows the absorbance spectra of SnSe as a function of wavelength given in nm. The absorbance decreases with the increment of wavelength, and on higher values of wavelength the absorbance remains constant. DRS (diffuse reflectance spectroscopy) measurement was carried out to find the band-gap of the materials. A Tauc plot is used to determine the optical bandgap in topological crystalline insulator SnSe which is given by the formula $A(Eg - h\upsilon)^n = (\alpha h\upsilon)$; where α is the absorption coefficient, A is constant, h is the Planck`s constant, υ is frequency and n for band measurements. i.e n=1/2 for direct and n=2 for indirect bandgap materials, n=3/2 for direct forbidden band and n=3 for indirect forbidden. The direct band gap of SnSe nanoflakes calculated from "Kubelka Munk" or Tauc plot is ~1.03eV as shown in the figure 4(b).

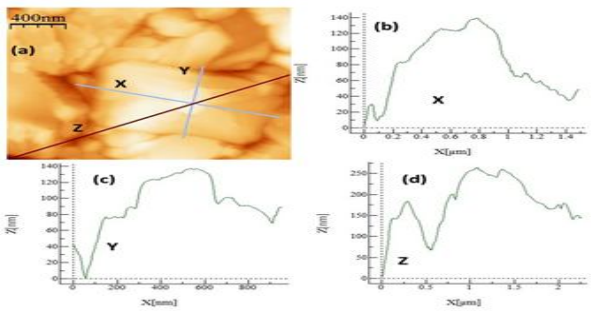

Figure 3

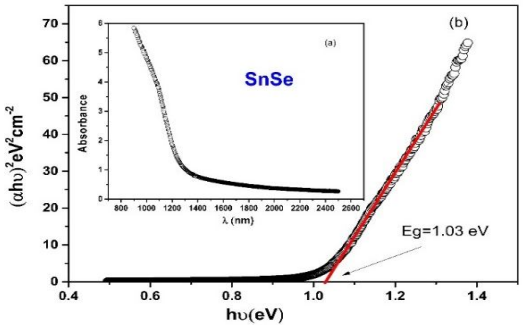

Figure 4

Figure 3a-3d.AFM images of nanocrystalline SnSe with the measurement along X,Y and Z directions. **Figure 4**. Inset a) shows the absorbance graph. b) shows the direct band gap of the nanocrystalline SnSe.

3.Result and Disscusion

The structural properties of nanocrystalline SnSe as determined by powder X ray diffraction shows a single phase orthorhombic structure with a unit cell volume of 206.77 $Å^3$ which is lesser than the reportedvalue of 214.24 $Å^3$ (JCPDS No.0089-0236, Pnma) for bulk SnSe. This is in accordance with the EDS data where the presence of 9% sulphur is observed in compositional analysis. The doping of sulphur (atomic radius 103.5pm) in Sn site (atomic radius 140.5pm) might have reduced the overall volume of the unit cell in our SnSe nanostructure. The source of sulphur doping is inferred to be from the Thioglycolic acid (TGA) [8] which is used as the shape directing and reducing agent. Morphology studies indicate the presence of 2-dimentional layered structure of SnSenanoflakes with edge to edge length of 1.6μm. Thesenanostructure with enhanced surface to volume ratio is also advantageous for probing surface dependent TCI properties. The optical properties indicate direct bandgap of 1.03 eV which is in between the value of end composition SnS (1.07 eV) and SnSe (0.97eV). The increment in band gap when compared to bulk SnSe can be attributed to the sulphur doping in SnSe which is in corroboration with the EDS and structural measurements[9]. The interesting presence of sulphur attributed to Thioglycolic acid which can be finetuned by changing the TGA content and microwave dosage. The sulphur doping also inhibit oxidation as well as can manipulate the carrier type for achieving high power factor which would be beneficial for thermoelectric applications.The effect of TGA in SnSe nanostructure in its sulphur content and morphology is in progress which would be published elsewhere.

Conclusion

Nanostructures of SnSe has been successfully synthesized in Microwave assisted solvothermal synthesis. The structural properties in the presence of very small percentage doping of sulphur is attributed to TGA which is used as the surfactant (shape directing)andreducing agent. Structural properties, compositional analysis and optical properties are in corroboration with each other. Square type of two dimensional nanoflakes of SnSe with 1.6μm dimension and sulphur doping in SnSe composition via this facile,scalable and fast microwave assisted synthesis is advantageous for thermoelectric application as well as to probe the surface properties of this TCI material.

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