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Enhanced thermoelectric performance of n-type bismuth selenide doped with nickel

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ABSTRACT

Bismuth selenide (Bi_2Se_3) and transition metal (nickel) doped (5 and 7.5 mol %) Bi_2Se_3 have been prepared by solvothermal approach for investigation of thermoelectric properties of the materials. The morphological characterization reveals plate and flake like structures for undoped and doped samples respectively. There is a decrease in lattice constant, computed from Rietveld refinement data and crystallite size, found using Debye-Scherrer equation for doped samples. Doping by nickel increases the electrical conductivity and reduces both thermo power and thermal conductivity of the materials than pure Bi_2Se_3. Reduction in thermal conductivity of the doped samples by 42%, results in an increase in figure of merit (ZT) of nickel doped (5%) materials by one order of magnitude (0.02–0.22) compared to pure Bi_2Se_3.

1. Introduction

Increasing energy shortage and environmental pollution are the two urgent issues in recent days for rapid population and industrial growth [1]. The search of high performance thermoelectric materials is a challenging area of research in these days to realize efficient mutual conversion between heat and electricity directly [2–7]. Thermoelectric materials are characterized by dimensionless figure of merit, $ZT = (S^2\sigma/\kappa)\ T = (P/\kappa)\ T$ where S is thermo power, σ is electrical conductivity, κ is thermal conductivity, P is power factor and T is absolute temperature. Interdependence of these parameters limits the efficiency of the material for practical applications. But ZT can be enhanced by decreasing κ, through phonon scattering at the numerous grain boundaries [8] and increasing power factor ($S^2\sigma$) through quantum confinement effects in nanostructured materials [9]. Among group V-VI binary and ternary compound semiconductors, bismuth telluride (Bi_2Te_3) [7,10–14], bismuth selenide (Bi_2Se_3) [15,16], antimony telluride [17,18] and $Bi_2Te_{1-x}Se_x$ [19–23], $Bi_xSb_{1-x}Te_3$ [24–26] are some of the efficient thermoelectric materials at or above room temperature. Theoretical prediction of high ZT for Bi_2Se_3 has led researchers to experiment with nanostructured Bi_2Se_3 for thermoelectric applications. There are reports on synthesis of nanostructured Bi_2Se_3 by methods like thermo chemical [9], solvothermal [27–29], hydrothermal [30], scalable interaction [31], melting and hot pressing [32,33], electro deposition [34]. Some of these materials have been characterized through the measurement of figure of merit ZT which is presented in Table 1. Various efforts have been made for improving ZT of Bi_2Se_3 like synthesis method [9,27–34], doping [15,16,32] and alloying [19–23] with other materials. Doping Bi_2Se_3 with transition metal like copper [32] and nickel [present work] is an interesting approach to increase ZT by tuning the carrier concentration.

Bi_2Se_3 has a rhombohedral layered crystal structure belonging to space group $R\bar{3}m$, each layer containing either Bi or Se atoms perpendicular to c axis in the sequence – [$Se^{(1)}$-Bi-$Se^{(2)}$-Bi-$Se^{(1)}$] –, weekly bound by Van der Waals forces with a slightly covalent nature [35]. The layered structure of Bi_2Se_3 where the Van der Waals gap permits for intercalation by other materials is very much beneficial to enhance the ZT through reduction of κ as has been observed in TiS_2 [36,37] and Cu doped Bi_2Se_3 [32]. To deepen the understanding of role of transition metal towards improvement of ZT, nickel, which is a transition metal of the same group as copper, has been chosen as a dopant in the present case.

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Table 1
Comparison of thermoelectric parameters of Bi_2Se_3 sample at room temperature with other's work.

Sample	Synthesized by	Electrical conductivity (S/cm)	Thermo electric power (μV/K)	Thermal conductivity (W/mK)	Power factor ($\mu W/cmK^2$)	Figure of merit (ZT)	Reference
Ni (5%) doped Bi_2Se_3	Solvothermal	38	−165	0.14	1.04	0.22	This work
High quality Bi_2Se_3 nanoplatelets	Thermochemical	551	−92	0.97	4.66	0.14	Ali et al. [9]
Bi_2Se_3	Solvothermal	21	−115	0.751	0.28	0.011	Kadel et al. [28]
Single layer based Bi_2Se_3	Scalable interaction/ exfoliation strategy	180	−90	0.43	1.5	0.11	Sun et al. [31]
Cu doped Bi_2Se_3	Melting and hot pressing	278	−170	0.65	8.03	0.33	Sun et al. [32]
Ca doped Bi_2Se_3	Melting	208	+180	2	6.73	0.10	Hor et al. [33]

2. Experimental

2.1. Synthesis of bismuth selenide

We have prepared the samples by solvothermal process as reported in our earlier work [38]. First, we added, 1 g bismuth nitrate (Bi $(NO_3)_3 5H_2O$; 99%, Merck, India) within 20 ml ethylene glycol (from Merck) in a beaker. The solution was sonicated in magnetic stirrer for 15 min in support of uniform dispersion, each time, after consecutive addition of 0.125 g EDTA (from Sigma Aldrich) and 0.34 g selenium dioxide (SeO_2; 98%, Spectrochem, India). For nickel doping, we have added 0.02 and 0.03 g (5 & 7.5 mol %) nickel nitrate (Ni $(NO_3)_2$, $6H_2O$; 99%, Merck, India) in the solution. After well dispersion of all chemicals, the solution was put into a 20 ml container. Then it was sealed and kept in an autoclave at 165° C for 24 h. After reaching room temperature, the solution was washed with absolute ethanol and distilled water several times and centrifugally separated at 3000 rpm for 15 min to remove all impurities. After that, the solid product was dried at 60 °C for 4 h in a vacuum oven.

2.2. Characterization

2.2.1. Structural characterization

X-ray diffraction pattern (XRD, BRUKER D8 ADVANCE) of the prepared samples were executed using Cu–Kα radiations (λ = 1.5418 Å) with scan range 10°–80° at a rate of 5°/min. Surface morphologies of the prepared samples were obtained from field emission scanning electron microscopic (FESEM, Hitachi, S-4800) images, operating at 20 KV along with energy dispersive X-ray (EDAX) pattern. Morphologies of the prepared samples were recorded by transmission electron microscopic (TEM, JEOL JEM-2011) images.

2.2.2. Thermoelectric characterization

Thermo power and electrical conductivity were measured in the temperature range 300–410 K. The prepared samples were pelletized (length ~1, breadth ~0.7 and thickness ~ 0.074 cm) by using hydraulic pressing machine under pressure of 5 ton. Thermo power measurement was carried out, creating a temperature difference (5–10 K) along the length of the sample by heating one end of sample by auxiliary heater in a vacuum chamber, and corresponding potential drop was recorded from a Hewlett-Packard data acquisition system (34970A) as explained elsewhere [39,40]. DC electrical conductivity measurement in the temperature range 300–410 K, was carried out by a four probe method with a PID controlled oven (Scientific Equipments, Roorkee, India). Thermal constant analyzer (Hot Disk, Model no. TPS 2500S, Sweden) was used for the measurement of thermal conductivity. Pellet (length ~1, breadth ~0.7 and thickness ~ 0.074 cm) samples were placed below and above the sensors and then it was kept thermally insulated. Input parameters-thickness, power and time of measurement were provided to the programme to get value of thermal conductivity. Carrier concentrations were evaluated from Hall effect measurements [39,40]. All the electrical properties were measured in plane direction. Sample densities (D) were evaluated from Archimedes principle as given in Table 2.

3. Result and discussions

3.1. XRD analysis

X-ray diffraction pattern of the prepared samples has been analyzed to determine phase purity, lattice parameter and crystallite size. The entire peaks have been indexed to the hexagonal structure of Bi_2Se_3 (JCPDS 33-0214), and no impurity phase related to the nickel doping is found. Due to transition metal ion doping, the crystal structure of Bi_2Se_3 is not affected but peak intensities are changed [41]. The diffraction peak of nickel is not found, and it may be due to low content and highly dispersion. Structural Rietveld refinements were executed on XRD data of the prepared sample as shown in Fig. 1 (a, b and c). The lattice parameters obtained from Rietveld refinement are presented in Table 2 (Fig. 1(d)). We see that lattice parameters decreases with higher doping. Preferred orientation can be described by an orientation factor,

$\gamma = (P-P_0)/(1-P_0)$ where P is the fractional intensity of the (00*l*) planes, P_0 is the value of P in the case of ideal isotropy and $P = \sum I$ (0

Table 2
Density (D), relative density (D_r), porosity (Φ), lattice constant (a and c), orientation factor (γ), crystallite size (D) and chemical formula of different samples.

Sample	D (g cm^{-3})	D_r (%)	Φ (%)	a in Á	c in Á	Orientation factor (γ)	Crystallite size (D) in nm	Chemical formula from EDX
Bi_2Se_3	6.14	90	10	4.1392	28.6220	0.034	55	$Bi_{2.3}Se_{2.7}$
Ni (5 mol %) doped Bi_2Se_3	5.79	85	15	4.1374	28.5804	0.080	47	$Bi_{2.2}Se_{2.7}Ni_{0.1}$
Ni (7.5 mol %) doped Bi_2Se_3	5.66	83	17	4.1364	28.5704	0.045	45	$Bi_{2.15}Se_{2.7}Ni_{0.15}$