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The effect of quenching from different temperatures on $Bi_{0.88}Sb_{0.12}$ alloy

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ABSTRACT

Structural, thermal, resistive and magnetic properties of melt quenched $Bi_{0.88}Sb_{0.12}$ alloys are reported. The samples are heated at three different temperatures, followed by rapid quenching in liquid nitrogen. Large temperature difference between liquidus and solidus lines, led to microscopic in-homogeneity in the alloy. The effect of quenching from different temperatures in polycrystalline $Bi_{0.88}Sb_{0.12}$ alloy has been studied. The parameters such as strain, unit cell volume, and resistivity are found to increase with temperature. Thermal variation of resistivity depicts non-monotonic temperature dependence. The total negative susceptibility increases and band gap of semiconducting $Bi_{0.88}Sb_{0.12}$ samples decreases with increasing temperature.

1. Introduction

Semiconducting Bi–Sb alloy is a well known n type thermoelectric material. Bi, having rhombohedral crystal structure, is a semimetal, with overlap energy of 184 meV between the valance and conduction band [1,2]. Bi, however when alloyed with semimetal Sb constitutes a continuous solid solution for the entire range of Sb concentration [3–5]. The Bi–Sb alloy have received special attention due to their attractive physical properties [3,6–9], emerging from peculiarities of its band structure. Electron–electron and electron–phonon scattering plays an important role in transport properties of this alloy and thus influence its thermoelectric properties [10]. $Bi_{1-x}Sb_x$ alloy shows semiconducting behavior for a small range of Sb content [$(0.07 \le x \le 0.22)$]. The band gap (E_g) of semiconducting $Bi_{1-x}Sb_x$ alloy depends extensively on Sb concentration and shows a transition from direct ($0.08 \le x \le 0.12$) to indirect ($0.12 < x \le 0.22$) band gap at $x=0.12$. These are narrow E_g semiconductors with maximum E_g of about 20 meV [3,11]. However, it should be pointed out that several groups have reported maximum E_g around $x=0.15$ [12–14]. But there are different reports also: viz., Rodionov et al. [15] reported maximum E_g around $x=0.13$, whereas Jain [1] and Malik et al. [11] reported for $Bi_{0.88}Sb_{0.12}$ sample. Bi possesses interesting diamagnetic property and the anomalous diamagnetism of elemental Bi has been discussed qualitatively by Adams [16]. The relation between E_g and diamagnetic susceptibility in $Bi_{1-x}Sb_x$ alloy has been elaborately discussed by Brandt et al. [17]. Sengupta et al. studied the effect of inhomogenity on the band parameters and magnetic property of single crystalline semiconducting and semimetallic Bi–Sb alloys [18]. Though limited works have been reported, but studies on magnetic property of the semiconducting $Bi_{1-x}Sb_x$ are still illusive in literature.

Moreover, synthesis and characterization of semiconducting Bi–Sb polycrystalline alloy is also important from the application point of view. But it is difficult to prepare a homogeneous Bi–Sb alloy. The underlying reason is inherent in the phase diagram [3]. Large temperature difference (ΔT) between the liquidus and the solidus lines, with constitutional super cooling causes macrosegregation of elemental Bi and Sb during synthesis, resulting in microscopic in-homogeneity of the alloy [19,20]. Improvement in homogenization can be achieved by rapidly freezing the homogeneous melt [21] or long time annealing of a quenched alloy [22]. Some methods have been developed to obtain homogeneous single or polycrystalline alloy such as traveling heater method [20], mechanical alloying (MA) [23,24], spark plasma sintering of the MA sample [21,25] etc. It was also reported that, sample

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synthesized by MA like ball milling technique is bound to increase thermodynamic defects, which in turn might be helpful in increasing the efficiency of a thermoelectric material [24].

In this work, an attempt has been made to study the effect of quenching from different temperatures on $Bi_{0.88}Sb_{0.12}$ alloy. The effect of synthesis temperature on E_g of $Bi_{0.88}Sb_{0.12}$ alloy has been studied. An in depth analysis of the structural properties as well as micro-structural characteristics of the melt quenched alloys are reported here. Finally, the effect of in-homogeneity on the structural, resistive and magnetic property of polycrystalline $Bi_{0.88}Sb_{0.12}$ is also analyzed.

2. Experiment

Polycrystalline $Bi_{0.88}Sb_{0.12}$ samples were synthesized by melting of high-purity Bi and Sb powder. It is an emerging and popular technique for the synthesis of Bi–Sb alloy as well as other related metal chalcogenides based thermoelectric materials [26–29]. Stoichiometric quantities of Bi and Sb powders (each of purity 99.999%; Alfa Aesar, UK) were loaded into an evacuated (10^{-3} torr) quartz tube of 10 mm and 11 mm, inner and outer diameters, respectively. The evacuated quartz tube were heated upto three different temperatures viz., 973 K, 1273 K and 1473 K and soaked for 10 h and finally rapidly quenched in liquid Nitrogen. Powder X-Ray Diffractometer [Model: *X'Pert PRO* (PANalytical)] was used for structural characterization of the synthesized samples. All the X-Ray Diffraction (XRD) measurements were performed in θ–2θ geometry with Cu-K_α radiation. In-depth structural analysis was performed using Rietveld (MAUD software) refinement technique [30]. Standard Si was used to determine the instrumental profile [31]. Field Emission Gun Scanning Electron Microscope (FEGSEM: FEI make Helios Nanolab 600i) equipped with a Ocatne Pro Energy Dispersive X-Ray (EDX) detector was used for microstructural and microchemical analysis of the samples. Microhardness measurements were carried out using a Leitz Miniload 2 microhardness tester with an applied load of 100 g and dwell time of 15 s. Each reported hardness value is an average of three measurements. Resistivity of all the synthesized samples, as a function of temperature down to 100 K, was measured using conventional four probe method. Silver paste cured at room temperature was used for achieving good ohmic electrical contacts. Differential thermal analysis (DTA) of the synthesized samples was performed in nitrogen atmosphere. Temperature dependent diamagnetic susceptibility of all the melt quenched polycrystalline $Bi_{0.88}Sb_{0.12}$ alloys was measured in the temperature range 30–300 K using Superconducting Quantum Interference Device Vibrating Sample Magnetometer (SQUID VSM, Quantum Design).

3. Result and discussion

XRD patterns of the three $Bi_{0.88}Sb_{0.12}$ samples treated at three different temperatures are shown in Fig. 1. Variation of the most intense diffraction peak, i.e. (012), for samples quenched from different temperatures, is demonstrated in Fig. 1(inset). All the (012) peaks of the synthesized $Bi_{0.88}Sb_{0.12}$ alloys shift to lower angle with increasing temperature. The synthesized samples are soaked at 973 K, 1273 K and 1473 K, respectively followed by rapid quenching at liquid nitrogen. This help the melt quenched samples to retain its phase as obtained at respective temperature. Since treatment temperature is consecutively higher in the three respective samples, the unit cell volume and lattice parameter of the melt quenched samples increases with increasing temperature due to thermal expansion [32]. It is correctly reflected in the shifting of XRD peaks to lower angle. Bi and Sb are isoelectronic

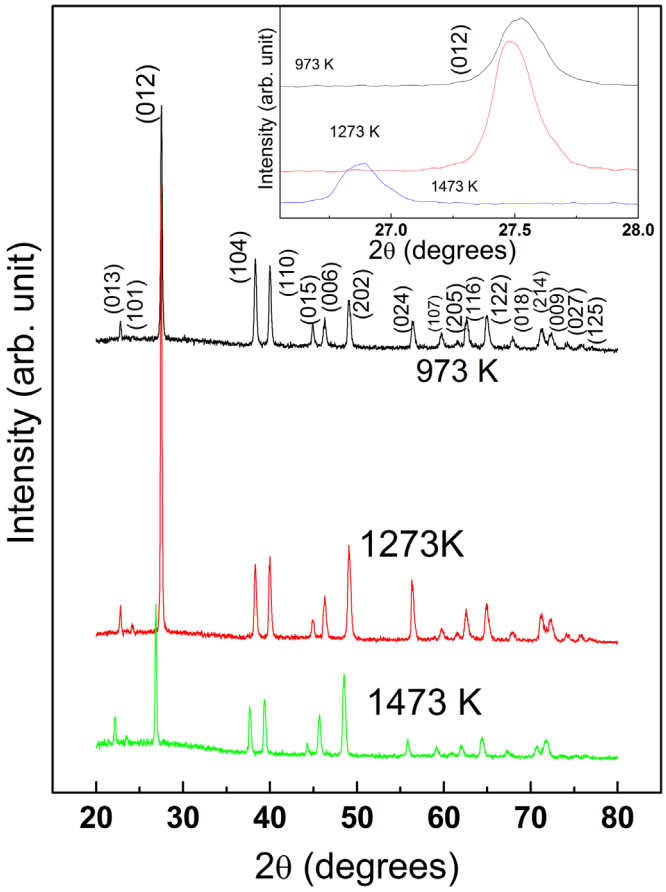

Fig. 1. XRD Patterns of $Bi_{0.88}Sb_{0.12}$ alloys quenched from 973 K, 1273 K and 1473 K, respectively. Inset shows (012) peak of rhombohedral $Bi_{0.88}Sb_{0.12}$ alloys.

and both belong to rhombohedral crystallographic structure with $R\bar{3}m$ space group. In-depth structural analysis has been carried out by Rietveld refinement technique using MAUD software. The experimental XRD pattern and theoretical XRD curve, as obtained after Rietveld refinement, for all the synthesized $Bi_{0.88}Sb_{0.12}$ alloys are presented in Fig. S1 (see the Supplementary information for Fig. S1) [33]. The refinement has been carried out using both atomic position and substitution. Space group $R\bar{3}m$ and point group D_{3d} with hexagonal coordinate system are used for refinement. Refined hexagonal unit cell volume as well as the corresponding lattice parameters, a_H and c_H (within error limit) of the melt quenched samples increases with increasing temperature (Table 1). This is in confirmation with the shift of the XRD peak towards lower angle as observed in Fig. 1(inset). The effect of temperature on the strain of the samples is also analyzed. As depicted in Table 1, strain increases monotonically with increasing temperature. In addition to Rietveld technique using the MAUD software, Williamson–Hall (WH) plot has also been employed to extract the strain in the synthesized samples. WH analysis, as depicted in Fig. S2 (see the Supplementary information for Fig. S2), indicates similar trend [34]. The saturation vapor pressure of Bi and Sb at around 973 K, 1273 K and 1473 K, are 1 and 10 Pa, 100 and 10^3 Pa and 10^3 and 10^4 Pa, respectively [35]. It is further observed that, the difference between saturation vapor pressures of Sb and Bi increase with increasing temperature. Hence Sb is more volatile than Bi and volatilization of Sb increases with temperature. In the melt quenched samples, Sb is thus segregated in the matrix of Bi–Sb alloy and Sb precipitation increases with increasing temperature. Here, it is noteworthy to mention that Lenoir et al. predicted Bi segregation in Bi–Sb alloy and in order to avoid precipitation of Bi in their samples, they adopted traveling heater