Investigation of Micro-indentation Hardness of Bi_2Te_3Based Composite Thermoelectric Materials

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Abstract. We have successfully synthesized $Bi_{0.5}Sb_{1.7}Te_{3+x}$ (x = 0, 0.12, 0.14) composite thermoelectric materials via solid state reaction followed by Spark Plasma Sintering (SPS). The structural characterization of these materials carried out by X-ray diffraction reveals to be composite phase consisting of Bi_2Te_3-type phase with small amount of Te and Sb phase. The micro-hardness performed on samples $Bi_{0.5}Sb_{1.7}Te_{3+x}$(x =0, 0.12, 0.14) reveals the reduction of VHN with increasing Te concentration as compared to that of single phase state –of-the-art $Bi_{0.5}Sb_{1.5}Te_3$ thermoelectric materials.

INTRODUCTION

The utilization of energy by eco-friendly technology with high efficiency is necessary in today's era. Thermoelectric materials enable us to convert directly heat into electricity and vice versa. Hence, thermoelectric devices are being used for recovery of waste heat which is exhausted by automobiles and power generation for sensors, and refrigeration [1-4]. In order to develop thermoelectric devices, the TE legs must be mechanically integratible with their counterparts. With this perception in mind the investigation of mechanical properties owe a great interest to be explored.

Bi2Te3 thermoelectric materials have been explored as potential thermoelectric materials for power generation and cooling devices. However, the mechanical properties are rarely studied. Bi_2Te_3 has a rhombohedral structure with space group R -3 m (#166). It exhibits layered structure assembled in three quintuple layers of Te(1)-Bi-Te(2)-Bi-Te(1). In order to optimize the performance of thermoelectric device, proper evaluation of mechanical properties will be required which will provide sufficient data to scientist and manufacture to integrate into practical thermoelectric device [5].

Hardness is one of the crucial mechanical properties which measure the resistance of material to plastic deformation induced by mechanical indentation and further movement of large dislocations. The hardness of material can be controlled by varying the presence of density of dislocations. On increasing of density dislocation, anchor points will be added which impede the movements of dislocations and the material will become harder [6].

In the present work, Bi_2Te_3-based composites namely $Bi_{0.5}Sb_{1.7}Te_{3+x}$(x = 0, 0.12, 0.14) have been developed to study the hardness behavior for finding the feasibility of materials to be deployed in making thermoelectric devices.

EXPERIMENTAL

The high purity elements of Bi (99.5%), Sb (99%) and Te (99.5%) were weighed according to stoichiometric ratio and mixed well. The mixed powder was then sealed into a quartz tube under the pressure of 10^{-5}Torr. The sealed tube was placed in the electronically controlled furnace for 8 hours at 800 °C. The phase confirmation of reacted samples was performed using powder X-ray diffractometer (PXRD, Model: Rigaku Mini Flex II) operated at 30 kV and 20 mA using Cu-Kα(λ =1.54 Å)in the range 20° to 80° of 2Θ.The reacted ingots were then mixed with help of mortar

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pestle and the mixed powders were then loaded in the graphite die of diameter 12.7mm for consolidation through Spark plasma sintering technique which were sintered at temperature 673 K and pressure of 50 Pa. The disc shaped samples were cut and polished to obtain the smooth surfaces. The micro-hardness measurements were carried out on samples $Bi_{0.5}Sb_{1.7}Te_{3+x}$(x = 0, 0.12, 0.14) through Vickers microindenter (model: OMNITECH 24450312/530) with micro load attachment. The indentations were performed at different loads between 5 g and 100g for 10seconds and average of 5 indentations for one sample was taken at each loads. Microstructure study was performed by transmission electron microscopy (TEM). Results and Discussions

Structural Investigation

Figure 1 shows the XRD diffraction pattern for samples $Bi_{0.5}Sb_{1.7}Te_{3+x}$(x = 0, 0.12, 0.14) which were synthesized via solid state reaction. All the XRD peaks were primarily indexed with the structure Bi_2Te_3 –type (rhombohedral with space group R -3 m) structure with other peaks of Sb and Te.

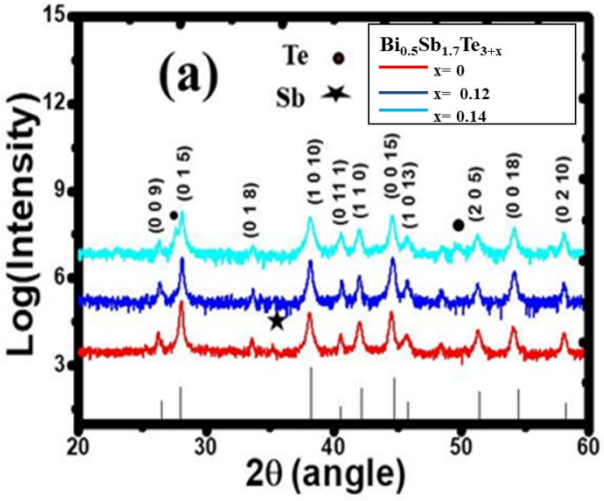

FIGURE 1. XRD pattern of composite samples $Bi_{0.5}Sb_{1.7}Te_{3+x}$(x = 0, 0.12 and 0.14)

Micro Hardness Investigation

Figure 2 (a) shows the micro hardness measurement (VHN) performed on $Bi_{0.5}Sb_{1.7}Te_{3+x}$(x = 0, 0.12, 0.14) at different loads (P) which is compared with the hardness of single phase state-of-the-art $Bi_{0.5}Sb_{1.5}Te_3$. One may notice that with Sb doping; $Bi_{0.5}Sb_{1.7}Te_3$, the hardness was found to be decreased when compared with that of matrix $Bi_{0.5}Sb_{1.5}Te_3$ phase material which could be due to the precipitation of soft metallic Sb within the matrix phase. However, with further increase of Te in $Bi_{0.5}Sb_{1.7}Te_{3+x}$, hardness starts to slightly increase which describes more prominent in case of $Bi_{0.5}Sb_{1.7}Te_{3.14}$ but less than that of state-of-the-art $Bi_{0.5}Sb_{1.5}Te_3$ materials. For instance, the VHN for $Bi_{0.5}Sb_{1.7}Te_{3.14}$ was observed to be 61.6kg/mm^2 at load 100g while VHN at 100 gm for $Bi_{0.5}Sb_{1.7}Te_3$ and $Bi_{0.5}Sb_{1.7}Te_{3.12}$ were noted to be 61.3 kg/mm^2 and 43.84 kg/mm^2 respectively. The rationale behind this is that $Bi_{0.5}Sb_{1.7}Te_{3.14}$ contains high density of dislocations which is presented in TEM micrograph (Figure 2b). This prominent enhancement of hardness in $Bi_{0.5}Sb_{1.7}Te_{3.14}$ is considered to be associated with increased dislocation density (Fig 2b) in this sample. Basically the dislocation moving through the materials enables the flip of planes of atoms from one side of the dislocation to other side and this movement causes a decrease in hardness. When the dislocation density increases, the dislocation interacts with other dislocation which protects the movement of dislocation through the materials and these interaction between dislocations creates an anchor point and will not allow the flipping of planes of atoms and movement is disrupted [6]. If more anchor points will be added by these interactions which means introducing the more dislocations will enhance the hardness of material. Thus based on this analogy, enhancement of hardness in $Bi_{0.5}Sb_{1.7}Te_{3.14}$ can be expected similar to earlier reports [7]. One can clearly notice that on increasing the loads, the hardness is increased and after 75grams the hardness was observed to be saturated for all samples.

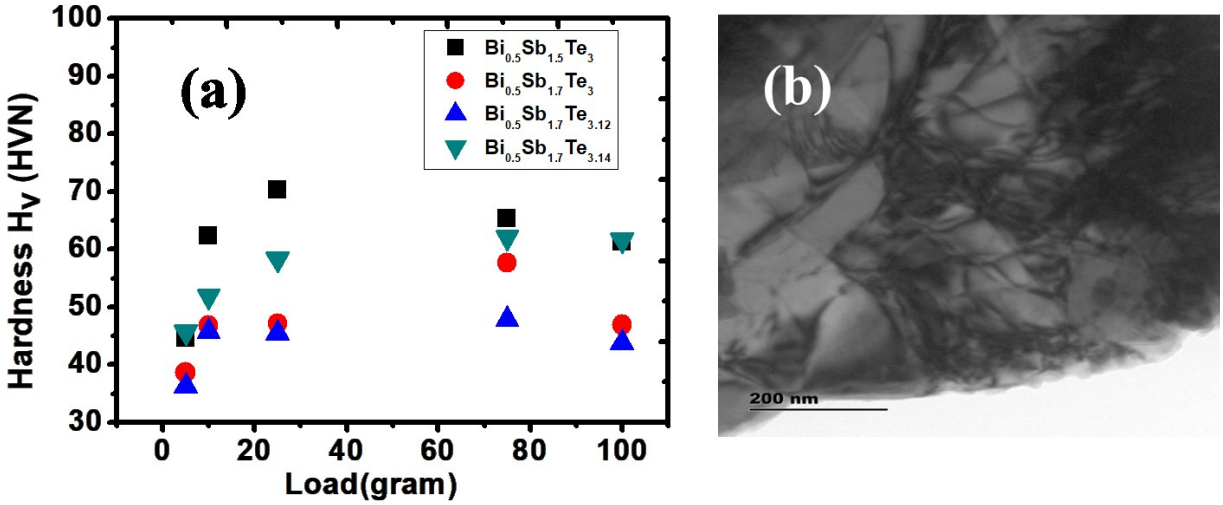

FIGURE 2: a) The micro hardness measurement performed on samples $Bi_{0.5}Sb_{1.7}Te_{3+x}$(x = 0, 0.12, and 0.14) and $Bi_{0.5}Sb_{1.5}Te_3$ b) TEM micrograph of sample Bi0.5Sb1.7Te3.14 showing high density of dislocations.

CONCLUSION

The several stoichiometry compositions $Bi_{0.5}Sb_{1.7}Te_{3+x}$(x = 0, 0.12, 0.14) were successfully synthesized by solid state reaction followed by SPS technique. The addition of excess Te (x = 0.12) leads to formation of dislocation and on further addition of Te with x= 0.14, the high density of dislocation was created which corresponds to large value of hardness in comparison to other composites. Overall, the VHN of composites was found to be decreased in comparison with that of matrix $Bi_{0.5}Sb_{1.5}Te_3$. The decrease in VHN of composite materials is attributed due to the precipitation of soft metallic Sb and Te within the matrix phase.

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