Effect of deformation and annealing effect on Thermoelectric Properties of flexible $Ag_2S_{1-x}Se_x$ (0 < x < 0.55) Material for Energy Applications

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The development of thermoelectric generators for alternate source of energy are currently a major focus as devices capable of supplying an input power (μW to mW) to many sensors, electronic gadgets, and wearable devices in low temperature range around 300 – 400 K [1]. Improvement of *figure of merit*, *ZT*, of the thermoelectric materials used in such device are very important. Besides, if these materials are flexible [2], the number of applications would be significantly enlarged.

Recently, Ag_2S is found to be an interesting material, as near room temperature it possesses good flexible properties with very low thermal conductivity (~ 0.5 W/m K) and large Seebeck coefficients (~ –900 μV/K) [3]. However, due to large electrical resistivity (~ 10^6 mΩ cm), the value of *ZT* was found to be very low. To improve the *ZT*, the partial substitutions of Se, Te at sulfur site are investigated [4,5]. Interestingly, the ductile nature of Ag_2S material found to be excellent with Se substitutions at sulfur site for $Ag_2S_{1-x}Se_x$ ($0 < x < 0.55$) compositions, and the maximum *ZT* of ~0.6 at 300 K is achieved near room temperature [4]. Although the value of *ZT* is significantly improved, however, the investigations in literature are mainly focused on mechanical properties and their TE properties are studied on bulk samples only [3,5]. In order to know the real performance of flexible, Ag_2S-based thermoelectric devices, it is of great importance to investigate the thermoelectric properties of flexible thin ribbon samples made by mechanical rolling.

In this study, therefore, the TE properties of deformed samples for all the compositions are investigated as function of temperature for both bulk and rolled samples (typical thickness of ~30 μm). The annealing effect treatment on rolled samples is found to be very effective in recovering the value of *ZT* which is same as obtained for the bulk. This is due to the relaxation of mechanical stress introduced in rolled sample during mechanical deformation.

Polycrystalline samples were prepared by using standard melting method. The rolled samples were annealed in vacuum sealed Pyrex glass tube above the phase transition of each composition. The measurements of bulk and rolled samples were made for several cycles to check the reproducibility of TE properties.

Structural characterization of as-prepared powder sample was carried out by using Bruker D8 Advance Cu K_α source, and found to be in single phase. Chemical composition and grain structure analyses were performed using Scanning Electron Microscope-Energy Dispersive X-ray spectroscopy (SEM-EDX), HITACHI SU 6600. Heat and electron transport properties were measured on hot-pressed bulk samples. Thermal conductivity measurement was done by using Laser flash analysis (NETZSCH LFA 457); whereas for Seebeck coefficient and electrical resistivity measurement, experimental systems developed in our laboratory were used [4].

The electrical resistivity (ρ) and Seebeck coefficients (S) of the rolled samples were found to be decreased in comparison to the bulk sample, this is due to change in local electronic structure upon mechanical deformation. After annealing, the internal stress of rolled sample become relaxed, and TE properties get recovered. Thus, we obtained the power factor ($PF = S^2/\rho$) similar to the bulk samples.

Thermoelectric properties bulk and rolled samples were measured over the whole composition range of $Ag_2S_{1-x}Se_x$ ($0 < x < 0.55$) in the temperature range of 300 – 650 K. The maximum value of *ZT* ~ 0.6 near room temperature reported for the bulk $Ag_2S_{0.45}Se_{0.55}$ [4] is well reproduced for the rolled sample of provided that the sample is annealed at the temperature slightly higher than the transition temperature. This result suggests that annealing at rather low temperature is good enough to recover the TE properties of deformed silver chalcogenide materials for the flexible TE device fabrications.

In this JSAP meeting, we will discuss in more details about the annealing effect on TE properties of high-performance flexible $Ag_2S_{1-x}Se_x$ ($0< x <0.55$) samples.

References

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