Development of Non-Toxic and Flexible Ag_2S Based Thermoelectric 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 substitutions of Se, Te at sulfur site are investigated [4,5]. Although significant enhancement in *ZT* is achieved but limited to *n*-type only. Also, it contains the toxic elements, therefore it is not appropriate to make the flexible TE devices which directly used with human body heat. To overcome this issue, modification in electronic structure of Ag_2S is of crucially importance. For such a purpose partial substitution at the Ag site can play an important role. Investigations using this approach have not been widely performed yet, and study in this direction is required. Therefore, we carried the electronic structure calculations on $Ag_{2-x}TM_xS$ (TM = transition metal element using DFT, and successfully achieved both *p* and *n*-type TE property of these material experimentally.

In the present work, we performed the first-principles calculations based on the density functional theory (DFT) with generalized gradient approximation (GGA) in the form of Perdue–Burke–Ernzerhof (PBE) for the exchange-correlation energy functional, as implemented in the VASP code. Firstly, with different transition metals substitutions at Ag site, we observed the formation of impurity peak in density of states, either of the valance (VB) or conduction band (CB) edge depends upon the elements used. The small impurity peak near VB and CB edge is very effective in modifying the thermoelectric properties of Ag_2S and to get the better TE property of *p*-type and *n*-type materials, respectively. We also computed the transport coefficients using BoltzTraP code under constant relaxation approximation. Secondly, in order to confirm the theoretical results, we synthesized the selected compositions of $Ag_{2-x}TM_xS$, and investigated thermoelectric properties of in the 300-450 K temperature range where only the low temperature phase is obtained. Polycrystalline samples were prepared by using standard melting method. 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].

For all the samples with substitutions of different atomic percentage in between 0.0 to 2.0 we observed *n*-type behavior in case of V, whereas with some other elements substitutions we observed *p*-type behavior. The electrical resistivity and Seebeck coefficient were monotonically decreased with increasing the amount of substituted elements while thermal conductivity remains low. Interestingly, both *p* and *n*-type of materials with non-toxic composition showed ductile nature which is very useful feature to make the flexible TE device. The detail results about synthesis, chemical compositions and figure of merit obtained in study will be presented in the conference.

References

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