AES
ISSN: 2096-3246
Volume 54, Issue 02, December, 2022
Special Issue

A BRIEF REVIEW ON THE THERMOELECTRIC PROPERTIES OF CHALCOGENIDE GLASSES

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Abstract

Chalcogenide glasses (ChGs) have unquestionably become the most widely used materials in the field of electronics, medicine, detection etc. ChGs are being actively studied to enhance their future uses. Among many of their magnificent properties is the thermoelectric (TE) property which is attracting many researchers towards these materials. By implementing advanced nanoscience and nanotechnology, numerous fresh TE materials with high figure of merit (ZT) are produced. This is particularly true for materials based on metal chalcogenides, which among all the various types of thermoelectric materials have relatively high ZT and low cost. In the present work, we have summarized the main parameters which decides whether the material is suitable for TE applications or not like Seebeck Coefficient (S), electrical conductivity (σ) and power factor (P) for various systems.

Keywords: Chalcogenide glasses, Thermoelectric properties, Seebeck effect

1. Introduction

Chemical compositions called chalcogenide glasses (ChGs) have at least one chalcogen atoms (*S*, *Se*, or *Te*) among their constituent elements. Scientists have been quite interested in ChGs over the past few decades, and this subject is still in its early stages of growth. ChGs are sometimes referred to as amorphous semiconductors because of the intermediate energy band gap values, which gives them a wide range of uses in the fields of electrical switching [1], memory [2], solar applications [3], among others. These glasses are suited for use in memory [4], photoelectrochemical cell [5], LEDs [6], Infrared (IR) [7], and optical limiting [8] applications because they display phase change properties and have optical transparency from visible to IR regions.

ChGs have several noteworthy properties such as electrical, thermal, optical, thermoelectric etc. The urgency of our energy and environmental problems has drawn significant attention to a number of affordable and pollution-free technologies, among which thermoelectric technology has made remarkable achievements. Chalcogenide-based TE materials have a greater power factor than oxide-based ones because their bonds are less covalent due to their low electronegativity values. As compared to some other TE materials, ChGs' heavier atomic weight is advantageous for lowering thermal conductivity. Additionally, ChGs are simple to produce into a variety of structures, providing a solid foundation for examining and enhancing TE performance. Numerous studies have demonstrated the superior performance of Chalcogenide TE materials. The advantage of chalcogenide-based TE materials also comes from their affordability, both in terms of production and use. [9].

2. Review of Thermoelectric Properties of ChGs

Thermoelectric properties of *Cu-Ge-Te* films (ternary system) have been studied [10]. The properties under studies for the composition Ge_{26}-Cu_x-Te_{74-x} (for at. % $2.5 \leq x \leq 12.5$) are dark dc-electrical conductivity (σ_{dc}) and S or Thermoelectric Power (TEP) for the temperature range 300-450 K. For evaluation of σ_{dc} and TEP, two electrodes of gold with a spread of 0.015 m and having length of 0.014 m were used. These evaluations were done in a vacuum ~ 10^{-1} Pa. The ln (σ_{dc}) vs $1/T$ graph was plotted from the calculated values of σ_{dc} and a linear behavior was seen. This confirms that for the temperature between 300 to 450 K, the electric conduction was executed by an activated step with a distinctive activation energy (AE). S or TEP is a valuable parameter for the characterization of amorphous semiconducting glasses. It is mainly based on the density of states. All samples have substantial positive values for TEP and there exists a negative relationship between TEP and temperature [11]. The values of σ_{dc} were seen to be increasing when *Cu* content is increased while on the other hand values of TEP decreased on increasing *Cu* content in the sample. Chemical bond approach (CBA) has been used to explain these findings. The *Te-Te* homopolar bonds, which act as defects, increase significantly on the *Cu* addition. Calculated TEP of all samples shows positive values and a descending temperature dependence. The glass transition temperature (T_g) and electrical conduction have a strong correlation.

Se doped In_2Te_3 thin films were studied for their TE properties [12]. These thin films, prepared via thermal evaporation, were annealed at 250 °C and 300 °C in *Ar* gas. For ternary system $In_2(Te_{1-x}Se_x)_3$ (x = 0.04,0.06,0.08 and 0.1) thermoelectric properties (σ_{dc} and TEP) were calculated in the temperature range 300-430K. Large values for S and σ are desired in an ideal thermoelectric material. High thermoelectric efficiency is achieved when thin film of the material is deposited as it minimizes the material's dimensions and thermal conductivity [13]. At room temperature, with the samples illuminated by white light of 150 Klux, photocurrent through the films was measured. Dark current of few nA was observed in the films which indicates the presence of charge carrier traps in the films. The negative values of S confirmed the n-type semiconducting behavior. For the films annealed at 300 °C, the corresponding S value ranged from -338 to -510 μVK^{-1}. In contrast to the films that had just been deposited, the values of S for the annealed films were marginally higher. The obtained values for the S closely match those reported in the literature for n-type *In-Se* and Bi_2Te_3-In_2Te_3 nanocomposites. It is possible that the structural transition of the $In_2(Te_{1-x}Se_x)_3$ phase into the In_2Se_3 and In_2Te_3 phases is what causes the change in thermoelectric characteristics in respect of annealing temperature.

The p-type *Cu* doped $As_{30}Se_{55}Sb_{15-x}Cu_x$ ($2.5 \leq x \leq 10$ at. %) films produced by vacuum thermal evaporation from bulk glasses were studied [14]. When *Cu* is added, the electron concentration is improved, which dramatically improves σ across the whole temperature range. Authors have investigated the thermoelectric behaviour between 300 to 420 K. The calculated σ_{dc} values increased with the enhancement of *Cu* atomic percentage. The performance of thermoelectric energy converters is governed by the power factor *P*. Using σ_{dc} and *S* in respect to $P = S^2\sigma_{dc}$, the succeeding values of *P* for $As_{30}Se_{55}Sb_{15-x}Cu_x$ thin films were determined. Observations indicated that *P* exhibits typical semiconductor behaviour, in contrast to how *P* was represented as a function of temperature. Additionally, it was discovered that *P* increased as temperature rises. *P* was also observed to rise when the concentration of *Cu* did, indicating that increasing *Cu* is more efficient at improving σ than at decreasing *S*. The noticed rise in *P* values by either rising temperature or *Cu* concentration is much in line with that which has already been published [15] In temperatures between 300 and 420 K, it has been demonstrated that electrical conduction occurs by an active process with a single AE. Result shows that the films under study may be applicable as TE.

Experimental measurements were made on the σ_{dc} and thermoelectric power for compositions $(SbSn)_xSe_{100-x}$ with *x* varying from 4 to 20 at. % [16]. The σ_{dc} has been measured for the temperature range 300-450 K and different conduction mechanisms, such as thermally triggered charge carrier mobility, tiny polaron hopping, and non-bipolar conduction, have been linked to the difference in activation energies between the σ and *S*. Melt quenching technique has been used to produce bulk glassy chalcogenides $(SbSn)_xSe_{(100-x)}$ ($x = 4$, 8, 12, 16 and 20 at. percent). Thin films of *Sb-Sn-Se* were deposited onto glass substrates then their σ_{dc} was measured at various compositions and temperatures where it was observed that the fluctuation of σ_{dc} with temperature often exhibits an Arrhenius pattern. So, above room temperature conduction continues through inter-band transitions. An increase in the conductivity values with *SbSn* atomic percentage at a particular temperature is related to an increase in the carrier concentration and reduction in bandgap values. The thermoelectric power value and the associated AE, ΔE_s, are both reduced by increasing atomic percentage of *SbSn* at a specific temperature. According to how *S* changes with temperature, one-band conduction with holes as charge carriers is the predominating situation. The ΔE_s derived from measurements of TE is lower than that derived from measurements of electric conductivity (ΔE_σ). The barrier to polaron hopping may be related to the difference $\Delta E = \Delta E_\sigma - \Delta E_S$. This mechanism is referred to as small polaron conduction. This effect is linked to *Se* presence in the glass network [17]. The calculated *S*, power factor, and the inferred electronic contribution to σ_{dc} were displayed, from which it can be implied that holes are the majority carriers and additional measurements of contribution of lattice vibration to σ_{dc} are required to assess how the merit of these alloys changes with composition. The polaron's hopping energy was raised with *SbSn* content, owing to the rise in cross-linking density. This energy is related to the difference of AE of electric conduction and *S*.

The impact of inclusion of *As* in the ternary system $Bi_{0.02}As_xSe_{0.98-x}$ system has been discussed by Dahshan *et al* [18]. From σ_{dc} and *S*, the activation energies of electrical and TE conductions were estimated respectively. σ_{dc} was measured and according to the Arrhenius rule, the linearity of the plots of $\ln(\sigma_{dc})$ vs $1/T$ demonstrated that the electrical conduction in *Bi-As-Se* glasses occurs by an activated process with a single AE spanning over the temperature 300-420 K. For *Bi-As-Se* films, it was discovered that σ_{dc} rises but ΔE_{dc} falls with an increase in *As* content. $\Delta E_{dc} = 0.64$ eV for $x = 0.02$ glass but drops to 0.53 eV for $x = 0.08$. *Bi-As-Se* thin films' carrier mobility (μ) may be estimated at various temperatures since μ is directly related to the free carriers lifetime via the equation: $\mu = e\tau/m^*$). ΔEs can be estimated in non-crystalline semiconducting materials by the *S* values or TE power via the relationship: $S = k_B e^{-1}(\Delta E_s/k_B T + AA)$ [19]. S was discovered to decline as temperature rose. All sample's S values are positive, suggesting that the holes are majority charge carriers in these films, making the *Bi-As-Se* thin films p-type semiconductors. S lowers as the *As* content rises and the energy difference between the E_F (Fermi level) and transport level cand be determined by looking at how the values of S change as a function of temperature. For *Bi-As-Se* thin films, the electrical conduction occurs via an activated process with a single AE in the temperature range 300-420 K. As the *As* content rises, the electrical conductivity rises along with the thermoelectric power and AE of electrical and TE conduction.

PbTe-based alloys, which are among the many thermoelectric materials, typically exhibit outstanding thermoelectric properties and are frequently employed in a variety of industries. When $(PbTe)_x(Ga_2Te_3)_{100-x}$ and $(PbTe)_x(In_2Te_3)_{100-x}$ alloys were compared, it became clear that low entropy of fusion (ΔS_m) and a deep eutectic manner are the two factors that determine an alloy's ability to form glass (GFA) [20]. By using the melt quenching technique, the pseudo-binary alloys were synthesized. High pure *PbTe*, $Ga2Te_3$, and $In2Te_3$ compounds were weighed according to the proper molar ratio and then vacuum sealed into quartz ampoules. To encourage the degree of mixing, ampoules were heated to a highest temperature of 1300 K in a rocking furnace and maintained isothermally for 12 hours. The ingots were then cooled to normal temperature in the furnace. The composition range of $x = 52$ to 64 was recognized as the glass-forming region, and the ideal glass composition was found to be $(PbTe)_{61}(Ga_2Te_3)_{39}$. It has been established that the two main criteria that cause *PbTe*-based alloys to vitrify were low fusion entropy and deep eutectic fashion. Bulk glasses with the best glass composition were made using SPS having a very low thermal conductivity of 0.1 $Wm^{-1}K^{-1}$ at 300K.

TE features of the kesterite-structured Ag_2CdSnS_4 and $Ag_2CdSnSe_4$ compounds were reported by Mohammed *et al* [21]. The change in heat energy that causes heat gradients is caused by the flow of charge carriers and phonon frequencies, which is how the induced potential difference is achieved. Positive values of the S show that the system is p-type, while negative values indicate at n-type semiconductors. S exhibits two distinct peaks for n-/p-types near E_F, with the maximum value being found at 300 K. The critical points of Ag_2CdSnX_4 ($X = S, Se$) for S for both p-type and n-type are ±1.5. (μeV). Beyond these ranges, S almost completely disappears; these key points reflect the range in which the materials display good thermoelectric capabilities. The efficiency of power generation by thermoelectric devices is shown by the FOM parameter, defined by $ZT = S^2\sigma\ T/k$. At room temperature, ZT is typically equal to unity for the p-/n-type of both compounds. Furthermore, the largest ZT peaks were found to be in the region of ±0.5 μ(eV) for Ag_2CdSnS_4 and ±0.25μ (eV) for $Ag_2CdSnSe_4$, which supports the findings that these materials have the highest thermoelectric efficiency. It has been established that the materials with ZT value of one or above are regarded attractive choices for TE devices.

First-principles computations were used to analyze the TE properties of the *Cd* chalcogenides *CdX* monolayers, where $X = S, Se$ and *Te* [22]. The WIEN2k package, which employs the full-potential linearized augmented plane wave (FP-LAPW) formalism, is used to conduct studies. The BoltzTraP code, which utilises the semi-classical Boltzmann transport theory along with the constant scattering time and rigid band approximation, is used to calculate the TE properties of the *CdX* monolayers [23]. *S* has positive values over the temperature range of 200-1200 K, demonstrating that holes are the primary charge carriers. The thermopower increases for temperatures up to 750 K in the same order as the chalcogenides' atomic number. The *CdS* monolayer thermopower increases than that of the *CdSe* single layer at 750 K, and it reaches its maximum value at 1050 K. For *CdSe* and *CdTe* monolayers, this parameter falls significantly as the temperature rises, whereas the influence of temperature on the *CdS* monolayer thermopower is quite minimal. The analyzed monolayer's σ_{dc} increases approximately linearly as temperature rises. In contrast to thermopower, a trait of semiconductor materials, this behaviour exhibits an opposing temperature-dependent fluctuation. The *CdS* monolayers are discovered to have the lowest electrical conductivity at a particular temperature. The σ_{dc} of the *CdTe* single layer is greater than the *CdS* single layer for temperatures up to 800 K. When the temperature rises, thermal excitation causes an increase in the charge carrier concentration, which causes the electrical conductivity to rise.

Strontium Chalcogenides (*SrX*, *X = O, Se, S* and *Te*) were studied for the temperature dependent transport properties in their rock salt (rs-SrX) and hexagonal monolayer (h-SrX) phases. *S*, σ and ZT (Figure of merit) were measured using BTE. When compared to their multi-layer counterparts (with smaller energy gaps), single layer systems with wide energy gaps exhibit better TE characteristics. A wide range of temperature, 100–1200 K, has been used to record the response of heat transfer. The chemical composition of the material, structural symmetry, grain size, temperature, phase transition, and pressure are the primary determinants of the heat response behaviour. In comparison to their hexagonal monolayer counterparts, in general the heat response in σ is shown to be greater in the case of rock-salt phases. The hexagonal monolayers of *SrS* and *SrTe* show the least thermal conductivity, while the *SrO* in rock-salt phase exhibits the most thermal conductivity if compared to their respective bulk counterparts also. σ was measured over a range of temperature 100-1200 K. The dimensions, chemical compositions, and stress states of a material have a major impact on its electrical conductivity. It should be emphasised that all the materials under consideration have significant electrical conductivities, with *SrSe* monolayers having the highest and *SrS* and *SrTe* monolayers having the lowest values in the series. Due to the fact that wide band gap semiconductors' availability of charge carriers determines a material's σ, the presence of few charge carriers in the materials under consideration fundamentally causes their conductivity to decrease as temperature rises. With respect to the temperature increase, there is a minor decrease in σ for both phases. It is known that a material's internal temperature differences cause charge carriers to flow from the hot to the cold side, creating a potential difference which is known as TE voltage that is used to determine the S of *SrX* compounds. The majority charge carrier type in the system is mainly determined by the sign of *S*. The positive Seebeck zone contains the monolayer *SrS* and *SrSe* as well as rock-salt *SrO*, whereas the negative Seebeck region contains the rest material. Thermoelectric materials with ZT > 0.8 for temperatures above 600 K were discovered to include a few monolayers (*h-SrTe* and *h-SrS*) and rock salt phases (*rs-SrO* and *rs-SrS*), with monolayers exhibiting only marginally higher efficiency [24].

3. Conclusion

Several binary, ternary and quaternary systems were studied for their thermoelectric properties. Thin films were generally synthesized using thermal evaporation technique. It was observed that value of *S* decides the majority charge carriers in the glass. If value of *S* iss positive, majority charge carriers are holes and thin films behave as p-type semiconductors and if *S* is negative, majority charge carriers are electrons, hence, thin films behave as n-type semiconductors. Generally, σ_{dc} was seen to be increasing with the content of dopant and temperature. σ_{dc} followed Arrhenius pattern. Power Factor (*P*) was also seen to follow the above behavior. At room temperature ZT, usually have value equal to unity for both type of semiconducting films. The major applications of chalcogenides as Thermoelectric materials are in sensors, thermoelectric generators, memory devices, etc.

4. References

[1] T. Cao, M. Cen, Fundamentals and Applications of Chalcogenide Phase-Change Material Photonics, Advanced Theory and Simulations, Vol. 2, Issue 8, (2019), https://doi.org/10.1002/adts.201900094

[2] Y. Xu, X. Wang, W. Zhang *et al* , Materials Screening for Disorder-Controlled Chalcogenide Crystals for Phase-Change Memory Applications, Advanced Materials, Vol. 33, Issue 9, 2006221 (2021), https://doi.org/10.1002/adma.202006221

[3] T. Gille, K. De Meyer, D. J. Wouters, Amorphous–crystalline phase transitions in chalcogenide materials for memory applications, Phase Transitions, vol. 81, no. 7–8, pp. 773–790, (2008), DOI: 10.1080/01411590802024852

[4] V Rao, P K Singh, P Lohia and D K Dwivedi, Non-isothermal crystallization kinetics of $Se_{82-x}Te_{18}Ge_x$ $(0 \leq x \leq 12)$ for memory applications. *Indian J Phys* 96, 1075–1085 (2022). https://doi.org/10.1007/s12648-021-02036-x

[5] J Henry, T Daniel, V Balasubramaninan, K Mohanraj and S Sivakumar, Chemically deposited p-type MoBiCuS4 thin film for photoelectrochemical cell applications, Phosphorus, Sulfur, and Silicon and the Related Elements, 197 (2022) 152-157. https://doi.org/10.1080/10426507.2021.1990921

[6] Ganesha Krishna V S, S Chattopadhyay, and K P Misra, Spectroscopic investigation of $Cu_xMg_{0.2-x}Zn_{0.8}S$ (x = 0, 0.05, 0.10, 0.15) thin films for deep and dilute blue LED applications, Luminescence, 37 (2022) 28-39. https://doi.org/10.1002/bio.4143

[7] I Kebaili, I Boukhris, Z A Alrowaili, M M Abutalib, and M S Al-Buriahi, Characterization of physicochemical properties of As2Se3–GeTe–AgI chalcohalide glasses for solar cell and IR applications: influence of adding AgI, J. Mater. Sci.: Mater. Electron., 33 (2022) 800-809. https://doi.org/10.1007/s10854-021-07350-y

[8] K Wang, W Wang, C Lin, X Shen, S Dai, and F Chen, Study on third-order optical nonlinear properties of transparent chalcogenide glass ceramics within Ge–S binary system, Ceram. Int., 48 (2022) 11209-11214. https://doi.org/10.1016/j.ceramint.2021.12.341

[9] C. Han, Q. Sun, Z. Li, S.X. Dou, Thermoelectric Enhancement of Different Kinds of Metal Chalcogenides, Advanced Energy Materials, 1600498, (2016), DOI: 10.1002/aenm.20160049

[10] S.R. Alharbi, K.A. Aly, Electrical and thermoelectric properties of ternary Cu-Ge-Te films, Journal of Alloys and Compounds, (2019), https://doi.org/10.1016/j.jallcom.2019.05.112

[11] E.R. Sittner, K.S. Siegert, P. Jost, C. Schlockermann, F.R.L. Lange, M. Wuttig, (GeTe)x(Sb2Te3)1-x phase-change thin films as potential thermoelectric materials, Physica Status Solidi (A) Applications and Materials Science, 210 (2013) 147-152, https://doi.org/10.1002/pssa.201228397

[12] P. Mannu, M. Palanisamy, G. Bangru, S. Ramakrishnan, M. Ramcharan, A. Kandasami, Structural and thermoelectric properties of Se doped In2Te3 thin films, American Institute of Physics ADVANCES 8, 115015 (2018), https://doi.org/10.1063/1.5057734

[13] L. L. Zhao, X. L. Wang, J. Y. Wang, Z. X. Cheng, S. X. Dou, J. Wang, and L. Q. Liu, Superior intrinsic thermoelectric performance with zT of 1.8 in single-crystal and melt-quenched highly dense Cu(2-x)Se bulks, Scientific Reports, vol. 5, 7671 (2015), https://doi.org/10.1038/srep07671

[14] H.H. Hegazy, A. Dahshan, K.A. Aly, Effect of Copper Addition on the Thermoelectric Power Factor and Electrical Conductivity of As-Se-Sb-Cu Thin Films, https://doi.org/10.1088/2053-1591/ab1efc

[15] A.P. Goncalves, G. Delaizir, E.B. Lopes, L.M. Ferreira, O. Rouleau, C. Godart, Chalcogenide Glasses as Prospective Thermoelectric Materials, Journal of Electronic Material, vol. 40, 1015 (2011), doi: 10.1007/s11664-010-1486-8

[16] R. Neffati, K. Aly, A. Dahshan, Electric and thermoelectric properties of (SbSn)xSe100−x chalcogenide glasses, Applied Physics A (2021) 127:639, https://doi.org/10.1007/s00339-021-04777-2

[17] H.A.V. Plas, R.H. Bube, Thermoelectric power of amorphous compound semiconductors Journal of Non-Crystalline Solids Vol. 24, 377–398 (1977), https://doi.org/10.1016/0022-3093(77)90106-5

[18] A. Dahshan, S. R. Alharb, K. A. Aly, Y. Saddeek, Thermal, mechanical, electrical and thermoelectric properties of Bi–As–Se glasses, Journal of Thermal Analysis and Calorimetry, (2019), https://doi.org/10.1007/s10973-019-08810-8

[19] H. Fritzsche, A general expression for the thermoelectric power, *Solid State Communications, (1971),* DOI:10.1016/0038-1098(71)90096-2

[20] P. Li, X. Qi, L.M. Wang, A comprehensive study of lead telluride (PbTe)-based amorphous alloys: Glass formation and thermoelectric properties, Journal of Non-Crystalline Solids 571 (2021) 121057, https://doi.org/10.1016/j.jnoncrysol.2021.121057

[21] H.M. Mohammed, F. Chiker, H. Khachai, N. Benosman, R. Khenata, R. Ahmed, S. Bin Omran, A. Bouhemadou, Xiaotian Wang, Structural, optoelectronic, optical coating and thermoelectric properties of the chalcogenides type Kesterite Ag2CdSnX4 (with X=S, Se): A computational insight, Materials Science in Semiconductor Processing 134 (2021) 106031, https://doi.org/10.1016/j.mssp.2021.106031

[22] M. Naseri, D.M. Hoat, J.F. Rivas-Silva, G.H. Cocoletzi, Electronic structure, optical and thermoelectric properties of cadmium chalcogenides monolayers, Optik, Volume 210, (2020) 164567, https://doi.org/10.1016/j.ijleo.2020.164567

[23] G.K. Madsen, D.J. Singh, BoltzTraP. A code for calculating band-structure dependent

quantities, Computer Physics Communications 175 (1) (2006) 67–71, https://doi.org/10.1016/j.cpc.2006.03.007

[24] K. Rajput, D.R. Roy, Structure, stability, electronic and thermoelectric properties of strontium chalcogenides, Physica E: Low- Dimentional Systems and Nanostructures, vol. 119 (2020) 113965, https://doi.org/10.1016/j.physe.2020.113965