Effective thermal conductivity and effective thermal diffusivity of $Se_{100-x}Zn_x$ chalcogenide system

N. S. SAXENA, R. SHARMA, K. SINGH, T. P. SHARMA
Condensed Matter Physics Laboratory, 5-6 Vigyan Bhawan, Department of Physics, University of Rajasthan, Jaipur 302004, India
E-mail: n_s_saxena@hotmail.com

In recent years, much attention has been given to II–VI group chalcogenide materials, mainly due to their wide range of applications as solid state devices both in scientific and technological fields [1]. These materials have come under increased scrutiny because of their wide use in cost reduction of devices for photovoltaic applications [2]. The research on renewable energies includes the photovoltaic conversion of solar energy and important investigations of novel materials and structures. In particular Selenium alloys are used in X-ray imaging and photonics [3]. ZnSe is one of the most promising materials for use in white LEDs and blue laser diodes [4].

The scattering of photons with the defects, impurities, and dislocations in the crystals influences the thermal transport properties i.e., thermal conductivity, thermal diffusivity and specific heat. Attempts have been made from time to time to investigate the thermal transport properties of loose granular materials, insulating building material, composites, plastics [5], and chalcogenide glasses [6] using transient methods. Nevertheless, very little effort has been made to understand the heat energy dissipation through polycrystalline materials [7].

Thermal conductivity investigations yield useful information on several properties of the material. Studies of the variation of thermal conductivity and thermal diffusivity of Se-Zn at different Zn concentrations provides a deep knowledge of thermal energy transfer through random process (conduction and diffusion). Thus it can be used as a tool in the study of imperfections, dislocations, and voids, as the carrier mean free path is mainly affected by the lattice defects [8]. In the present work, an investigation has been undertaken to study the variation of effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) of the Zn_xSe_{100-x} ($x = 0$, 10, 20, 30, 40, and 50) system using the transient plane source (TPS) technique.

High purity (99.99%) selenium granules and fine Zn dust in appropriate atomic percentage were weighed and simply mixed by grinding with the help of a mortar and pestle for about 10 hrs at room temperature. The alloys were prepared through a simple solid state reaction. Solid solutions can be formed between two or more components provided that their atomic radii, electronic structures, and crystal structures are similar [9]. In Se-Zn systems these conditions are fulfilled and therefore solid solutions are formed. In the present study a binary solid solution of Zn and Se has been prepared in the powder form. Then pellets of thickness 2 mm and diameter 12 mm were prepared by compaction. The pellets were made at a constant pressure of 433 MPa. The surfaces of these pellets were smooth so as to ensure good thermal contact between the samples and the heating elements as the TPS sensor is sandwiched between the two pellets of sample material in the sample holder as shown in Fig. 1. The change in the voltage was recorded with a digital voltmeter, which was connected to a personal computer.

The power output to the sample was adjusted according to the nature of the sample material and was, in most cases, in the range 6×10^{-6}– 16×10^{-6} W/m^2. The measurements reported in this paper were performed with a TPS element. It was made of a 10 μm-thick nickel foil (having a resistance of about 3.26 Ω and a temperature coefficient of resistance (TCR) around (4.6×10^{-3} k^{-1}) with an insulating layer made of 50 μm-thick kapton, on each side of the metal pattern. Analysis of the data obtained through these measurements was done in a way that was outlined by Gustafsson [10]. In experiments with insulating layers of such thickness, it is necessary to ignore the voltage recorded during the first few seconds because of the influence of the insulating layers. However, owing to the size of the heated area of the TPS element, the characteristic time of the experiment is so long that it is possible to ignore a few seconds of recorded potential difference values and still obtain very good results.

An important aspect of the design of any TPS element is that the pattern should be such that the largest part of the “hot” area should be covered by the electrically conducting pattern. This is due to the fact that there is insulation between the different parts of the pattern. This becomes more important because insulating layers are covering the conduction pattern and also the surface(s) of the sample. It should be noted that the temperature difference across the insulating layer could, after a short initial transient, be considered constant.

Simultaneous measurements of effective thermal conductivity and effective thermal diffusivity of pellets of the Zn_xSe_{100-x} ($x = 0$, 10, 20, 30, 40, and 50) systems compacted under a load of 433 MPa, were carried out at room temperature using the TPS technique. Variations of effective thermal conductivity and effective thermal diffusivity with the composition (x) of Zn have been plotted in Figs 2 and 3.

0022–2461

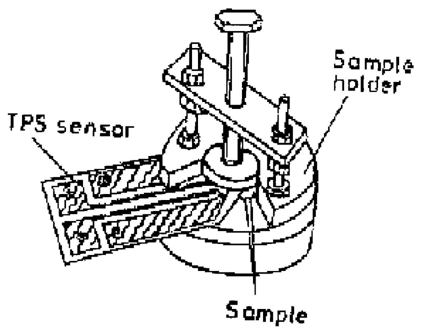

Figure 1 Sample holder diagram with TPS sensor.

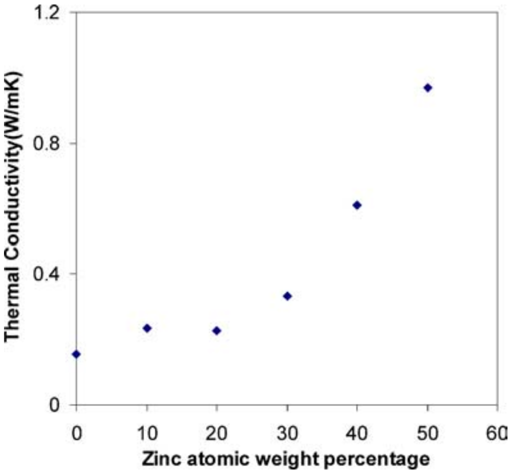

Figure 2 Thermal conductivity with Zn atomic weight percentage.

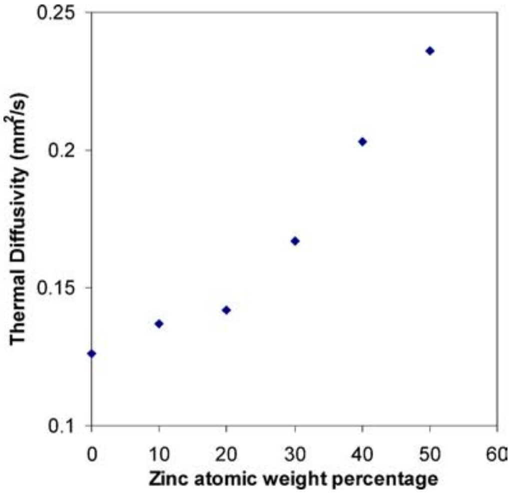

Figure 3 Thermal diffusivity with Zn atomic weight percentage.

The results indicate that both the values of λ_e and χ_e increase slightly upto 10 atomic weight percent of Zinc and then remain constant from $x = 10$ to 20. It is interesting to note that for Zn concentration from $x = 20$ to $x = 50$, a rapid increase both in λ_e and χ_e has been observed. This behavior of λ_e and χ_e with zinc percentage can be explained by different types of bond formation in this system for different Zn concentrations in the solid solutions of Se-Zn.

Zn is a metal and Se is a semiconductor (specific resistivity $\approx 2 \times 10^{11} \mu\Omega$-cm) and therefore at small Zn concentration the thermal behavior of the system is similar to that of pure Se. But on increasing the Zn concentration, the behavior of the system changes and both λ_e and χ_e start increasing.

The increase in λ_e and χ_e may be described in terms of the formation of different bonds between Zinc and Selenium at different concentrations. Both λ_e and χ_e increase slightly at 10 atomic weight percent of Zn because of the metallic nature of Zn.

Se, which in its stable state consists of gray trigonal, metal-like crystals, has "infinite" spiral chains of atoms. Although there are fairly strong single bonds between adjacent atoms in each chain, there is evidently weak interaction of a metallic nature between the neighboring atoms of different chains. When Zn is added in lower concentration ($x = 10$ to 20) probably the Zn is fully absorbed in Se_8 rings and these show effectively no change in their structure over the Se. This in turn gives no change in λ_e and χ_e in the concentration range of Zinc from $x = 10$ to 20. As soon as the concentration of Zn is increased in the solid solution of Se-Zn beyond $x = 20$, λ_e and χ_e starts increasing rapidly. In the presence of a growing concentration of Zn in Se, the two electrons of the outermost shell of Zn are given to Se, which has a two-electron vacancy in its outermost unfilled shell, thus forming Iono-covalent bonds of Se-Zn. It has been observed that the single bond between Se-atoms in an infinite spiral chain of Se is changed to a double bond (iono-covalent bond) of Zn with Se. This in turn increases the polar nature of the sample and hence the dissociation energy. Iono-covalent bonds formed in such a fashion provide longer chain lengths and hence higher thermal conductivity with the addition of Zn to Se.

Thus the enhancement in the effective thermal conductivity and effective thermal diffusivity with increasing concentration of Zinc in Selenium is suggestive of the fact that a change from covalent bonding to iono-covalent bonding takes place.

Acknowledgments

Authors are thankful to the Defence Research and Development Organization (DRDO), Govt. of India, for providing us the financial assistance to carry out the present work.

References

1. A. B. SEDDON, *J. Non-Cryst. Solids* **184** (1995) 44.
2. M. HUSAIN, B. P. SINGH, S. KUMAR, T. P. SHARMA and P. J. SEBASTIAN, *Solar Energy Mater. Solar Cells* **76** (2003) 399.
3. K. SINGH and N. S. SAXENA, *Ind. J. Pure Appl. Phys.* **41** (2003) 466.
4. R. N. BHARGAVA, in "Properties of Wide Band Gap II–VI Semiconductors," edited by R. Bhargava (INSPEC, IEE, London UK, 1997) p. 27.
5. N. S. SAXENA, P. R. PRADHAN, G. D. LADIWALA, K. BALA and M. P. SAXENA, *Solid State Ion.: Mater. Appl.* (1992) 723.
6. K. SINGH, N. S. SAXENA and N. B. MAHARJAN, *Phys. Stat. Sol.* (a) **189**(1) (2002) 197.
7. N. SANKAR, K. RAMCHANDRAN and C. SANJEEVIRAJA, *J. Cryst. Growth* **235** (2002) 195.
8. S. R. OVSHINSKY, *Phys. Rev. Lett.* **21** (1986) 1450.
9. L. V. AZAROFF, "Introduction to Solids" (Tata McGraw-Hill Publishing Company Limited, 1988) p. 289.
10. S. E. GUSTAFSSON, *Rev. Sci. Instrum.* **62** (1991) 797.

Received 23 October 2003
and accepted 23 June 2004