

Effect of indium additive on thermal transport properties of Se–Te–Cd multi-component chalcogenide glasses

Sunil Kumar · Kedar Singh

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Abstract The thermal conductivity, thermal diffusivity and specific heat per unit volume of twin pellets of $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($x = 0, 5, 10$ and 15) glasses, were carried out at room temperature by transient plane source technique. Results indicated that both values of thermal conductivity (λ) and thermal diffusivity (χ) are varied with In (indium) content and highest for 5 at.% of In, whereas the specific heat per unit volume is almost constant with increase of indium concentration. This shows that $\text{Se}_{75}\text{Te}_{10}\text{Cd}_{10}\text{In}_5$ glass can be considered as a critical composition at which the alloy becomes chemically ordered and most thermally stable than other compositions. This compositional dependence behaviour of thermal conductivity and thermal diffusivity can explained in terms of ionic-covalent type bond which In makes with Se and Te as it is incorporated in Se–Te–Cd glasses.

Keywords Chalcogenides glasses · Transient plane source · Thermal conductivity

Introduction

Chalcogenide glasses are vitreous materials composed of chalcogen elements of Group VI of the periodic table. They exhibit a continuous variation in physical properties with change in chemical composition [1]. In general, chemical bonds determine the structures and all the properties of a material in any state of aggregation [2, 3]. Chalcogenides glassy materials have many useful properties and have

recently drawn great attention because of their use in various solid-state devices. These glasses based on transition metals are soft magnetic materials and are extensively used in the electronics and power industries [4, 5]. Moreover, they are interesting as core materials for optical fibres for transmission especially, when short lengths and flexibility are required [6, 7]. In recent years, much attention has been given to II–VI group chalcogenide materials, mainly due to their wide range of applications both in scientific and technological fields [8]. These materials have come under increased scrutiny because of their wide use in cost reduction of devices for photovoltaic applications [9]. The research on renewable energies includes the photovoltaic conversion of solar energy and important investigation of novel materials and structures. In particular, Selenium alloys are used in X-ray imaging and photonics [10]. Amorphous chalcogenides based on Se and Te elements has been extensively studied by various workers [11–13] and such compounds have potential applications in semiconductor devices, transistors and detectors [14]. The shortcomings of Se–Te alloys are the limited reversibility and ageing effect due to low glass transition and crystallization temperatures [15]. These problems can be removed by addition of third element as a chemical modifier in Se–Te alloys. So, many works have been done on Se–Te–Sb, Se–Te–Sn and Se–Te–In ternary chalcogenide glasses [16–21]. Addition of impurities in chalcogenide glasses can alter their structural, electrical, thermal and optical properties without changing the p-type class of the semiconductor. The addition of third element improves glass forming ability, thermal stability and hardness of Se–Te glasses. The addition of Cd element is useful to explain transport mechanism in chalcogenide glasses and the results obtained discussed in terms of topological and structural transitions in chalcogenide glasses [22]. Addition

S. Kumar · K. Singh (✉)
Department of Physics, Faculty of Science, Banaras Hindu
University, Varanasi 221005, India
e-mail: kedarbhp@rediffmail.com

of Cd impurity also increases thermal stability and hardness of Se–Te chalcogenide glasses. We have reported the calorimetric studies of glassy Se–Te–Cd–In alloys by means of non-isothermal DSC [23]. In the present work, we have discussed the thermal conductivity, thermal diffusivity and specific heat of indium-based multi-component chalcogenide glasses.

Material preparation

High purity (99.999 %) Se, Te, Cd and In elements in appropriate atomic percentages were weighed by electronic balance and put into a quartz ampoule (5-cm length and 12-mm internal diameter). The contents into ampoule (5 g) were sealed into a vacuum of 10^{-5} Torr and heated in a furnace, where temperature was raised at a rate of 3–4 K/min up to 1,123 K and kept around that temperature for 12 h to ensure the homogeneity of the samples. The molten samples were then rapidly quenched in ice cooled water. Samples obtained by quenching were in the form of glasses. The X-ray diffraction (XRD) pattern of as-prepared samples were recorded using Philips PW-1700 powder diffractometer (operating at 20 keV) with Cu- K_{α} ($\lambda = 1.54056 \text{ \AA}$) radiation to confirm the glassy nature of alloys. Glassy nature of alloys were confirmed by XRD (see Fig. 1), which have been reported by our group elsewhere in the calorimetric measurements on multi-component chalcogenide glasses of Se–Te–Cd–In system [24]. These bulk glasses were then crushed to fine powders by grinding process. Pellets of 2 mm thickness and 12-mm diameter were prepared by a pressure machine at a load of 4 tons.

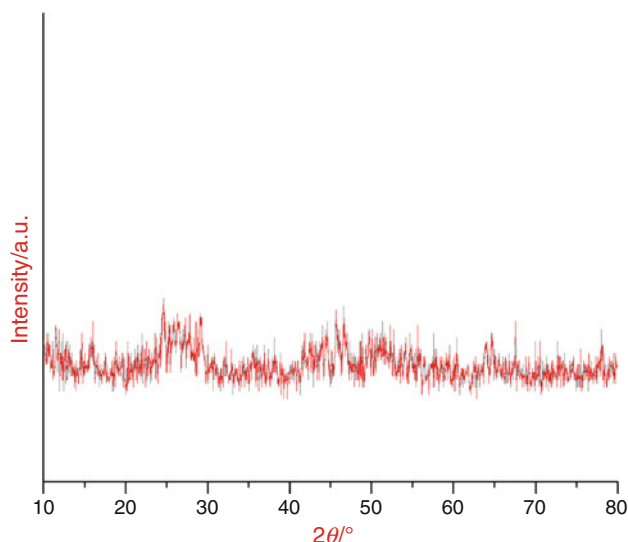


Fig. 1 XRD pattern of $\text{Se}_{75}\text{Te}_{10}\text{Cd}_{10}\text{In}_5$ chalcogenide glass

Experimental arrangement

The measurements reported in this paper were performed using a transient plane source (TPS) element. TPS element is made of 10- μm thick nickel foil with an insulating layer made of 50- μm thick kapton, on each side of the metal pattern. Evaluation of these measurements was performed in a way that was outlined by Gustafsson [25]. 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 values potential difference [18]. These connecting leads had the same thickness on each side metal pattern of the TPS element. Each TPS element had a resistance at room temperature of about 3.69Ω and a TCR of around $4.6 \times 10^{-3} \text{ K}^{-1}$. An important aspect of design of any TPS element is that the pattern should be such that as large a part of the ‘hot’ area as possible should be covered by the electrically conducting pattern, as long as there is insulation between different parts of the pattern. This is particularly important when insulating layers are covering the conduction pattern and the surface(s) of the sample. It should be noted that the temperature difference across the insulating layer can, after a short initial transient, be considered constant. The samples are in the form of pellets of 12-mm diameter and 2-mm thickness, and the surfaces of these pellets are smooth so as to ensure perfect 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 holders using pressure contacts [18]. The change in the voltage was recorded with a digital voltmeter, which was online to the 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 $0.01\text{--}0.02 \text{ W cm}^{-2}$.

Result and discussion

The measurements of thermal conductivity and thermal diffusivity of pellets of $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($x = 0, 5, 10$ and 15) multi-component glasses, were carried out at room temperature by TPS technique. The variation of thermal conductivity (λ), thermal diffusivity (χ) and specific heat per unit volume (ρC_p) with indium content have been plotted in Figs. 2, 3, 4, respectively. It can be observed from Figs. 2 and 3, that the thermal conductivity and thermal diffusivity have been varied with In content and the highest at 5 at.% of In. Thermal conductivity and thermal diffusivity could be explained by considering the structural changes due to the

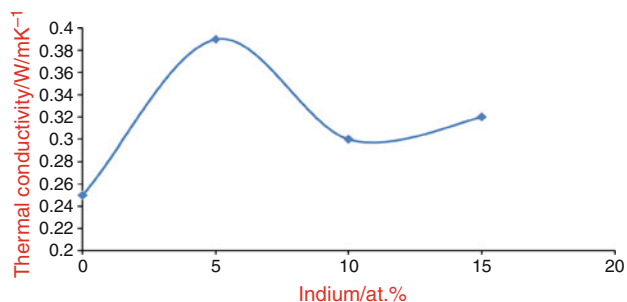


Fig. 2 Thermal conductivity versus indium percentage

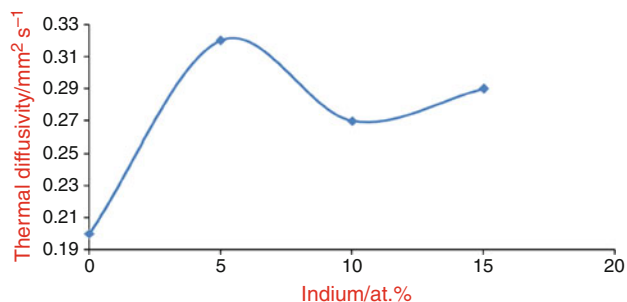


Fig. 3 Thermal diffusivity versus indium percentage

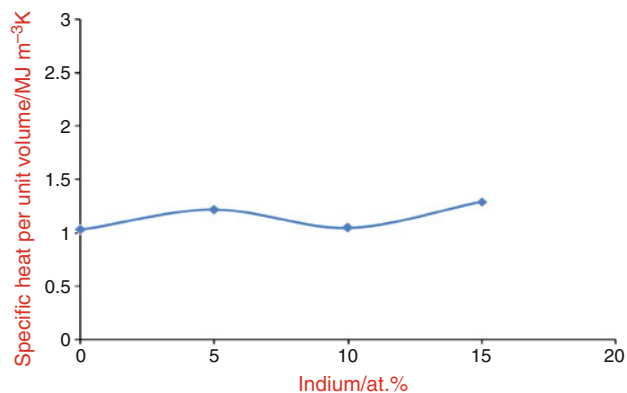


Fig. 4 Specific heat per unit volume versus indium percentage

addition of more and more indium concentration. The structure of the Se–Te system prepared by melt quenching is regarded as a mixture of Se₈ member rings, Se₆Te₂ mixed rings and Se–Te copolymer chains. A strong covalent bond [26] exists between the atoms in the ring, whereas between the chains only the van der Waals forces are dominant. It is reported [27] that a–Se contain about 40 % of the atoms in ring structure and 60 % are bounded as polymeric chains. With the increase of In concentration in Se, a slight increase of polymeric chains of Se is also observed. The addition of In is at the cost of Te concentration and increases the chain length. The (λ) and (χ) increase up to 5 at.% of In, and with further addition of In the chain as well as the ring structure are effected, and as the effects of these on (λ) and (χ) are

opposite at 10 and 15 at.% of In as shown in Figs. 2 and 3. The Se–Se bonds (bond energy 206.1 kJ/mol) will be replaced by In–Se bonds which have higher bond energy (bond energy 257.5 kJ/mol) [28, 29]. Hence, the cohesive energy of the system increases with the increasing of In content. These results show that the increase of (λ) and (χ) up to 5 at.% of In and the peak value of (λ) and (χ) is at 5 at.% of In content. This composition can be considered as a critical composition at which the system can become a chemically ordered alloy containing high energy In–Se heteropolar bonds. Further addition of In favours the formation of In–In bonds (bond energy 125.58 kJ/mol), thus reducing the In–Se bond concentration. This in turn results in a decrease of bond energy of (In–In) – (In–Se) = –131.92 kJ/mol. Thus, the cohesive energy decreases, resulting in a decrease of (λ) and (χ). It has noticed that the bond formation energies in the case of Te–Te and Te–In are also small so that the overall structure does not show any change. This could be further explained in the following way. The bond length of Se–Se and In–In is 232 and 325 pm, respectively. The bond length of Se–Se is smaller than In–In. The effective molecular weight of glasses decreases as the bond lengths increase and hence the density of localized states decreases [30]. This decrease in the density of localized states increases the porosity and produces more disordered structure [31], which is responsible for the decrease of thermal conductivity and thermal diffusivity at the higher percentage of indium. It is also observed that crystallization activation energy, rate constant (K_p) are lower and crystallization temperature (T_c) and glass transition temperature (T_g) their difference ($T_c - T_g$) is highest [24] for the glass containing 5 at.% of indium. The small value of activation energy and highest value of ($T_c - T_g$) gives the highest thermal stability of Se₇₅Te₁₀Cd₁₀In₅ glass. Therefore, this composition has the lowest tendency towards crystallization as compared to other compositions.

Specific heat per unit volume (ρC_p) as obtained from the experimentally measured values of thermal conductivity and thermal diffusivity for different compositions of indium. Figure 4 shows the variation of specific heat per unit volume with the composition of indium in glassy Se–Te–Cd–In alloys. It can be observed that the variation in specific heat is almost constant. Slightly high values of specific heat at higher composition of indium are due to the availability of the large number of degrees of freedom in the alloy, which could release heat energy.

Conclusions

The investigation of simultaneous measurement of thermal conductivity and thermal diffusivity of Se–Te–Cd–In glassy system varies with In content suggests that 5 at.% of

In glass is most thermally stable than other glasses of this series, which is also confirmed by crystallization kinetic studies.

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