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Short communication

Comparative analysis of some thermo-physical properties of $Se_{90}Zn_{10}$ and $Te_{90}Zn_{10}$ alloys

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ABSTRACT

The present paper reports a comparative study of some thermo-physical properties (thermal conductivity, diffusivity and specific heat per unit volume) of $Se_{90}Zn_{10}$ and $Te_{90}Zn_{10}$ alloys. Simultaneous measurements of effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) of twin pellets of $Se_{90}Zn_{10}$ and $Te_{90}Zn_{10}$ alloys using transient plane source (TPS) technique have been made at room temperature. From the measured values of λ_e and χ_e, the specific heat per unit volume (C_v) has been calculated. The results indicate that the measured values of these parameters are higher for $Te_{90}Zn_{10}$ alloy as compared to $Se_{90}Zn_{10}$ alloy. This is explained in terms of thermal conductivity of chalcogen elements Se and Te.

1. Introduction

Chalcogenide alloys are used as photographic materials and have gained much importance in past one decade due to new optimistic applications of chalcogenide alloys in the field of lasers and fiber techniques [1–3]. Recently Zn-based alloys of Se and Te chalcogen elements have found various attractive applications [4–8].

The wide band gap zinc selenide (ZnSe) semiconductor is an example of potential applications in optoelectronic devices, such as blue light emitting diodes and blue diode lasers. These ZnSe diode lasers operate in blue–green region [4]. It can also be used in short-wavelength visible-light laser devices [5]. Also, ZnSe is one of the most promising materials for use in white LEDs and infrared lenses [6]. The use of ZnSe for industrial applications needs that the alloy should be synthesized inexpensively.

ZnTe is of special technological interest, as it is a potentially low-cost semiconductor for switching devices and multi-junction solar cells. Polycrystalline ZnTe material and its alloys like CdZnTe were successfully utilized in the fabrication of tandem solar cell structures with a tailored band gap and quantum well structures. ZnTe was also proposed as passivation layer for HgTeCd surfaces for MIS (metal–insulator–semiconductor) devices [7,8].

In order to make use of this material in industrial applications, a better understanding of their physical properties is desirable. The knowledge of thermo-physical properties of a material in bulk form has useful significance from structural point of view. Thermo-physical properties like thermal conductivity, thermal diffusivity and specific heat per unit volume of these materials are influenced by the scattering of phonons with crystal defects, impurities and dislocations present in them. Studies of the variation of λ_e and χ_e of these materials with temperature provides an insight about the various scattering processes that serve to limit the mean free path of heat carriers, i.e., phonons. Thus it can be used as a tool in the study of structural changes in the material with temperature, as carrier's mean free path is affected by the lattice defects and porosity which changes with temperature [9].

Attempts have been made from time to time to investigate the thermal transport properties at room temperature in both binary and ternary alloys of chalcogenide materials [10–12] using transient methods by changing the composition of chalcogen element. However, no serious attempt has been made to study the effect of chalcogen element on the thermo-physical properties of binary systems of chalcogenide materials by changing the chalcogen element itself keeping it concentration constant in a particular binary alloy, which is an interesting problem from research point of view. In the present paper, an investigation has been undertaken to compare the thermo-physical properties of two important chalcogen materials $Se_{90}Zn_{10}$ and $Te_{90}Zn_{10}$.

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2. Material synthesis

High purity (99.99%) selenium and tellurium granules were weighed in two separate quartz glass ampoules (length 5-cm and internal diameter 8-mm) with fine Zn dust in appropriate atomic percentage. The content of the ampoules was sealed in a vacuum of 10^{-6} Torr and heated in a furnace where temperature was raised at a rate of 3–4 K/min up to 1500 K and kept around at that temperature for 10 h. The ampoules were frequently rocked to ensure the homogeneity of the samples. The molten samples were then rapidly quenched in ice-cooled water. Ingots of the quartz ampoules were crushed into fine powder and the pellets of thickness 2 mm and diameter 12 mm were prepared by a pressure machine. The pellets were made at a constant load of 5 tonnes. The surfaces of these pellets were made smooth so as to ensure good thermal contact between the samples and the heating elements. Transient plane source (TPS) element, which is source of heat as well as sensor of temperature increase in the sample, was sandwiched between the two pallets of sample material [13,14].

3. Theoretical basis

The TPS method consists of an electrically conducting pattern (Fig. 1(a)) in the form of a bifilar spiral, which also serves as a sensor of the temperature increase in the sample. Assuming the conducting pattern to be in the y–z plane of a co-ordinate system placed in an infinite solid material, the rise in the temperature at a point y–z at time (t), due to an output power through the spiral per unit area Q is given by [13]:

$$\Delta T(y,z,\tau) = \frac{1}{4\pi^{3/2}a\lambda}\int_0^{\tau}\frac{d\sigma}{\sigma^2}\int_A dy'\,dz'\,Q\left(y'z't-\frac{\sigma^2a^2}{\chi}\right) \times \exp\left[\frac{-(y-y')^2-(z-z')^2}{4\sigma^2a^2}\right] \qquad (1)$$

Here $\chi(t-t')=\sigma^2a^2$, $\theta=a^2/\chi$ and $\tau=\sqrt{t/\theta}$. a is the radius of the hot disc (source and the sensor) which gives a measurement of the overall size of resistive pattern and θ is known as the characteristic time. σ is a constant variable, λ is the thermal conductivity in units of W m^{-1} K^{-1} and χ is the thermal diffusivity in unit of mm^2/s of the sample.

The temperature increases at $\overline{\Delta T(y,z,\tau)}$ because the flow of current through the sensor gives rise to a change in the electrical resistance $\Delta R(t)$ which is given as

$$\Delta R(t)=\alpha R_0\overline{\Delta T(\tau)} \qquad (2)$$

Here R_0 is resistance of TPS element before the transient recording has been initiated at room temperature, α is the temperature coefficient of resistance (TCR) and $\overline{\Delta T(\tau)}$ is the properly calculated mean value of the time dependent temperature increase of the TPS element. $\overline{\Delta T(\tau)}$ is calculated by averaging the increase in temperature of TPS element over the sampling time because the concentric ring sources in TPS element have different radii and are placed at different temperatures during the transient recording. During the transient event, $\overline{\Delta T(\tau)}$ can be considered to be a function of time only, where as, in general, it will depend on such parameters as the output power in TPS element, the design parameters of the resistive pattern, and the thermal conductivity and thermal diffusivity of the surroundings. It is possible to write down an exact solution [13] for the hot disc if it is assumed that the disc contains a number 'm' of concentric rings as sources.

From the ring source solution [14] we immediately get

$$\overline{\Delta T(\tau)}=\frac{P_0}{\pi^{3/2}a\lambda}D_s(\tau) \qquad (3)$$

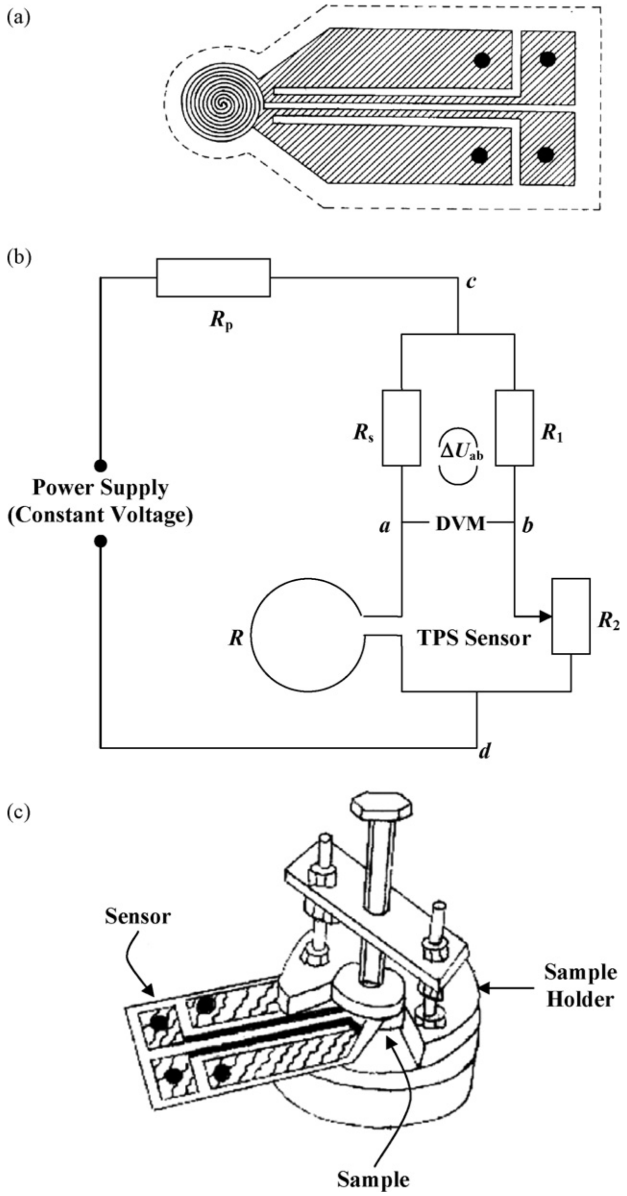

Fig. 1. (a) Schematic diagram of TPS sensor. (b) Bridge circuit diagram used to monitor the voltage variation. (c) Sample holder diagram with TPS sensor.

Here

$$D_s(\tau)=\frac{1}{[m(m+1)]^2}\int_0^{\tau}\frac{d\sigma}{\sigma^2} \times\left[\sum_{l=1}^{m} l\left\{\sum_{k=1}^{m} k\exp\frac{-(l^2+k^2)}{4\sigma^2m^2}L_0\left(\frac{lk}{2\sigma^2m^2}\right)\right\}\right] \qquad (4)$$

In Eqs. (3) and (4), P_0 is the total output power, L_0 is the modified Bessel function and l, k are the dimensions of the resistive pattern. To record the potential difference variations, which normally are of the order of a few millivolts during the transient recording, a simple bridge arrangement as shown in Fig. 1(b) has been used. If we assume that the resistance increase will cause a potential difference variation $\Delta U(t)$ measured by the voltmeter in the bridge, the analysis of the bridge indicates that

$$\Delta E(t)=\frac{R_s}{R_s+R_0},\quad I_0\,\Delta R(t)=\frac{R_s}{R_s+R_0}\frac{I_0\alpha R_0P_0}{\pi^{3/2}a\lambda}D_s(\tau) \qquad (5)$$

Table 1
Thermo-physical properties (thermal conductivity, diffusivity and specific heat per unit volume) of $Se_{90}Zn_{10}$ and $Te_{90}Zn_{10}$ alloys

Sample	λ_e ($W\,m^{-1}\,K^{-1}$)	χ_e (mm^2/s)	C_v ($MJ/m^3\,K$)
$Se_{90}Zn_{10}$	0.4	0.123	3.25
$Te_{90}Zn_{10}$	0.8	0.198	4.04

Here

$$\Delta E(t) = \frac{\Delta U(t)}{[1 - C\Delta E(t)]} \tag{6}$$

and

$$C = \frac{1}{R_s I_0[1 + (\gamma R_p/\gamma(R_s + R_0) + R_p)]} \tag{7}$$

The definition of various resistances is found in Fig. 1(b). R_p is the lead resistance, R_s is a standard resistance with a current rating that is much higher than I_0, which is the initial heating current through the arm of the bridge containing the TPS-element. γ is the ratio of the resistances in two ratio arms of the bridge circuit, which is taken to be 100 in the present case.

4. Experimental

The measurements reported in this paper were performed with a TPS element. It is made of a 10-μm thick nickel foil (having a resistance of about 3.26 Ω and temperature coefficient of resistance (TCR) around ($4.5 \times 10^{-3}\,K^{-1}$) with an insulating layer made of 50-μm thick Kapton, on each side of the metal pattern. The surfaces of these pellets are smooth so as to ensure a 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 (Fig. 1(c)). The change in the voltage was recorded with a digital voltmeter, which was online to the personal computer. In experiments with insulating layers of such thickness, we ignore the voltage recorded during first few seconds because of the influence of the insulating layers. It is important to note that the size of the heated area of the TPS element is such that the characteristic time becomes quite long. Therefore, it is possible to ignore first few seconds of recorded potential difference values and still get good results.

The design of any TPS element is based on the fact that as large a part of the 'hot' area as possible should be covered by the electrically conducting pattern to the dimensions up to which there is insulation between the different parts of the pattern. We can consider the temperature difference across the insulating layer, as a constant, after a short initial transient.

5. Results and discussions

Simultaneous measurements of effective thermal conductivity (λ_e) and effective thermal diffusivity (χ_e) of pellets of $Se_{90}Zn_{10}$ and $Te_{90}Zn_{10}$ alloys, compacted under a load of 5 tonnes, were carried out, at room temperature using TPS technique. Specific heat per unit volume (C_v) of the sample has been obtained using the measured values of λ_e and χ_e. The deviations from the measured values are on the average 3% for thermal conductivity, 7% for thermal diffusivity and 3% for the specific heat per unit volume as suggested by Gustafsson [13]. The values of λ_e, χ_e and C_v for $Se_{90}Zn_{10}$ and $Te_{90}Zn_{10}$ alloys are given in Table 1. From this table it is clear that the all the three measured thermo-physical quantities are higher in case of $Te_{90}Zn_{10}$ alloy. This shows that the out of the chalcogen elements Se and Te, Te-based alloys with Zn as chemical modifier may have comparatively larger thermal conductivity, diffusivity and specific heat per unit volume. The higher vale of λ_e in case of $Te_{90}Zn_{10}$ alloy as compared to $Se_{90}Zn_{10}$ alloy can be explained in terms of higher value of thermal conductivity of Te ($\lambda_e = 2.67\,W\,m^{-1}\,K^{-1}$) as compared to that of Se ($\lambda_e = 0.52\,W\,m^{-1}\,K^{-1}$) at room temperatures. This may be probably reason of the higher values of λ_e, χ_e and C_p for $Te_{90}Zn_{10}$ alloy too as compared to $Se_{90}Zn_{10}$ alloy.

Table 2
Strength of chemical bonds expected in the present alloys

Chemical bond	Strength of chemical bond (kJ/mol)
Se–Se	206.1
Se–Zn	170.7
Te–Te	158.8
Te–Zn	117.6

The above results can also be explained in terms of average strength of different bonds formed in chalcogenide alloys. The thermo-physical properties like activation energy of crystallization of chalcogenide alloys depend on the average bond strength [15,16]. Hence other thermo-physical properties of these materials can also be governed by average bond strength of the system. It can be assumed that when $Te_{90}Zn_{10}$ and $Se_{90}Zn_{10}$ alloys are heated, then initially the heat is consumed for bond breaking or formation in these materials and after some structural relaxations, steady-state condition is achieved. Thus, the alloy having lower average bond strength probably takes less time in achieving the steady-state condition. The bond strengths of Te–Te and Te–Zn bonds are comparatively lower than that of Se–Se and Se–Zn bonds (see Table 2). Thus the comparatively lower average bond strength of $Te_{90}Zn_{10}$ alloy is also thought to be responsible for the present results.

6. Conclusions

Comparative analysis of some thermo-physical properties (thermal conductivity, diffusivity and specific heat per unit volume) of $Se_{90}Zn_{10}$ and $Te_{90}Zn_{10}$ has been made. The results show that the thermal conductivity measured in the present study is higher for $Te_{90}Zn_{10}$ alloy as compared to $Se_{90}Zn_{10}$ alloy. The results are explained in terms of thermal conductivity of parent elements Se and Te. The higher values of other two thermo-physical parameters for $Te_{90}Zn_{10}$ alloy are interpreted in terms of lower average bond strength of $Te_{90}Zn_{10}$ alloy.

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