Creep activation energy of flow process in $Bi_2Te_{2.8}Se_{0.2}$ single crystals

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Abstract. Temperature dependence of the Vickers microhardness of $Bi_2Te_{2.8}Se_{0.2}$ single crystals has been studied. Loading time dependence of microhardness at different temperatures has been used for creep study in the temperature range 303 K–373 K. The activation energy for indentation creep of the crystals has been evaluated.

Keywords. Vickers microhardness; cleavage surface; creep; activation energy.

1. Introduction

The V_2–VI_3 (V = Bi, Sb; VI = Se, Te) binary compounds and their pseudobinary solid solutions are highly anisotropic and crystallize into homologous layered structures parallel to the c-axis and known to find applications ranging from photoconductive targets in TV cameras to IR detectors (Stolzerm *et al* 1986; Arivuoli *et al* 1988). V_2–VI_3 compounds are narrow band gap semiconductors: $E_g \sim 0.2$ eV, ~ 0.35 eV and ~ 0.16 eV for Sb_2Te_3, Bi_2Se_3 and Bi_2Te_3, respectively. There are also a few applications for temperature control of laser diodes (Rowe and Bhandari 1981), optical recording system (Watanabe *et al* 1983) and strain gauges (Atakulov *et al* 1982). Among these, Bi_2Te_3 is the most potential material for thermoelectric devices such as thermoelectric generators, thermocouples, thermocoolers and IR sensors with the best figure of merit near room temperature (Roy *et al* 1978; Jeon *et al* 1981; Rowe and Bhandari 1981; Goodman 1985; Jansa *et al* 1992). It also finds widespread application in electronic, microelectronic, optoelectronic and electromechanical devices (Sakai *et al* 1981; Arivuoli *et al* 1988). It crystallizes into a rhombohedral structure with space group $R\bar{3}m$ (Sagar and Faust 1967). Its melting point is 573°C and has p-type semiconductivity. There have been various studies on optical and electrical properties of single crystals and thin films of Bi_2Te_3 (Guha Thakurta and Bose 1970; Testardi and Burstein 1972; Rahman Khan and Akhtaruzzaman 1982; George and Pradeep 1985). There is also a report on microhardness of Bi_2Te_3 single crystals (Arivuoli *et al* 1988). However, there is hardly any work reported in literature on the microhardness of Bi_2Te_3 based pseudobinary crystals. This is particularly so in the case of solid solution, Bi_2Te_3 : Se. Microhardness is a general macroprobe for assessing the bond strength, apart from being

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a measure of the bulk strength. Further, the impurity addition is also known to modify band gap as has been observed by the authors (Desai and Soni 1998). The present paper reports the results of investigation of the microhardness of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ single crystals and indentation creep of the cleavage surfaces of these crystals.

2. Experimental

The single crystals were obtained from stoichiometric mixture of the respective elements of 5 N purity, using Bridgman–Stockbarger method. The crystal quality was such that it yielded a fairly plane cleavage surface. The vacuum pressure used to seal the quartz ampoules containing the charge was of the order of 10^{-4} Pa, the temperature gradient across the melting point at the lower end was set to 45°C/cm by controlling the furnace temperature within ± 5°C. It was lowered through the gradient zone at the rate of 0.35 cm/h.

The hardness indentations were carried out on freshly cleaved surfaces of samples of at least 2 mm thick, using Vickers diamond pyramidal hardness tester. The indentation diagonals were measured to an accuracy of 0.19 μm using a micrometer eye piece. For the study of load dependence of hardness, the applied load was varied in the range from about 10 mN to 1000 mN. The hardness was calculated using the standard formula

$$H_v = \frac{1854p}{d^2} \times 9.8065,$$

where p is the applied load in mN obtained as the product of the load in g and g the 9.81 ms^{-2}, d the average of the two indentation mark diagonal lengths in μm and H_v the Vickers hardness in MPa.

Since this equipment does not provide for high temperature hardness testing, a simple hot stage was prepared

which was attached to the hardness tester. The thermo-couple was connected to the input terminal of an operational voltage amplifier of gain 100 and the output was read to an accuracy of 1 mV. Before producing the indentation, the specimen to be indented was held at the desired temperature for at least 30 min to achieve thermal equilibrium.

It is known that microhardness has a complex load dependence for small applied loads. The zero load condition was assured to give a maximum load-error to be 1 mN and a load of 500 mN was selected to minimize microhardness variations due to error in applied load. Data obtained for different indentation times at different temperatures have been used for the creep study on these samples. The results, discussed below, are based on the observations averaged over at least three indentations produced at each variable value and a particular indentation set repeated on two to three samples.

3. Results and discussions

3.1 *Temperature variation of microhardness*

For studying the temperature dependence of micro-hardness, indentations were made at 10 K interval from room temperature 303 K to 373 K, on a number of specimens. Figure 1 shows the plot of $\ln H_v$ vs T/T_m, where H_v is the Vickers hardness and T and T_m, the indentation temperature and melting point, respectively, both in Kelvin. It can be seen that the plot is a straight line with a negative slope indicating a fast decrease in H_v with increase of temperature. The general behaviour may be described by the Shishokin–Ito empirical relation

$$H_v = A \exp(-BT),\qquad(1)$$
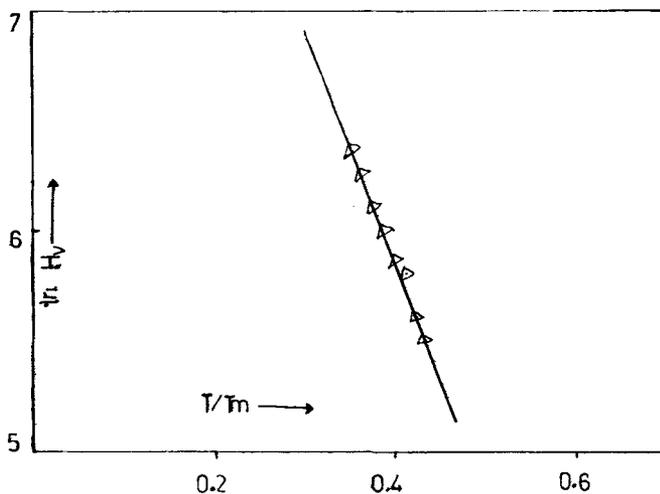
where the constant B is known as softening parameter

of the crystal and A, the extrapolated intrinsic hardness. From the graph the softening parameter B is found to be $\sim 84{\cdot}5 \times 10^{-4}\,\mathrm{K^{-1}}$.

3.2 *Creep and activation energy for flow process*

In the present study a relation based on the kinematic analysis of the creep process during indentation has been found to be satisfactory and it has been used to evaluate activation energy for creep (Atkins *et al* 1966),

$$\ln (H_v^{-3} - H_{vo}^{-3}) = \ln A + \ln (t^{1/3} - t_0^{1/3}) - Q/3RT,\qquad(2)$$

where, H_v is the hardness value at time t, H_{vo} the hardness value immediately after the full load at time t_0, Q the activation energy for creep, T the absolute temperature and R universal gas constant. The plots of $\ln H_v$ vs $\ln t$ obtained at different temperatures are shown in figure 2. It can be seen that $\ln H_v$ varies linearly with t and the slope of the straight line increases with temperature as predicted by Atkins (1973). For each temperature, H_{vo} was obtained for $t_0 = 1$ sec from the plots in figure 2. Figure 3 shows the plot of $\ln (H_v^{-3} - H_{vo}^{-3})$ vs $\ln (t^{1/3} - t_0^{1/3})$ at different temperatures. These are straight lines all of almost equal slopes close to unity in accordance with (2).

To evaluate Q, the usual method is to find difference between intercepts at two temperatures T_1 and T_2 in these graphs (figure 3) and to equate it to

$$Q(1/T_1 - 1/T_2)/3R,$$

under the assumption that Q remains constant with temperature. However, in many cases Q has been found to be different in different temperature ranges. Hence an alternative method (Bhatt and Desai 1982; Jani *et al* 1995), which does not assume Q to be constant with temperature has been used. From the plots of figure 3,
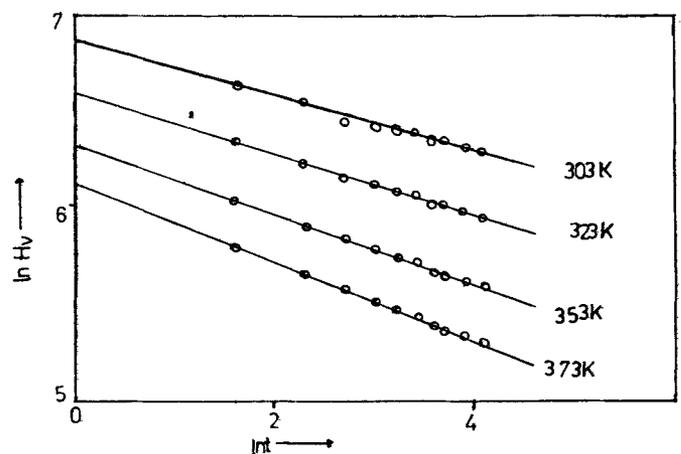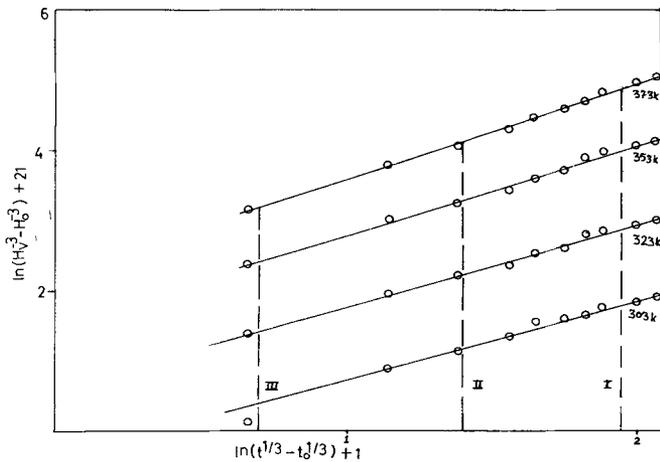

Figure 1. Plots of $\ln H_v$ vs T/T_m.

Figure 2. Plots of $\ln H_v$ vs $\ln t$.

Figure 3. Plots of $\ln(H_v^{-3}-H_{vo}^{-3})+21$ vs $\ln(t^{1/3}-t_0^{1/3})+1$.

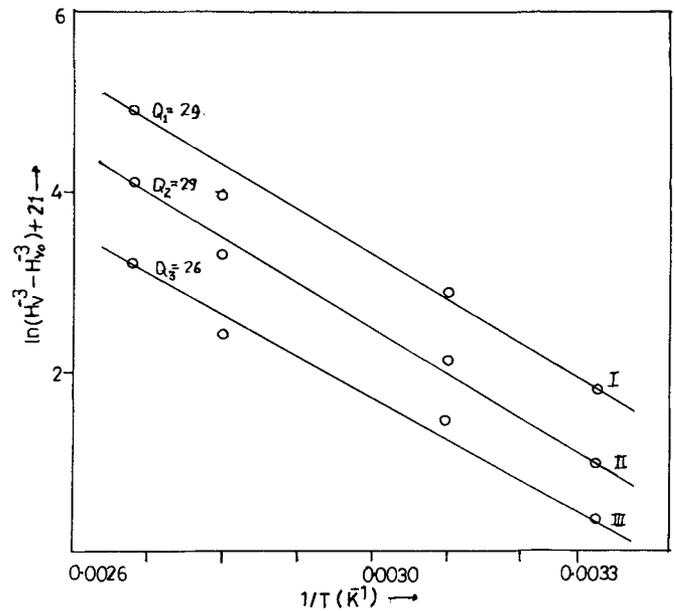**Figure 4.** Plots of $\ln(H_v^{-3}-H_{vo}^{-3})+21$ vs $1/T$.

three sets of $\ln(H_v^{-3}-H_{vo}^{-3})$ values at different temperatures were obtained for three different values of $\ln(t^{1/3}-t_0^{1/3})$ indicated by vertical broken lines. These values of $\ln(H_v^{-3}-H_{vo}^{-3})$ were plotted against the inverse of corresponding temperature (figure 4). Again these curves are straight lines with approximately equal slopes according to (2). The slope represents the value of $-Q/3R$. The energy value obtained in the present case, 117 kJ/mol, is similar to those at low homologous temperatures in the cases like Ag, Cu, Ni, Co etc. A dislocation pipe diffusion mechanism may explain this.

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References

Arivuoli D, Gnanam F D and Ramasamy P 1988 *J. Mater. Sci. Lett.* **7** 711

Atakulov Sh B, Azimov T and Shamsiddinov A N 1982 *Sov. Phys. Semicond.* **16** 1326

Atkins A G 1973 *The science of hardness testing and its research application* (eds) J H Westbrook and H Conard (Ohio: ASM) Ch. 17

Atkins A G, Silverio A and Tabor D 1966 *J. Inst. Metals* **94** 369

Bhatt V P and Desai C F 1982 *Bull. Mater. Sci.* **4** 23

Desai C F and Soni P H 1998 *Physics of semiconductor devices* (eds) V Kumar and S K Agarwal (Delhi: Narosa) **2** p. 1174

George J and Pradeep B 1985 *Solid State Commun.* **56** 117

Goodman C H L 1985 *Mater. Res. Bull.* **20** 237

Guha Thakurta S R and Bose A K 1970 *Indian J. Phys.* **44** 601

Jani T M, Pandya G R and Desai C F 1995 *Cryst. Res. Technol.* **30** K17

Jansa L, Lostak P, Sramkova J and Horak J 1992 *J. Mater. Sci.* **27** 6062

Jeon H W, Ha H P, Hyun D B and Shim J D 1981 *J. Phys. Chem. Solids* **52** 579

Rahman Khan M S and Akhtaruzzaman M 1982 *Indian J. Pure & Appl. Phys.* **20** 656

Rowe D M and Bhandari C M 1981 *Modern thermoelectronics* (London: Holt. Rinehort and Winston) p. 103

Roy B, Chakraborty B R, Bhattacharya R and Dutta A K 1978 *Solid State Commun.* **25** 937

Sagar A and Faust Jr J W 1967 *J. Appl. Phys.* **38** 482

Sakai N, Kajiwara N, Takemura T, Minomura S and Fuji Y 1981 *Solid State Commun.* **40** 1045

Stolzerm M, Stordeur M, Sobotta H and Riede V 1986 *Phys. Status Solidi* **B138** 259

Testardi L R and Burstein E 1972 *Phys. Rev.* **B6** 460

Watanabe K, Sato N and Miyaoka S 1983 *J. Appl. Phys.* **54** 1256