Temperature Dependence of Vickers Microhardness and Creep Study of $In_x\ Bi_{2-x}\ Te_3$ Crystals

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Abstract

Temperature dependence of Vickers microhardness of $ln_x\ Bi_{2-x}\ Te_3$ single crystals with x ranging from 0.1 to 0.5 has been studied. Loading time dependence of microhardness at different temperatures has been used for creep study in the temperature range 300 K to 400 K. The activation energy for indentation creep of the crystals has been evaluated.

Introduction

Solid solutions based on bismuth telluride $Bi_2\ Te_3$ are an important group of semi-conducting materials which find applications in thermoelectric devices. For example, in view of the pronounced Peltier effect and high value of the Seebeck coefficient, $Bi_{2-x}\ Sb_x\ Te_3$ is used for the construction of cooling elements and generators operating in the range close to 300 K [1].

Although the electrophysical properties of $Bi_2\ Te_3$ and its solid solutions, particularly with $Sb_2\ Te_3$, have been studied to quite a good extent, there is hardly any report found in literature on the study of mechanical properties of these systems. Specifically, there is no report on microhardness study of these materials [2]. In the case of $Bi_{2-x}\ ln_x\ Te_3$ single crystals, the crystal growth and basic physical properties have been studied by Lostak et al [3]. Interestingly, the p-type Bi_2Te_3 is converted to an n-type crystal with x in the range 0 to 0.3 [4]. In this paper, the authors report the results of their study of microhardness and indentation creep of these crystals with x=0.1, 0.2 and 0.5.

Experimental

The crystals used in the present study were grown by zone melting method. The specimens were in the form of 2 mm to 3 mm thick (0001) cleavage slices obtained at ice

temperature to minimize deformation. Vickers diamond pyramidal indenter was used to produce indentations on the (0001) plane. Both the indentations and measurements were carried out on a Vickers projection microscope. Since this equipment is not equipped for high temperature hardness testing, a simple hot stage was prepared which was attached to the hardness tester. The thermocouple 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.
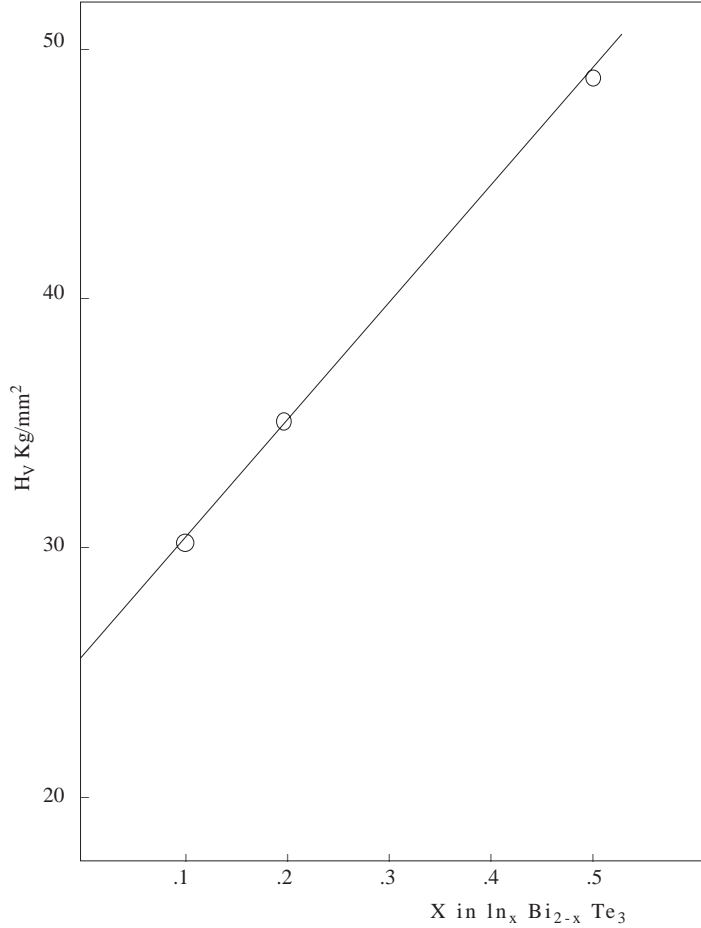

Figure 1. Plots of H_v vs X

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 of 0.200 gm and a load of 50 gm was selected to minimize microhardness variations due to error in

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the applied load. Data obtained for different indentation times at different temperatures have been used for the creep study on three samples of different compositions. At least three indentations were taken for each loading time. The result presented is the average of the data obtained.

Results and Discussion

The hardness was found to increase with increasing of concentration of indium as shown in Figure 1. For studying the temperature dependence of microhardness, indentations were made at 10°C intervals from room temperature to 100°C on a number of specimens. Figure 2 shows the plot of ln Hv versus T/Tm, where H_v is the Vickers hardness and T and Tm, the indentation temperature and melting point, respectively, both in Kelvin. It can be seen that the plot is a straight line with negative slope indicating a fast decrease in Hv with increase of temperature, in agreement with the hardness temperature relationship [5,6]:
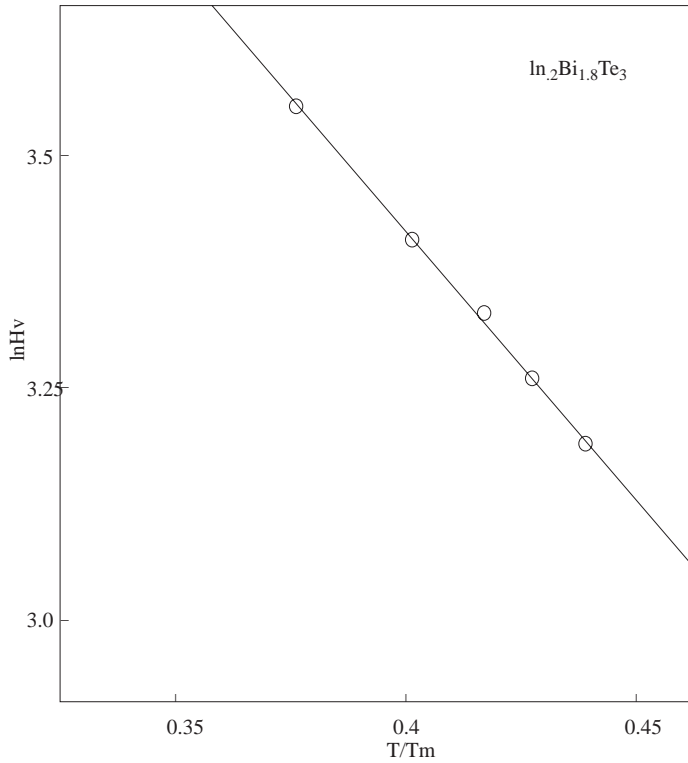

Figure 2. Plots of $\ln H_v$ vs T/T_m

$$H = A exp(-BT), \tag{1}$$

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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 was found to be $\sim 73.6 \times 10^{-4} K^{-1}$. The decrease in hardness with increasing temperature and the general behaviour of loading time dependence may be described by an overall empirical relation which incorporates the earlier equation [7]. 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. The equation used is

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

where, H_v is the hardness value at time t, H_{vo} is the hardness after attaining the full load at time t_o, Q is the activation energy for creep, and T is absolute temperature and R is universal gas constant. The plots of ln H_v versus ln t obtained at different temperatures are shown in Figure 3. It can be seen that ln H_v varies linearly with ln t and the slope of the straight line increases with temperature as predicted by Atkins et al [8]. For each temperature, H_{vo} was obtained for $t_0=1$ sec. from the plots in Figure 3. Figure 4 shows the plot of ln $(H_v^{-3} - H_{vo}^{-3})$ versus ln $(t^{1/3} - t_0^{1/3})$ at different temperatures. Note that arbitrary constants have been added in both x and y coordinates to avoid negative numbers. These are straight lines of almost equal slopes close to unity in accordance with equation (2).
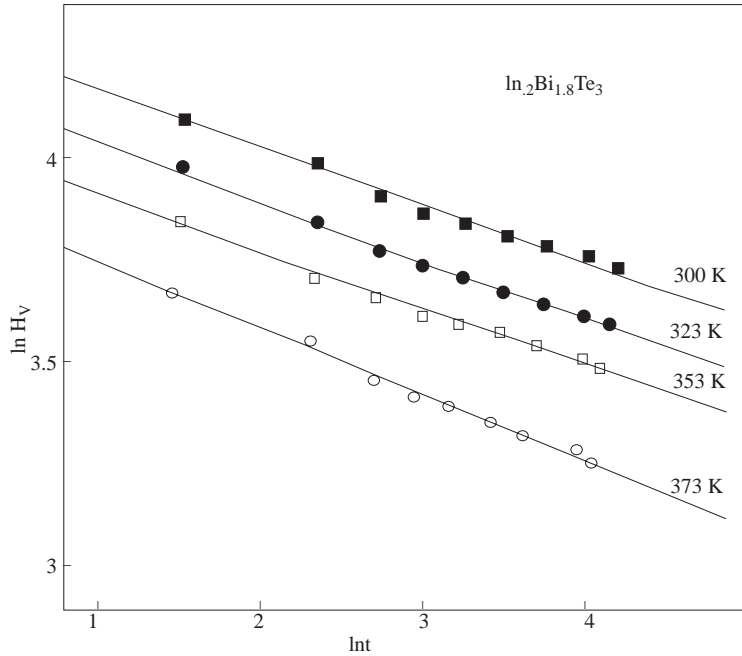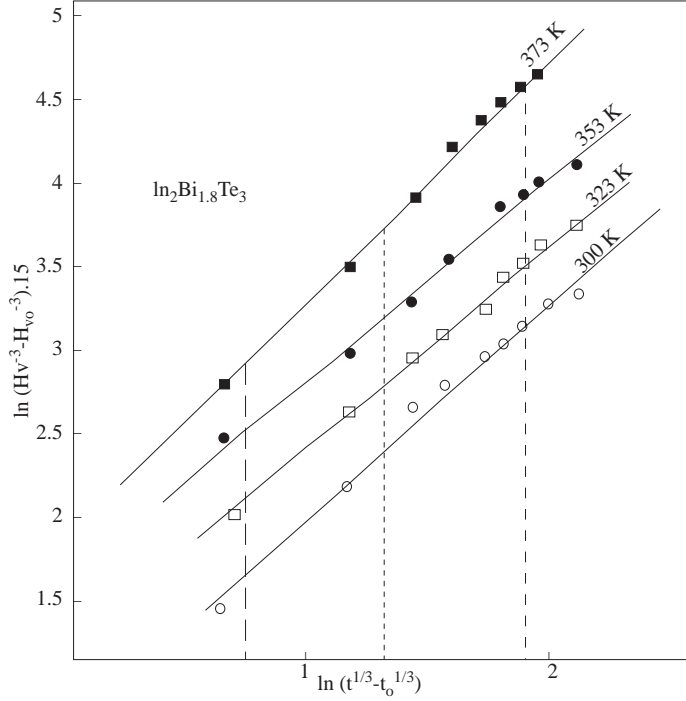

Figure 3. Plots of lnH_v vs lnt

Figure 4. Plots of $\ln H_v^{-3} - H_{vo}^{-3} + 15$ vs $\ln(t^{1/3} - t_0^{1/3})$

To evaluate Q, the usual method is to find the difference between the intercepts at two temperatures T_1 and T_2 in these graphs (Figure 4) and equate it to $Q(^1/T_2 - ^1/T_1)$ / 3R under the assumption that Q remains constant with temperature. However, in many cases Q has been found to vary with temperature. Hence, an alternative method which does not assume Q to be constant with temperature has been used. From the plots of Figure 4, 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 5). Again, these curves are straight lines with approximately equal slopes according to equation (2). The slope represents the value of Q/3R. The plots corresponding to Figure 2, 3, 4 and 5 were obtained also for other dopant concentrations and were found to be of similar nature. The values of hardness at room temperature and creep activation energy for the different crystals are shown in Table 1. The increase of creep activation energy with the increase in dopant concentration is a well established phenomenon. The energy values obtained in the present case are similar to those at low homologous temperatures in the cases like Ag, Cu, Ni, Co etc. A dislocation pipe diffusion mechanism has been proposed to explain the observed behaviour [9]. The dislocation loop growth by climb is aided by diffusion in a vacancy supersaturation environment such as existing at low

homologous temperatures. The pipe diffusion rather than bulk diffusion is favoured at such temperatures [10,11].

Table 1. Creep activation energy and hardness of crystals of different compositions.

X in $\ln_x Bi_{2-x} Te_3$	Hardness(kg/mm^2)	Creep Activation energy
0.1	30.6	12.10
0.2	36.2	13.16
0.5	49.0	18.10
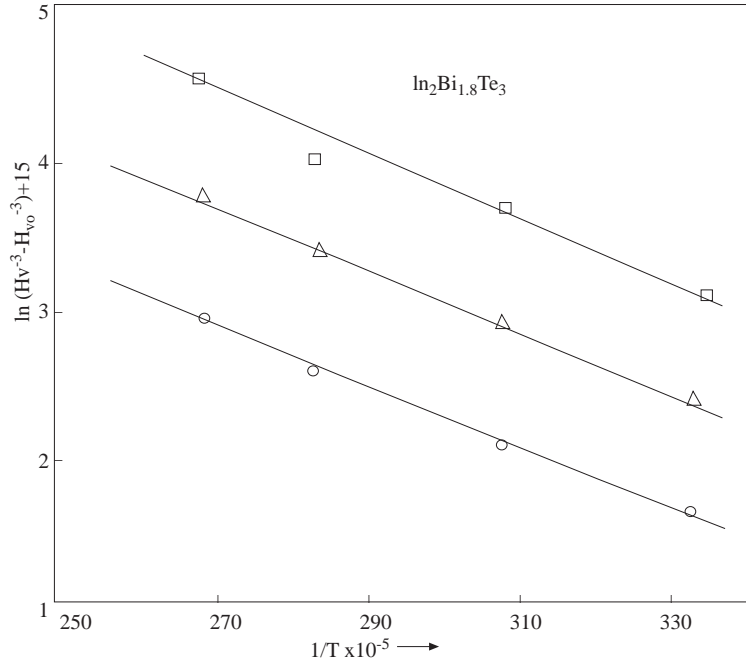
Figure 5. Plots of $\ln H_v^{-3} - H_{vo}^{-3} + 15$ $1/T \times 10^{-5}$

Acknowledgement

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