

Microhardness Creep in Single Crystals of Tin-chalcogenides

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Abstract

SnSe and SnS have been grown by Bridgman-Stockbarger method. Loading time as a function of vickers microhardness has been measured at different temperatures in the range 303 K to 388K. All measurements of hardness have been carried out on the cleavage planes. The activation energy for creep has been evaluated to be 2.92 and 1.75 K Cal/mole, respectively, for SnSe and SnS crystals.

1. Introduction

The layer-structured IV-VI chalcogenides SnSe and SnS are important for holographic recording and switching applications. They are also known for their promising prospects as opto-electronic materials. There have been reports on their crystal growth and electrical and optical properties of thin films. However, there are very scarce reports on microhardness studies on these tin chalcogenide crystals [1]. The authors have carried out indentation hardness creep study on these crystals. The results are reported.

2. Experimental Techniques

The crystals used in the present study were grown by Bridgman-Stockbarger method [2-4]. The specimens were in the form of 3 to 4 mm thick cleavage slices of cross-sectional area about 1cm² obtained by cleaving the crystal rod along the respective cleavage planes viz., (001) of SnSe and SnS. The cleavage was performed at ice-temperature to minimize the deformation. The indentations were carried out using Vickers diamond pyramidal indenter on the microhardness tester, supplied with Vickers projection microscope. Since this equipment does not provide for high temperature hardness testing, a simple hot stage was used with copper constantan thermocouple. The microhardness measurements were carried out on the cleavage plane of the specimen. Before producing the indentation, the

specimen was held at the desired temperature for at least 30 min. to achieve thermal equilibrium. We have observed [1] that the hardness of SnS & SnSe is insensitive to load of 100 gm or more. Therefore, in the present study, a load of 100 gm was kept constant. at least three indentations at each loading time and at each temperature were produced. The results represent the average.

3. Results and Discussion

For studying the temperature dependence of microhardness, indentations were made at 20 to 25^o intervals from room temperature, 303 K, to 388K. Figure 1 a and b show the plots of $\ln H_v$ versus T/T_m obtained for SnSe and SnS single crystals, where H_v =Vickers microhardness, T=indentation temperature and T_m =melting point of the material. It can be seen that the plots are straight lines with negative slope indicating a fast decrease in hardness with increasing temperature. Such steep fall in microhardness with temperature has also been observed in a number of cases like, Si, Ge, and Cu [5].

The use of indentation hardness as a means of studying the plastic yield properties of solids is well known. The hardness decreases with increasing loading time and the general behaviour may be described by an overall empirical relation which incorporates the earlier relations. The hardness behaviour is then found to closely parallel the creep characteristics of materials, obtained in unidirectional stress tests [6].

In the present study this relation, based on the kinematic analysis of the creep process during indentation has been found to be applicable.

The relation is

$$H_v^{-3} - H_0^{-3} = A \exp(-Q/3RT)(t^{1/3} - t_0^{1/3}) \quad (1)$$

where,

H_v = Vickers hardness at time t

H_0 = Vickers hardness value immediately after attaining the full load p at time t_0 .

Q = Creep activation energy

A = Constant, R =The gas constant

T = Absolute temperature.

This equation has been used to determine the activation energy for creep. The experimental observations needed to calculate Q are shown in the form of $\ln H_v$ versus $\ln t$ plots in Figure 2a and b respectively, for SnSe and SnS single crystals. These are straight lines obtained at different temperatures indicated near each graph. It has been predicted by Atkins et al [6] that the negative slope of such straight lines should increase with increasing temperature. However, the present author is unable to draw any such conclusion, due to limited range of temperatures used. The values of H_0 at time t_0 , selected as 1 sec, was obtained by extrapolating the straight lines to $\ln t = 0$. The intercepts on $\ln H_v$

axis give the values of H_0 for different temperatures using these values of H_0 and t_0 , $\ln(H_v^{-3} - H_0^{-3})$ versus $\ln(t^{1/3} - t_0^{1/3})$ were plotted [Figure 3 a and b]. From these plots, it is clear that the straight lines have nearly equal slopes as predicted by Eq(1). The values of activation energy Q for creep was claculated by finding the difference between the intercepts at two temperatures T_1 and T_2 in hese graphs and equaing them to $Q/3R(1/T_2 - 1T_1)$.

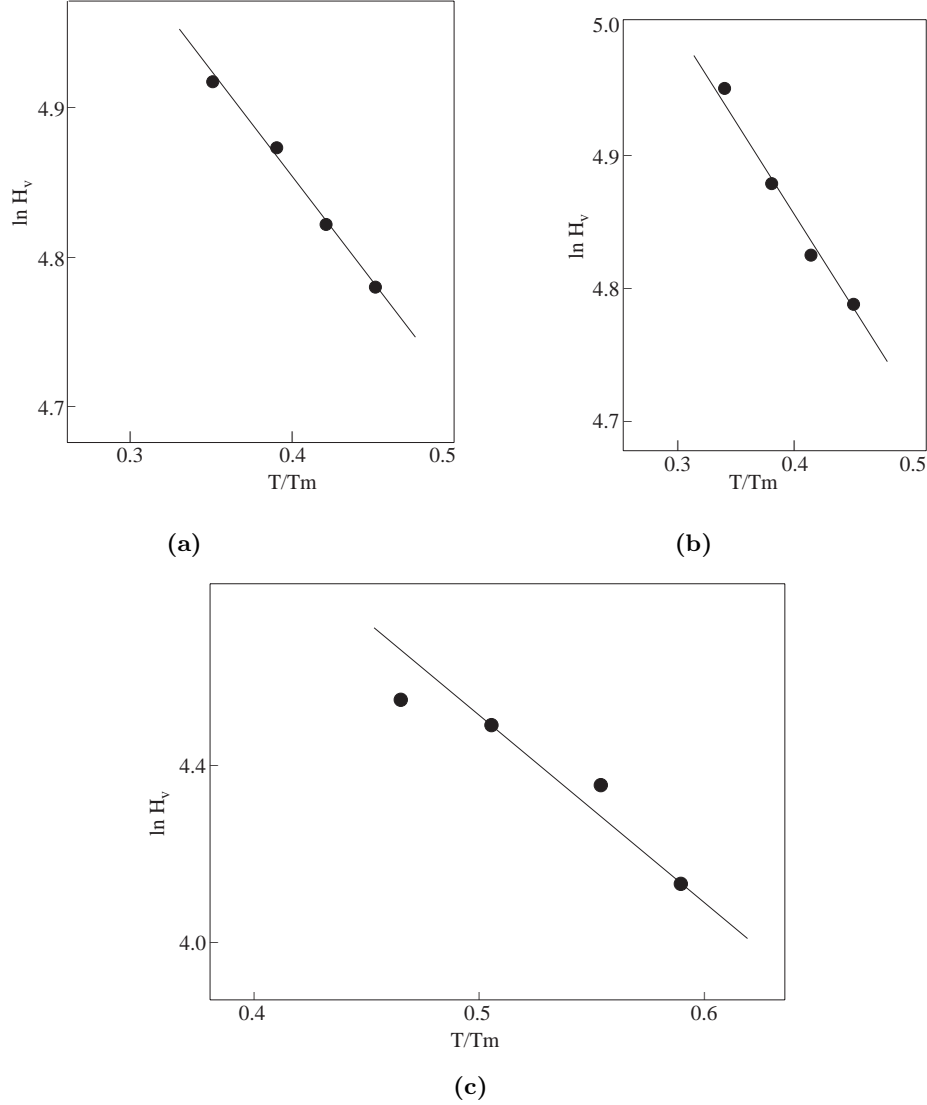
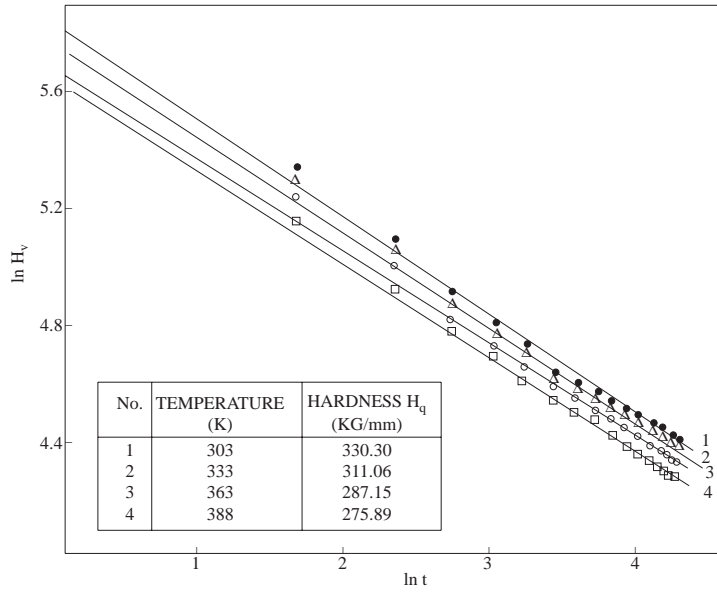
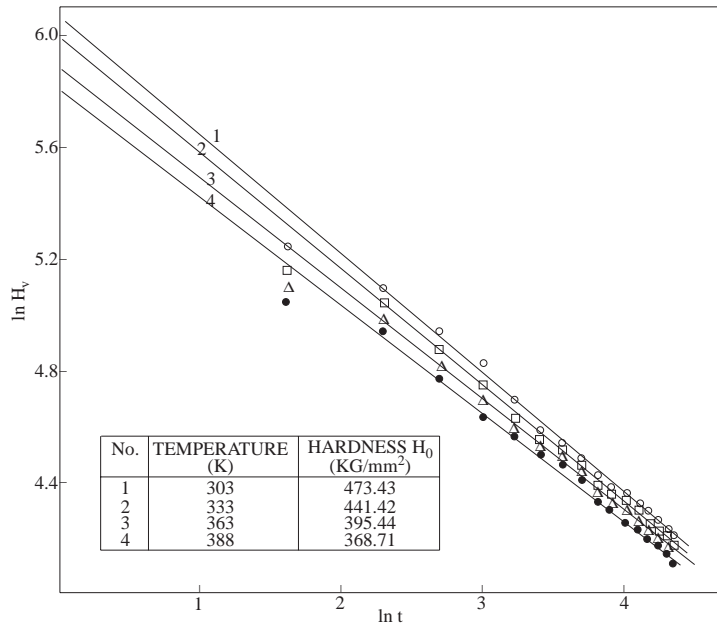


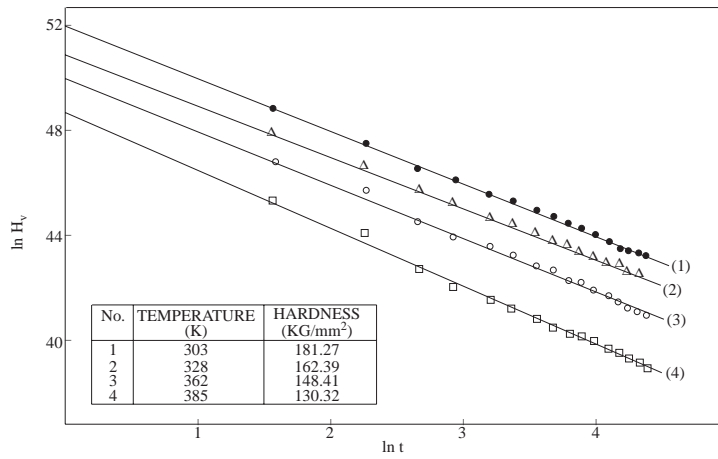
Figure 1. Plots of $\ln H_v$ versus T/T_m for (a) SnSe and (b) SnS crystals.



(a)

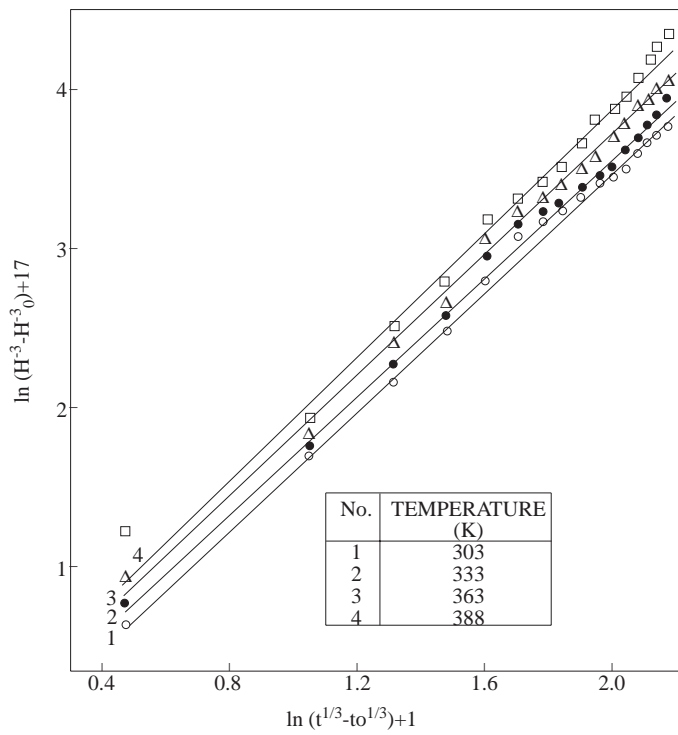


(b)

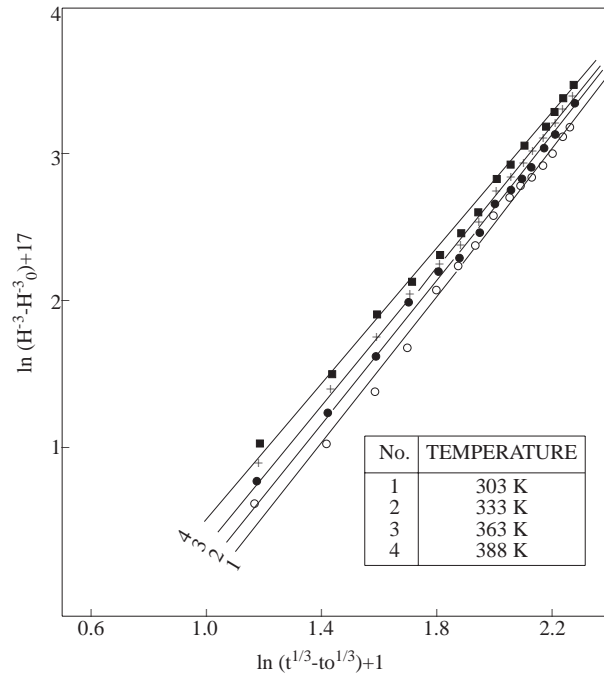


(c)

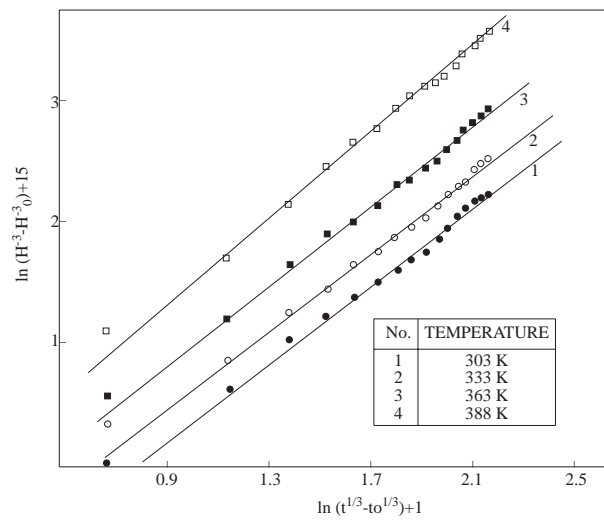
Figure 2. Plots of $\ln H_v$ versus $\ln t$ for (a) SnSe and (b) SnS and crystals.



(a)



(b)



(c)

Figure 3. Plots of $\ln(H^{-3} - H_0^{-3})$ versus $\ln(t^{1/3} - t_0^{1/3})$ (a) SnSe and (b) SnS crystals.

Thus if T_1 is selected as 304K, T_2 can be 333K, 385K. The calculations were made considering all combinations of T_2 and T_1 and average value of Q was found for each of the crystals. The activation energy values Q thus obtained for SnSe and SnS crystals are 2.92 and 1.75 K cal/mole respectively.

There is practically no report found in literature regarding creep and its activation energy in compound semiconductor crystals. The temperature range used in the present work is below half the melting points. The activation energies therefore cannot be correlated to self-diffusion mechanism [7]. The data available on elemental and alloy crystals and polycrystals indicate [8,9] the creep activation energies obtained in the present work to be quite low and hence may be associated with increased density of thermally generated carriers which may screen the dominance of strong bonds, like covalent and ionic, characteristic to these materials.

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