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Microhardness studies of SnI_2 and SnI_4 single crystals

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Abstract. The variation in the microhardness of tin-di-iodide (SnI_2) and tin-tetra-iodide (SnI_4) crystals has been determined using Vicker's microhardness indentor. It is observed that the microhardness of the crystals depends on the applied load and is independent of the duration of loading. Vickers Hardness Numerals (VHN) for SnI_2 is found to be greater than that of SnI_4 crystals. Mayer's equation and implications have been discussed.

Keywords. Single crystals; indentation; microhardness; Vickers hardness; tin-di-iodide; tin-tetra-iodide.

1. Introduction

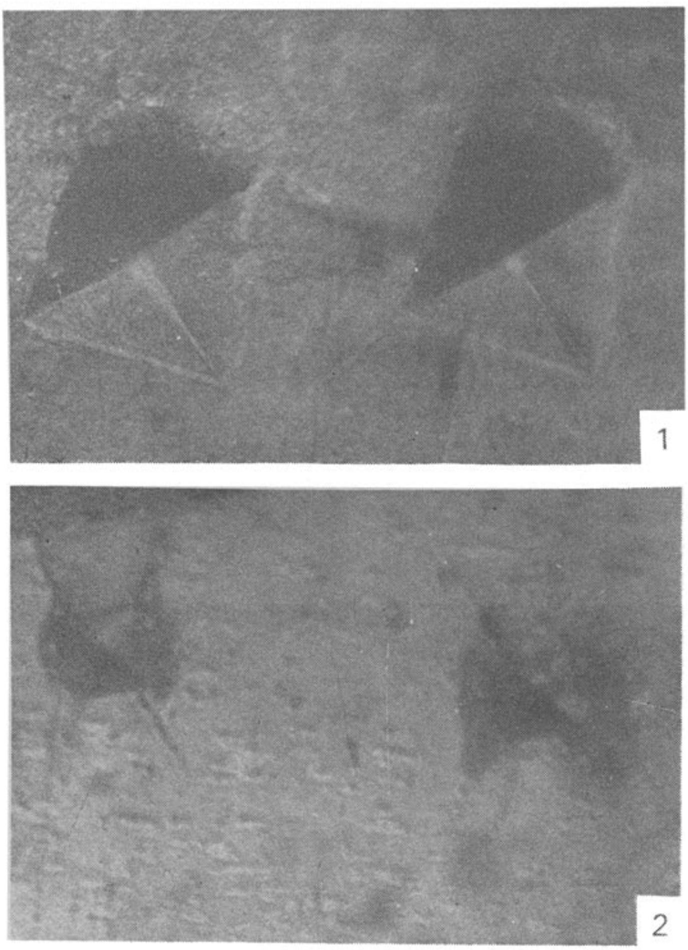
Hardness is a measure of the resistance to permanent deformation or damage. As the hardness properties are basically related to the crystal structure of the material, microhardness studies have been applied to understand the plasticity of the crystals. Boyarskaya *et al* (1969) reported the relation of microhardness to load for NaCl monocrystals. Morkievskii (1960) studied the dependence of the form of an indentation on the symmetry of the crystal face to determine the hardness by the penetration of a diamond pyramid.

Tin iodides *viz* SnI_2 and SnI_4, crystals have aroused great interest because of their several interesting electro-optical properties. Desai and Rai (1980) reported that single crystals of SnI_2 and SnI_4 can be grown by gel method. However information on the mechanical properties of these crystals is meagre. In this paper, studies on the mechanical properties from the plastic deformation of SnI_2 and SnI_4 single crystals are reported.

2. Experimental details

Single crystals of tin di-iodide (SnI_2) and tin tetra-iodide (SnI_4), were grown using the controlled reaction between $SnCl_2$ and KI by diffusion process in silica gels. The crystals were examined by scanning electron microprobe analysis, x-ray diffraction, density measurements and thermogravimetric analysis; these techniques confirmed that they were SnI_2 (monoclinic, space group C2/m) and SnI_4 (primitive cubic, space group Pa3). The SnI_2 (6–7 mm) and SnI_4 (4–4.5 mm) crystals with smooth surfaces and free of any microstructures were selected for indentation studies.

Microhardness was measured with a diamond pyramidal indentor, (M/s. Cuoke Troughton and Simms) which can be used with a Vickers projection microscope. The indentor is in the form of a square pyramid, the opposite faces of which make an angle of 136° with one another. The microhardness values of SnI_2 and SnI_4 samples were determined at room temperature and the time of indentation (t) was kept 15 sec. The load was varied from 5 to 80 g, so that the microhardness region, as defined by Buckle (1959) could be covered. In another set, the t was varied from 5 to 30 sec. These experiments were repeated for five trials, for each loading on a (010) face of SnI_2 and on a (111) face of SnI_4 crystals. Measurements were made of two diagonals of an identation mark and from the mean values diagonals and applied load, the Vickers Hardness Numeral (VHN) was computed using the relation : VHN $= 1.854\ P/d^2$, (kg mm^{-2}) where P is the applied load in kg and d is the diagonal measurement in mm (Mott 1956).



Figures 1 2. 1. Indentation marks on a (010) face of SnI_2 crystal at a load of 50 g. **2.** Indentation marks on a (111) face of SnI_4 crystal at a load of 50 g.

3. Results and discussion

Typical indentation marks with a load of 50 g are shown in figures 1 and 2, on SnI_2 and SnI_4 crystals respectively. It is seen that several median vents grow simultaneously from the stress concentration points, the sharp indenter edges. No preferred directions of venting was observed as in anisotropic materials where vents tend to have preferred orientation (Dekker and Rieck 1974). The fact that the observations are made on the (010) surface, which is normal to the unique axis and that the angle in monoclinic is close to the right angle ($\beta = 92°$). Even for low loads, the deformation was too severe and near the indentation mark, displaced matter chips off as observed frequently on minerals. However, this chipping off does not alter the size of the indentation if the diagonal ends can still be observed.

The basic sequence of crack propagation events has been explained as follows (Lawn and Wilshaw 1975). The sharp point of indentor produces an inelastic deformation and at some threshold a deformation-induced flow suddenly develops into a small crack, the median vent on a plane containing the contact axis and the increase in load causes further stable growth of the median vent. On unloading, median vents begin to clos but not heal. Relaxation of deformed material within the contact zone just prior to removal of the indentor superimposes intense residual tensile stresses upon the applied load and sideways extending cracks, called, "lateral vents" begin to appear. The lateral vents continue to extend and cause chipping.

The dependence of d and P for SnI_2 and SnI_4 crystals is shown in figure 3 where d^2 is plotted against P. The plots are straight lines, passing through the origin, indicating that the errors in loading are nil. However, in the studied range, the graph of log P against log d (figure 4) for both crystals, gave straight lines with slopes 1.927 and 1.936 for SnI_2 and SnI_4 respectively. This proves the validity of the relationship $P = ad^n$ where $n = 2$ (Mayer's equation). Microhardness experiments indicated that VHN was independent of loading time or dwell time, but was a function of indentor load. The observed variation of VHN as a function of

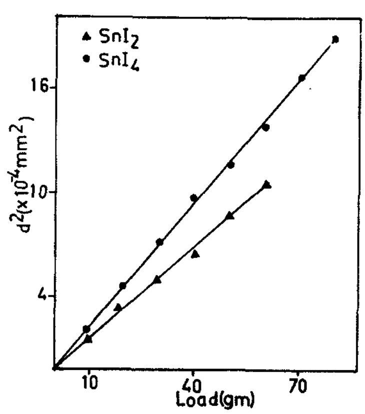
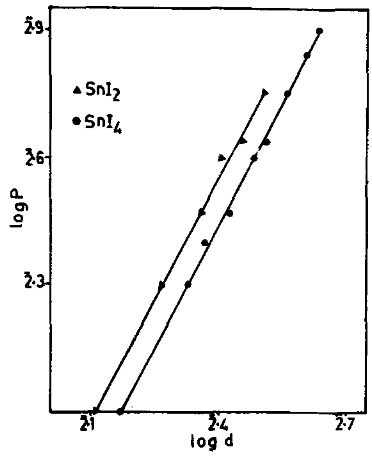
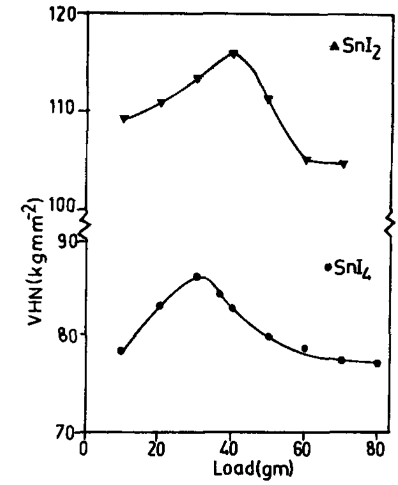


Figure 3. Graphs of square of indentation diagonal (d) plotted against the indentation load for (▲) SnI_2 and (●)SnI_4 crystals.



(4)



(5)

Figures 4-5. 4. Plots of a log P against log d for (▲) SnI_2 and (●) SnI_4 crystals. **5.** Vickers Hardness Numerals (VHN) as a function of load P for SnI_2 (▲) and SnI_4 (●) crystals.

indentor load (P) is graphically represented in figure 5. This can be explained by considering the effect of the distorted zone of the crystal on hardness as expressed by Berzina *et al* (1965). During indentation, the indentor penetrates to a depth comparable with, or greater than, the thickness of the distorted zone. Since this zone is penetrated by the indentor, its effect will be marked at comparatively low loads and hence we observe a steady increase in hardness with load (whence the chipping of materials from the surface is very intense). As the depth of the indentor increases with load, the effect of the distortion zone decreases and hence the load dependence of microhardness is less. For large loads (above 50 g) when the indentor reaches a depth at which undistorted material exists, the microhardness is independent on load.

4. Conclusions

SnI_2 and SnI_4 crystals are highly brittle and even at low indentation load fracture occurs at stress concentration points. The results suggest that the microhardness of the crystal depends on the applied load and is independent of the duration of loading. Further, irrespective of the relative orientation of the indentor and crystals, median vents are initiated at the sharp indentation edges. Maver's equation $P = ad^n$ has also been verified.

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