Vickers micromechanical indentation of $NaSb_2F_7$ and $Na_3Sb_4F_{15}$ single crystals

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Fluoro-complexes of antimony (III) and alkali metal fluorides are of both practical and theoretical interest. There have been several papers dealing with problems of the structure of compounds of this type [1-5]. Nuclear gamma resonance (NGR) spectra of complex antimony (III) fluorides of composition MSb_2F_7 (M = K, Na, Rb, Cs) have been carried out by Gukasyan *et al.* [6]. They have reported that the values of chemical shift for $NaSb_2F_7$ and KSb_2F_7 are equal and these complexes are made up of discrete structural units, namely trigonal bipyramidal SbF_4 ion and pyramidal SbF_3 molecule, which are bridged by fluorine ions. Since there is no information available on their micromechanical behaviour, a systematic study of the hardness characteristics of $NaSb_2F_7$ and $Na_3Sb_4F_{15}$ single crystals was undertaken.

The hardness of a crystal is generally defined as its resistance to structural breakdown under an applied stress. The general definition of indentation hardness, which relates to the various forms of indenter, is the ratio of the applied load to the surface area of indentation. Several investigations have been undertaken to correlate the indentation hardness with other physical properties. Even though the mechanism of deformation during indentation is clearly not understood, hardness testing provides useful information concerning the mechanical behaviour of solids. Several investigators [7-11] have used indentation techniques to study glide, deformation anisotropy, cracks etc. in various crystals.

Antimony trifluoride forms several complexes with sodium fluoride. Among these complexes, $NaSb_2F_7$ and $Na_3Sb_4F_{15}$ were synthesised by reacting antimony trifluoride with sodium fluoride in the appropriate molar ratio. The growth experiments were performed by slow and controlled evaporation of the solvent at constant temperature (305 K) using polyethylene containers and stirrers. The seed crystals are obtained by spontaneous nucleation. Single crystals of $NaSb_2F_7$ and $Na_3Sb_4F_{15}$ of dimensions up to 20 mm × 15 mm × 8 mm and 15 mm × 20 mm × 13 mm were grown in a period of three months.

The microhardnes of the crystals was determined using a Leitz-Wetzler hardness tester fitted with a Vickers diamond pyramid indenter. For the static indentation test, all the indentation measurements were made at room temperature using freshly cleaved samples of $NaSb_2F_7$ and $Na_3Sb_4F_{15}$. The time of indentation was maintained at 10 s for all trials. The centre of an impression should never be less than three times its own diameter away from any edge of the specimen or the edge of an adjacent impression. If the distance is too small a distorted indentation will be produced, resulting in inaccuracy in the measurement. The diagonals of the indentation are measured with the aid of a calibrated micrometer attached to the eyepiece of the microscope. Several indentations were made on each sample and the diagonal lengths (d) of the indented impressions were measured. The average value of the diagonal lengths of the indentation mark in each load was used to calculate the hardness. In addition, the indentation-induced crack lengths were also measured using the micrometer eyepiece.

The Vickers microhardness, H_v, was calculated using the relation [12]

$$H_v = 1.8544(P/d^2)\,\mathrm{kg\,mm^{-2}} \tag{1}$$

where P is the applied load in kg and d is the average diagonal length of the Vickers impression in mm after unloading. The Meyer relation can be represented by

$$P = \mathrm{a}d^{\mathrm{n}} \tag{2}$$

where P is the applied load, d is the diagonal length of the indentation and a and n are constants for a given material. In the present investigation, the microhardness is found to decrease with increase of load for both $NaSb_2F_7$ and $Na_3Sb_4F_{15}$ crystals as shown in Fig. 1. The value of n represents the work hardening coefficient and it was computed using the least squares fit method for $NaSb_2F_7$ and $Na_3Sb_4F_{15}$ crystals and found to be 1.36 and 1.29 respectively (Fig. 2). According to Onitsch [13], when the value of n is less than 2, then the hardness number should increase with decrease of load. Our results support this theory.

During the examination of Vickers indentation on the crystals $NaSb_2F_7$ and $Na_3Sb_4F_{15}$, interesting crack patterns were observed. When the load is 5 g, cracks were initiated on $NaSb_2F_7$ crystals, but in the case of $Na_3Sb_4F_{15}$ the cracks were observed only at 10 g. According to Arora *et al.* [14] when the Vickers indenter load is increased, a transition occurs from the purely inelastic deformation to the formation of penny-shaped cracks beneath and across the major diagonals of the Vickers indent. However, the radial cracks formed along the major diagonals or the edges of the Vickers indent, when the system is not overloaded, are probably the result of the unloading of the residual stresses [15, 16]. The toughness of the material is the resistance to fracture. The fracture toughness, K_c of a material is dependent on the microstructural features and is generally insensitive to the chemical species in the surrounding environment. The expression for a crack propagation under loading conditions, determined by the analysis of the deformation

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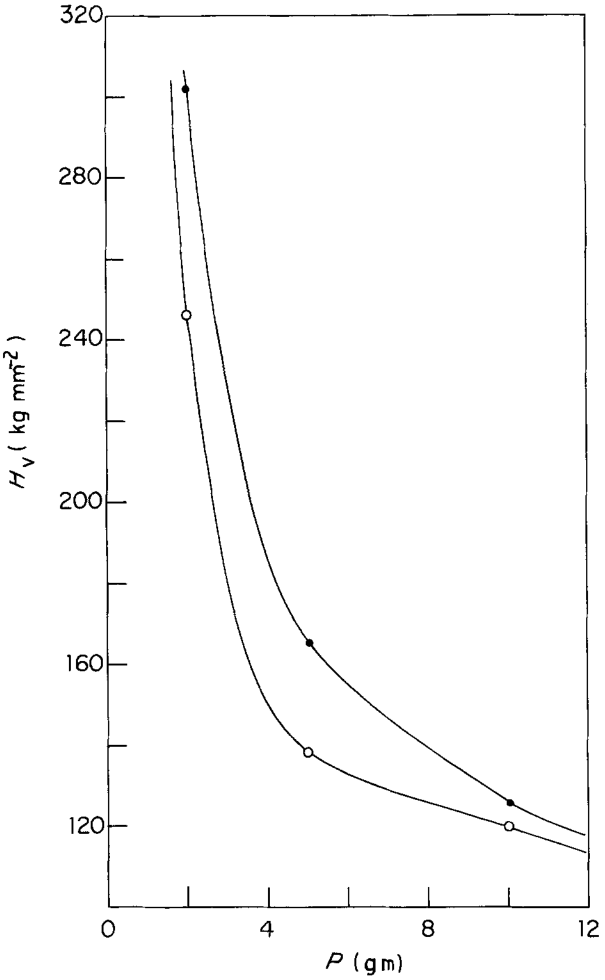

Figure 1 Variation of microhardness with indenter load. (○) $NaSb_2F_7$, (●) $Na_3Sb_4F_{15}$.

fracture mechanics of the indentation process can be represented under equilibrium conditions as [17]

$$P/l^{3/2} = \beta_0 K_c \quad \text{for} \quad l \geqslant d/2 \qquad (3)$$

where P is the applied load, l is the crack length measured from the centre of the indentation impression to the crack end, d is the diagonal length of the indentation impression and β_0 is the indenter constant, equal to 7 for a Vickers diamond indenter [18].

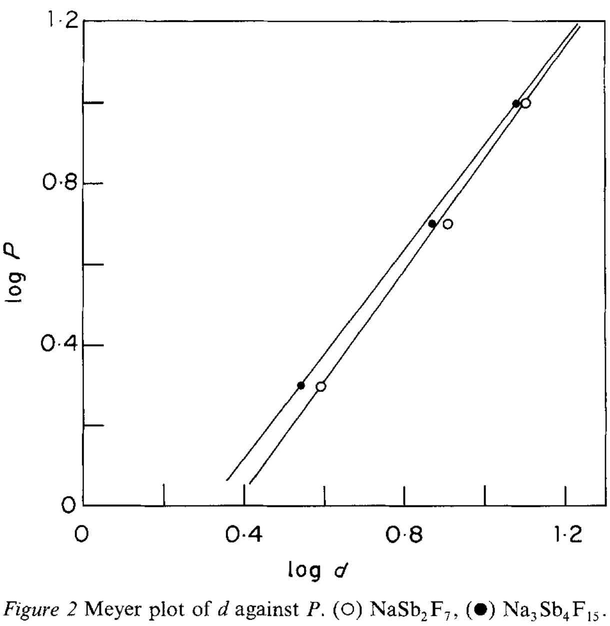

Figure 2 Meyer plot of d against P. (○) $NaSb_2F_7$, (●) $Na_3Sb_4F_{15}$.

TABLE I Mechanical properties of $NaSb_2F_7$ and $Na_3Sb_4F_{15}$

Crystal	Load (gm)	Fracture toughness MPa m$^{1/2}$	Brittleness index μm$^{-1/2}$
$NaSb_2F_7$	5	0.169	7.449
	10	0.157	7.513
$Na_3Sb_4F_{15}$	10	0.213	5.804

Brittleness is a property which affects the mechanical behaviour of a material. Brittleness indices have been calculated from the ratio between the hardness, H_v, and fracture toughness K_c. The crack length l from the centre of the indentation mark was measured. Knowing the crack length and microhardness values at 5 g and 10 g for $NaSb_2F_7$ and $Na_3Sb_4F_{15}$, the fracture toughness and brittleness index have been calculated (Table I).

From the above results we conclude that the microhardness decreases with increase of load. The radial crack lengths have been used to calculate the fracture toughness and brittleness index.

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