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Growth, Structural and Micro hardness studies of $KSbF_4$ and K_2SbF_5 crystals

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***Abstract*—Interest in Potassium Fluoro Antimonate crystals has been increased for the last four decades due its superionic conduction and its unusual electro-optic properties. Potassium tetra fluoro antimonate ($KSbF_4$) and Potassium penta fluoro antimonite (K_2SbF_5) crystals have been grown by slow evaporation method. $KSbF_4$ crystallizes into orthorhombic structure with a space group Pmmn. K_2SbF_5 belongs to orthorhombic crystal system with a space group Cmcm. Micro indentation analysis on these crystals indicates that they are moderately softer substances. Both crystals revealed reverse indentation size effect (RISE). Variation of stiffness constant with load has been discussed. Yield strength for $KSbF_4$ and K_2SbF_5 crystals have been found out as 16.72 and 16.941 MPa respectively.**

***Index Terms*—Micro indentation, Potassium fluoro antimonate crystal, Stiffness constant, Yield strength.**

I. Introduction

Although hardness has been defined in several ways it is now generally accepted that it is the resistance offered by the crystal for the movement of dislocations and practically it is the resistance offered by a material to localized plastic deformation [1]. The microhardness is a mechanical parameter that is strongly related to the structure and composition of the crystalline solids [2]. The hardness is estimated from the ratio of the load applied on indenter to the area of the impression left on the specimen. During the indentation process, the external work applied by the indenter is converted into the strain energy component proportional to the volume of the resultant impression and the surface energy component [3]. Hardness of the material depends on different parameters such as lattice energy, Debey temperature, heat of formation and interatomic spacing [4], [5]. It is well known that micro hardness of solids depends on the applied indentation test load. This phenomenon is known as the indentation size effect (ISE) [6]. In normal ISE we have been observed higher hardness values at lower loads and it decreases as the load is increased. It has been observed in a variety of materials like alkali halides [7] and alums [8]. In some cases, a different trend with initial increase of hardness with increase in load then followed by a decrease and finally hardness becoming independent at higher loads, known as reverse indentation size effect (RISE) [9]. Similar observations have been found out in our present study. $KSbF_4$ and K_2SbF_5 crystals have aroused great interest because of their several interesting electro-optical and super ionic properties [10]-[12]. Micro hardness studies have been made on various fluoro antimonate crystals such as Sodium fluoro antimonate crystals [13], [14] and Ammonium fluoro antimonate crystals [15], [16]. Researchers have devoted many pages for finding the characterization of Potassium fluoro antimonate crystals. However in the literature, information on the mechanical properties of Potassium fluoro antimonate crystals is meager. Therefore in this paper we report the growth, structural and micro hardness studies of $KSbF_4$ and K_2SbF_5 crystals.

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II. Materials And Methods

Antimony tri fluoride forms several complexes with Potassium fluoride. Among the complexes, $KSbF_4$ and K_2SbF_5 crystals have been synthesized by reacting Antimony tri fluoride with Potassium fluoride in the appropriate molar ratio.

$$KF + SbF_3 \rightarrow KSbF_4 \quad (1)$$
$$2KF + SbF_3 \rightarrow K_2SbF_5 \quad (2)$$

The reactants were stirred well using magnetic stirrer to ensure uniform temperature and concentration throughout the entire volume of the solution. The filtered solution was transferred into a crystallizer and allowed to evaporate slowly under room temperature. Small transparent rectangular shaped crystals were obtained in a period of about fifteen days. The grown $KSbF_4$ and K_2SbF_5 crystals are shown in Fig. 1 and Fig.2.

The X-ray diffraction patterns (XRD) of the powdered samples were obtained by using Philips X'pert Pro X-ray automatic diffractometer in the range of 10 – 70° with CuKα radiation of wavelength 1.54056 Å. The single crystal X- ray diffraction analysis of crystal was carried out using ENRAF NONIUS CAD-4 Diffractometer with MoKα radiation (λ=0.7107Å). Hardness measurements have been carried out using REICHERT MD 4000 E Vicker's Ultra Micro hardness tester attached to a metallurgical optical microscope. The well polished crystal was mounted on the platform of the microhardness tester and loads of different magnitudes were applied over a fixed interval time of 15 Sec. The average diagonal lengths of indentation for various loads were measured.

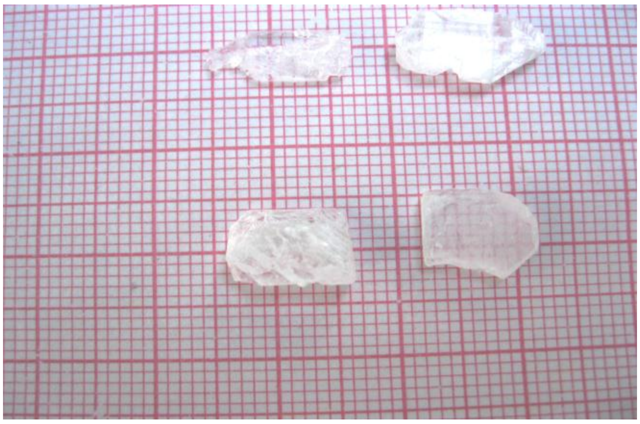

Fig. 1. Photograph of the grown $KSbF_4$ crystal

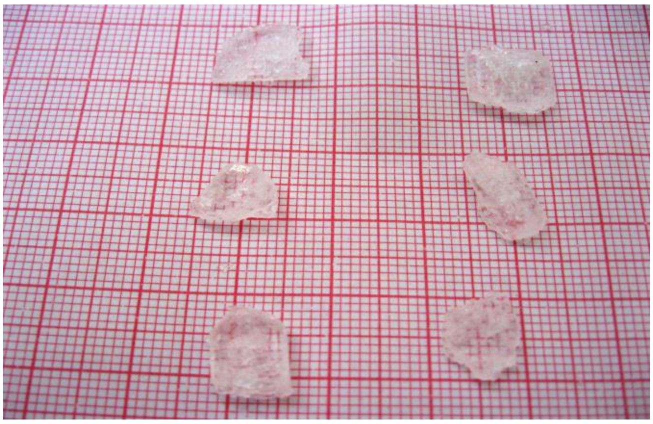

Fig. 2. Photograph of the grown K_2SbF_5 crystal

III. RESULT AND DISCUSSIONS

The observed indexed Powder XRD pattern for $KSbF_4$ crystal is shown in Fig.3.

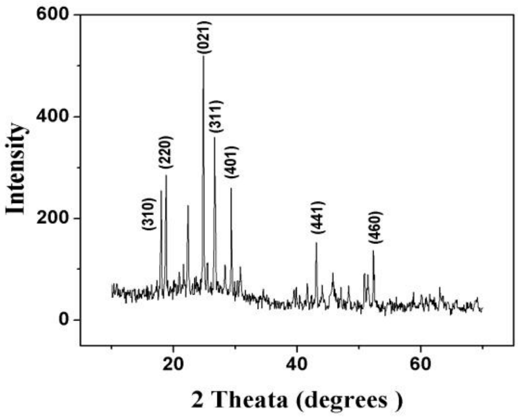

Fig. 3. Indexed observed XRD Pattern of $KSbF_4$ crystal

The XRD data match very well with the JCPDS file No. 85– 0626**,** which confirms the identity of the grown crystal. The result of single crystal XRD indicates that $KSbF_4$ crystallizes into orthorhombic structure with space group Pmmn. The lattice parameters are determined to be a=16.28 Ǻ, b=11.51 Ǻ, c= 4.543 Ǻ, $\alpha=\beta=\gamma=90^o$, V=857.33 Ǻ^3. These results have been found to be in agreement with the already reported values [17]. Observed indexed Powder XRD pattern for K_2SbF_5 crystal is shown in Fig. 4.

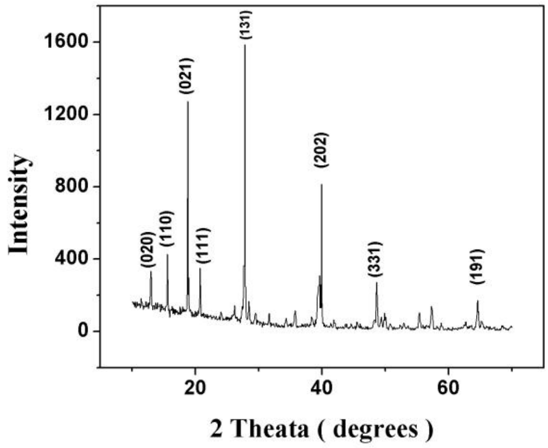

Fig. 4. Indexed observed XRD Pattern of K_2SbF_5 crystal

The pattern is very well in agreement with the JCPDS file 77-0878, which confirms the presence of K_2SbF_5 crystal structure. The result of single crystal XRD indicate that K_2SbF_5 crystal belongs to orthorhombic crystal system, having lattice dimensions a=6.27Ǻ, b=13.66 Ǻ, c=6.49 Ǻ and $\alpha=\beta=\gamma=90^o$, V=556 Ǻ^3 with a space group Cmcm, which are in agreement with the already reported values [18]-[21].

The Vicker's micro hardness value (Hv) was calculated using the relation [6],

$$Hv=1.8544P/d^2 \text{ kg/mm}^2 \quad (3)$$

Where P is the applied load and d is the average diagonal length of the indentation impression. A plot of hardness value (Hv) with the applied load (P) is shown in Fig.5.

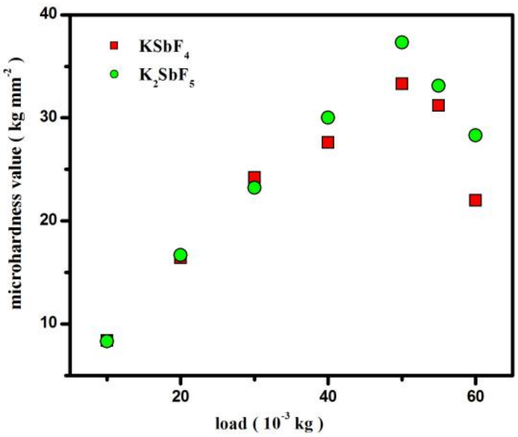

Fig. 5. Variation of microhardness with load for $KSbF_4$ and K_2SbF_5 crystals.

In the present study for both crystals the value of Hv increase as the load increase and finally decreases for higher loads (above 50gm), revealed reverse indentation size effect (RISE). Above 50 gm cracks were initiated on the crystal surface around the indenter. The major contribution to the increase in hardness is attributed to the high stress required for homogeneous nucleation of dislocation in the small dislocation free region indented [22]-[24].

When the applied load is small, the indenter penetrates only the surface layers, consequently dislocations are nucleated along a particular slip plane near the surface and therefore the effect is shown sharply. When the penetration depth increases with applied load, nucleation of dislocation involves in another set of slip planes just below the indenter in the crystal. After a certain penetration, the effect of inner slip planes becomes more prominent than that of slip planes along the surface layers and hence the microhardness is independent on load [25].

It can also be explained in another way. During indentation the thickness of the distorted zone is limited for small loads, hence we observe a steady increase in hardness with load. As the depth of the indenter increases with load, the effect of the distortion zone decreases and hence the dependence of microhardness is less. For large loads (above 50 g), the indenter reaches the undistorted zone, hence the microhardness in independent on load [26], [27]. From the literature it has been found that the reverse ISE occurs only in materials in which plastic deformation is dominant [28], [29]. Investigations showed that all semiconductors exhibit RISE [30]. The same phenomenon is observed in the present insulating crystals.

The relation between the load and size of the indentation is given by Meyer's law [31],

$$P = K_1 d^n \qquad (4)$$

Where P is load, d is the diagonal length of impression, K_1 and n are constants. Work hardening coefficient (n), a measure of the strength of the crystal, is computed from the slope of the log P versus log d plot (Fig.6) and K_1, the standard hardness is noted by the intercept of the graph.

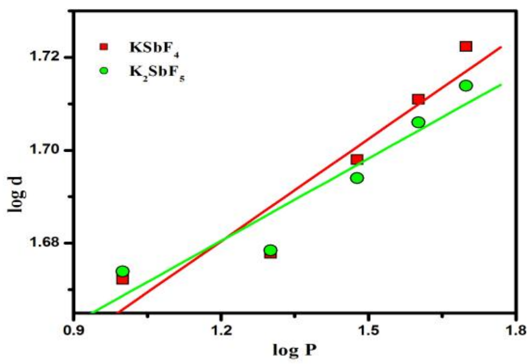

Fig. 6. log P versus log d Plot for $KSbF_4$ and K_2SbF_5 crystals.

The value of n for $KSbF_4$ and KSb_2F_5 crystals have been found out as 1.59 and 1.63 respectively using least square fit method. Low work hardening coefficient shows less dislocation in the grown crystal, since work hardening coefficient is caused by the dislocations present in the crystal [32], [33]. From many observations it has been found that the value of n lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials [34]. The values observed in the present study are just around 1.6 suggesting that $KSbF_4$ and K_2SbF_5 crystals are moderately softer substances. The value of n for K_2SbF_5 is in close agreement with that of mixed crystals of $(NH_4)_2SbF_5$ – K_2SbF_5 (n = 1.66) [35] and for Na_2SbF_5 (n = 1.5) [13]. The n value of $KSbF_4$ is slightly differ with $NaSbF_4$ (n = 1.3) [13] and suggest that $KSbF_4$ is softer crystal than $NaSbF_4$. The decreasing n value of $KSbF_4$ compared with $NaBF_4$ (n = 1.79) and NH_4BF_4 (n = 1.85) [36] may be attributed by the introduction of antimony in the place of Boron. From the n values, it has been found that K_2SbF_5 crystal is softer than $KSbF_4$ crystal.

Since the material takes some time to revert to elastic mode after every indentation, an additional correction factor x known as the measure of dislocation density of the material is applied to the observed d value [32] (Justin Raj et al 2008). Meyer relation may be satisfied as given below.

$$P = K_2 (d + x)^2 \qquad (5)$$

Substituting for P from Meyer relation we get.

$$K_1 d^n = K_2 (d + x)^2 \qquad (6)$$

$$d^{n/2} = (K_2/K_1)^{1/2} d + (K_2/K_1)^{1/2} x \qquad (7)$$

The correction factor x was determined from intercept of straight line obtained by plotting d versus $d^{n/2}$ (Fig.7). Slope yields $(K_2/K_1)^{1/2}$, where K_2 is a constant.

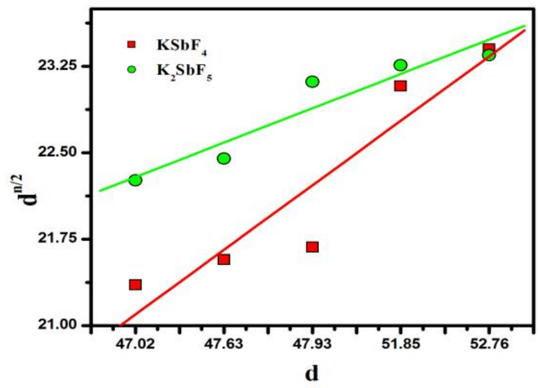

Fig. 7. Plot of d versus $d^{n/2}$ for $KSbF_4$ and K_2SbF_5 crystals

The micro hardness value correlates with other mechanical properties such as elastic constants and yield strength (**σ_y**). Yield strength is one of the important properties for device fabrication. (**σ_y**) Can be calculated using the relation [37]

$$\sigma_y = H_v/2.9\{[(1-(2-n)][(12.5(2-n)/(1-(2-n)]^{2-n}\}$$

The yield strength is calculated to be 16.72 and 16.941 MPa for $KSbF_4$ and K_2SbF_5 crystals respectively. The microhardness parameters are listed in Table. 1.

Table 1. Hardness parameters of $KSbF_4$ and K_2SbF_5 crystals.

Name of the crystal	n	K_1(kg/mm)	K_2(kg/mm)	x(µm)
$KSbF_4$	1.59	0.001074	0.02261	0.0777
K_2SbF_5	1.63	0.001041	0.02854	0.085

The elastic stiffness constant (C_{11}) gives an idea about tightness of bonding between neighbouring atoms. The stiffness constant for different loads has been calculated using Wooster's empirical formula [38],

$$C_{11} = Hv^{7/4}. \qquad (9)$$

The variation of elastic stiffness constant with load is depicted in Fig. 8. From the graph, it is clear that the stiffness constant increases with increase of load.

The higher value of stiffness constant for K_2SbF_5 than $KSbF_4$ may be due to the higher contribution of potassium and fluorine. Appreciable values of C_{11} indicates that the binding force between the $[Sb_4F_{16}]^{4-}$ anions and K^+ cations in $KSbF_4$ crystal and $[SbF_5]^{2-}$ anions and K^+ cations in K_2SbF_5 crystals are quite strong.

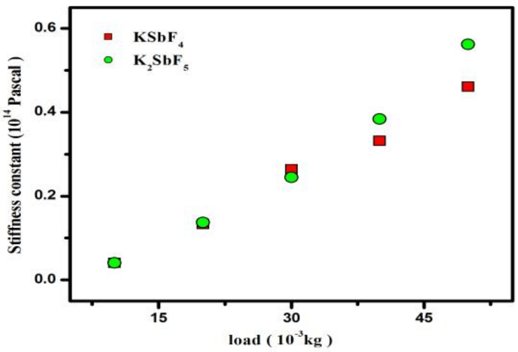

Fig. 8. Variation of stiffness constant with load for $KSbF_4$ and K_2SbF_5 crystals

IV. Conclusions

Optically clear single crystals of $KSbF_4$ and K_2SbF_5 have been grown by slow and controlled evaporation technique. The microhardness study shows that hardness steadily increases with load, then decrease for higher loads. The work hardening coefficient (n) for $KSbF_4$ and K_2SbF_5 crystals have been found to be 1.59 and 1.63 respectively and indicate that they are moderately softer substances. Yield strength has been found out as 16.72 and 16.941 MPa for $KSbF_4$ and K_2SbF_5 crystals. Stiffness constant revealed that the tightness of binding of ions is quite strong.

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