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Growth, structural, vibrational, microhardness and dielectric Studies of $$KSb_4F_{13}$\ crystal$

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ABSTRACT

Interest in Potassium Fluoro Antimonate crystals have been increased for the last four decades due its superionic conduction and its unusual electro-optic properties. The title compound KSb_4F_{13} crystal has been grown by slow evaporation technique at room temperature. The crystalline perfection was analyzed by powder X-ray diffraction method. From single crystal X-ray diffraction, it has been found that it belongs to tetragonal crystal system with a space group 14/m. The presence of functional groups were identified by FTIR spectral analysis. The microhardness studies indicate that the KSb_4F_{13} crystal is a moderately softer substance. It showed that the given crystal exhibit reverse indentation size effect (RISE). The dielectric and A.C. conductivity studies have been carried out at different frequencies with different temperatures , and the results analyzed.

INTRODUCTION

During the past few decades, researchers have shown much interest in the Fluoro antimonate crystals with chemical formula M_2SbF_5 , $MSbF_4$, MSb_2F_7 , MSb_3F_{10} , MSb_4F_{13} etc (where $M = NH_4$, Na, K, Tl, Cs, Rb) due to their intensive applications in the field of opto electronics and superionic conduction [1 - 13]. So many publications has been devoted their pages for the growth and characterization of Potassium fluoro antimonate crystals. But Microhardness and dielectric studies of KSb_4F_{13} crystal has not been reported in the literature. Therefore in the present investigation we report the growth, structural, vibrational, microhardness and dielectric and A.C. conductivity studies of KSb_4F_{13} crystal.

MATERIALS AND METHODS

Synthesis and Crystal growth

The title compound KSb_4F_{13} crystal has been synthesized from highly purified Hydrofluoric acid, Antimony trioxide and Potassium fluoride in the stoichiometric ratio 12:2:1 was dissolved in double distilled water to prepare the saturated solution. The chemical equation governing the reaction is,

$$12HF + 2Sb_2O_3 + KF \rightarrow KSb_4F_{13} + 6H_2O$$

$$\tag{1}$$

The saturated solution was purified further by repeated recrystallization and allowed to evaporate the excess amount of water at 305K to obtain seed crystals due to spontaneous nucleation within a week. The single crystals of KSb_4F_{13} were successfully grown from aqueous solution by slow evaporation technique in a period of two weeks. The grown crystals are shown in Fig. 1.



Fig.1 The photograph of the grown KSb_4F_{13} Crystal

Material Characterization

Powdered XRD spectrum of the crystal is recorded using Philips X' pert Pro X-ray diffractometer with CuK α radiation of wavelength 1.54056 Å. MESSERS ENRAF NONIUS CAD4 X- ray diffractometer with MoK α radiation (λ = 0.7107Å) was used to obtain the accurate cell parameters of the grown crystals at room temperature by the least squares refinement of the setting angles of 25 reflections. FTIR spectrum is recorded using Perkin Elmer RX1 FTIR Spectrometer in the region of 400 to 4000 cm⁻¹ by KBr pellet technique for its functional group confirmation and qualitative assignment. Microhardness studies have been carried out using REICHERT MD 4000E VICKERS ULTRA MICROHARDNESS TESTER. The well polished crystal was mounted on the platform of the microhardness tester and loads of different magnitude were applied over a fixed interval time of 15 Sec. The average diagonal lengths of indentation for various loads were measured. The dielectric study on the grown crystal has been carried out using Agilent 4284 A 20Hz-1 MHz precision LCR Meter. Graphite coating was applied on the opposite sides of the crystal, which was placed between two copper electrodes and thus a parallel plate capacitor was formed. The capacitance (C_P) and dielectric loss (tanð) of the sample were measured for various frequencies in the range of 100Hz to 1MHz, at different temperatures from 40°C to 150°C.

RESULTS AND DISCUSSION

XRD analysis

The standard and observed powder XRD pattern of the given KSb_4F_{13} crystal is shown in Fig. 2. It is in agreement with the JCPDS File No. 73 – 2186, confirm the identity of the grown crystal. From single crystal XRD data it is found that KSb_4F_{13} crystal belongs to the tetragonal system with a = 9. 636 Å, b = 9.636 Å C = 6.362 Å with a space group 14/m. It has two molecules in the unit cell with a volume of 611.7 Å³ which are in good agreement with the reported values [14-15].

FTIR analysis

The recorded FTIR spectrum of KSb_4F_{13} crystal is depicted in Fig. 3. The broad absorption band at 3524 cm⁻¹ corresponds to the stretching vibration of hydroxide ion participating in the O-H-F hydrogen bond [16]. A narrow band at 1644 and 1714 cm⁻¹ corresponds to the bending vibrations of O-H bond [16]. The bands formed at 1227 and 1367 cm⁻¹ represents the bending vibrations of Sb-O-Sb bonds [17]. The stretching vibrations of Sb-F bonds corresponds to the absorption band at 508cm⁻¹ [18].



Fig. 2 Standard and observed powder XRD pattern of KSb₄F₁₃ crystal



Fig. 3 FTIR spectrum of KSb₄F₁₃ crystal

Microhardness Studies Variation of load with hardness Hardness values of the grown crystal has been estimated from the expression

$$H_v = 1.8544 \text{ P/d}^2 \text{ kg/mm}^2$$

Here P is the load applied on indenter in kg and d is the diagonal length of the impression in mm [19]. The values of H_V were plotted against load (Fig.4).

In the present case, hardness steadily increases then decreases for higher loads (i.e after 50gm), known as reverse indentation size effect (RISE) [20]. This behaviour of independence of microhardness at higher loads can be explained on the basis of slip planes producing dislocations. At small loads, the indenter penetrates only the surface layers, dislocations are nucleated in slip planes close to the indented surface. When the penetration depth increases

(2)

with applied loads, another set of slip planes just below the indenter in the crystal producing dislocations and hence we observe a steady increase in hardness with load. At higher loads, the activity of the latter type of slip planes becomes more dominant than that of slip planes near the surface. This complex effect appears to be responsible for the effect of independence of hardness at higher loads [21].



Fig. 4 Variation of hardness with load for KSb_4F_{13} crystal



Fig. 5 Plot of log P versus log d for KSb₄F₁₃ crystal

log P vs log d plot

The relation between load and the size of indentation is given by Meyer's law [22],

$$\mathbf{P} = \mathbf{K}_1 \mathbf{d}^n \tag{3}$$

Here K_1 is the standard hardness, n is the work hardening index. From the slope of the log P vs log d plot (Fig. 5), the value of n has been estimated and K_1 is noted by the intercept. The value of n is expected to be 2, but it has not received wide acceptance especially in the low load region. Onitsch [23] from careful observations on various

(5)

materials pointed out that n lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials. The n value observed in the present study (n=1.615) suggests that KSb_4F_{13} is a moderately softer substance.

d vs d^{n/2} Plot

Crystal undergo elastic recovery after the release of the indentation stress. So a correction factor (x) is necessarily added to satisfy the eqn. (3)

$$\mathbf{P} = \mathbf{K}_2 \left(\mathbf{d} + \mathbf{x} \right)^2 \tag{4}$$

Simplifying eqn. (3) and (4)

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

The value of the correction factor x was determined from the intercept of straight lines obtained by plotting d versus $d^{n/2}$ (Fig.6). Slope gives $(K_2/K_1)^{1/2}$. The hardness parameters for KSb_4F_{13} crystal are listed in Table. 1.



Fig. 6 Plot of d versus $d^{n/2}$ for KSb_4F_{13} crystal

Table.1 Micro Hardness parameters of KSb₄F₁₃ crystal

n	K1(Kg/m)	K2(Kg/m)	x(µm)
1.615	0.001054	0.02153	0.0821

Yield Strength Studies

The microhardness value correlates with other mechanical properties such as elastic constants and yield strength(σ_y). Yield strength is one of the important property for device fabrication. From the hardness value the yield strength (σ_y) can be calculated using the relation [24],

$$\sigma_{y} = Hv/2.9 \{1 - (2-n)[(12.5(2-n)/1 - (2-n)]^{2-n}$$
(6)

The yield strength has been estimated as 1.619 MPa.

Elastic Stiffness Constant (C11)

The elastic stiffness constant gives an idea about the tightness of bonding between neighbouring atoms. It was calculated using Wooster's empirical relation $C_{11} = (Hv)^{7/4}$ [25]. The variation of elastic stiffness constant with load is shown in Fig. 7. Appreciable value of elastic stiffness constant indicates that the binding force between $(Sb_4F_{13})^-$ anions and K⁺ cations are quite strong.



Fig. 7 - Variation of stiffness constant with load for $KSb_4F_{13}\,crystal$



Fig. 8 Variation of dielectric constant with temperature at different frequencies in [100] axis for KSb₄F₁₃ crystal

Dielectric and A. C. conductivity Studies

Dielectric measurement is one of the useful methods for characterization of electrical response in crystalline and ceramic materials. A study of the dielectric properties provides information about electric fields within the solid materials. If the area of the crystal was smaller than the plate area of the cell, then the dielectric constant (ϵ_r) of the given crystal was calculated using the relation [26],

 $\epsilon_r = \{[(C_{crys}-C_{air})(1-A_{crys}/A_{air})]/C_{air}\}[A_{air}/A_{crys}]$

(7)

Variation of dielectric constant and dielectric loss (tan δ) with temperature at different frequencies in [100] and [010] axes are shown in 8, 9, 10, 11 respectively.



Fig. 9 Variation of dielectric loss with temperature at different frequencies in [100] axis for KSb₄F₁₃ crystal



Fig. 10 Variation of dielectric constant with temperature at different frequencies in [010] axis for KSb₄F₁₃ crystal



Fig. 11 Variation of dielectric loss with temperature at different frequencies in [010] axis for KSb4F13 crystal

It has been found that both dielectric constant and dielectric loss decrease with increasing frequency. This is the normal dielectric behaviour [27]. This can be understood on the basis of the mechanism of polarization. The high value of ε_r at lower frequencies may be due to the presence of space charge polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. As the frequency increases, the dipoles are unable to rotate rapidly so that their oscillations begin to lag behind with the external field and hence the polarization decreases gives raise to diminishing values of ε_r and tan δ [28].

The contribution from space charge polarization depends on purity and perfection of crystals, as the impurities and defects create potential barriers that limit the transport of charge carriers. Therefore the space charge (or diffusing) contribution involves a limited transport of charge carriers until they are stopped at a potential barrier, possibly a grain boundary or phase boundary [29]. The dielectric constant is observed to increase with temperature due to the orientation of dipoles.

The amount of power loss in a dielectric under the action of the applied voltage is commonly known as dielectric loss. The low values of dielectric loss suggest that the grown crystals are of moderately good quality [30].

A.C. conductivity is one of the studies done on solids in order to characterize the bulk resistance of the crystalline sample. The A.C. conductivity (σ_{ac}) is given by,

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta$$

(8)

Here $\omega = 2 \pi f$ and f is the frequency of the applied alternating field, ε_r is the dielectric constant and tan δ is the dielectric loss. The variation of A.C. conductivity with temperature at different frequencies in [100] and [010] axes are depicted in Fig. 12, 13 respectively.



Fig. 12 Variation of A. C. conductivity with temperature at different frequencies in [100] axis for KSb₄F₁₃ crystal



Fig. 13 Variation of A. C. conductivity with temperature at different frequencies in [010] axis for KSb₄F₁₃ crystal

It showed that σ_{ac} increases with increase of frequency. σ_{ac} also shows an intensive rise with increasing temperature at all investigated working frequencies is due to the creation of more and more charge carriers produced by thermal activation, which in turn increases the conductivity.

CONCLUSION

Good quality single crystals of KSb_4F_{13} have been successfully grown by conventional slow evaporation method. Powder and single crystal X-ray diffraction studies confirmed the Identity of the grown crystals. FTIR studies showed the functional groups present in the crystal. Vickers microhardness study on KSb_4F_{13} crystal reveals that the hardness number increase with increase of load and after 50gm it decreases with increase of load. Meyer's index n is around 1.6 suggesting that grown crystal falls under the moderately soft material category. The dielectric and A.C. conductivity studies have been carried out at different frequencies with different temperatures , and the results analyzed.

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