Growth and microhardness studies of mixed crystals of (NH₄)₂SbF₅-K₂SbF₅

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Mixed crystals of (NH₄)₂SbF₅-K₂SbF₅, an electro-optic material have been grown by isothermal evaporation technique. Powder X-ray diffraction method has been used for structural identification and determination of lattice parameters. Load dependent microhardness measurements on this crystal reveal the mechanical behaviour of the material. The work hardening co-efficient and the yield strength of the material were found to be 11.66 and 2.058 Mpa, respectively.

Keywords: Solution growth, Mixed crystals, Microhardness

IPC Code: B01D9/00

1 Introduction
Recently, there is an increasing demand for the synthesis and growth of new electro-optic materials having simple structures. Fluoro-complexes of antimony with the alkali fluorides are of considerable interest because of their high optical homogeneity and other pertinent characteristics such as superionic conductivity, low dielectric loss for battery and capacitor applications. Antimony (III) fluoride reacts with alkali metal fluorides to form numerous crystalline complexes of the general formulæ M₂(SbF₅), M(SbF₄) and M(Sb₂F₇) where, M is alkali metal ion with exception of Li⁺. Fluoro-antimonate crystals of ammonium for superionic properties and sodium fluoro antimonate for their electro-optic properties are realized in the literature. Non availability of literature references kindled interest on mixed crystals of fluoro-antimonate crystals. In recent years, attempts are made to grow mixed crystals which are used in optical information storage processes, Laser window materials and as neutron monochromators.

Measurement of hardness is an useful non destructive testing method to determine the bond strength. The microhardness value correlates with other mechanical properties such as elastic constants and yield strength. The microhardness of mixed crystals exceeds the microhardness of the component single crystals, so when hardness is of prime importance for a particular application, mixed crystals are more preferred than the component single crystals. In the present investigation the crystal growth, X-ray analysis and the microhardness measurements on the mixed crystal (NH₄)₂SbF₅-K₂SbF₅ are studied and the results are discussed.

2 Crystal growth
Ammonium fluoride, antimony trioxide and hydro-fluoric acid (48%) are the starting materials for the preparation of (NH₄)₂SbF₅ solution. These materials are mixed in water in equimolar ratio. The reaction can be represented as

\[ \text{Sb}_2\text{O}_3 + 4\text{NH}_4\text{F} + 6\text{HF} \rightarrow 2(\text{NH}_4)_2\text{SbF}_5 + 3\text{H}_2\text{O} \quad (1) \]

Similarly, K₂SbF₅ solution is prepared by mixing KF and Sb₂O₃ in water with HF. Equal volume ratio of both the saturated solutions are mixed thoroughly and concentrated in a hot water bath to obtain super saturation. The growth experiments are carried out by slow and controlled evaporation of the solvent at constant temperature (300 K) using PVC container and magnetic stirrer. Seed crystals obtained by spontaneous nucleation are further used to grow bulk crystals of (NH₄)₂SbF₅-K₂SbF₅ in a period of two months.

3 Results and Discussion
3.1 Powder XRD Analysis
X-ray diffraction technique is used to investigate the inner arrangement of atoms or molecules in a
crystalline material. The lattice parameters are identified by X-ray powder diffraction technique. The diffractogram of the mixed crystal is taken by STOE powder diffraction system loaded in Si-911 holder. The range of 2θ is scanned from 10-60 degree. Intensity versus 2θ is recorded and is shown in Fig. 1. The sharp intense peaks on the pattern reveal that the crystallites are pure and dislocation free. From the XRD analysis it is found that the crystal is crystallized into orthorhombic with space group CmCm, which is the same as that of the parent molecules13,14. The lattice parameters are determined to be a = 6.5219 Å, b= 13.7689 Å, c = 6.2914 Å and α = β = γ = 90°. The interplanar spacing d is calculated for all the observed values. The XRD data of (NH₄)₂SbF₅-K₂SbF₅ is tabulated in Table 1.

### 3.2 Microhardness

The hardness of a material depends on different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. According to Jianghong Gong15, during an indentation process, the external work applied by the indenter is converted into a strain energy component proportional to the volume of the resultant impression and a surface energy component proportional to the area of the resultant impression. Microhardness is a general microprobe for assessing the bond strength, apart being a measure of bulk strength. The crystals slices are well polished to avoid surface defects which influence the hardness values strongly. Microhardness

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Fig. 1—X-Ray Diffractogram of (NH₄)₂SbF₅-K₂SbF₅
studies are carried out at room temperature using Shimadzu HMV-2000 fitted with vickers pyramidal indentor. The load (P) is varied for 10, 15, 25 and 50 gms and the time of indentation is kept constant as 15 seconds for trials. Ten indentations are made on the sample and the average diagonal length (d) of the indentation impressions are measured.

The hardness of the material, \( Hv \) is determined by the relation

\[ Hv = 1.8544 \frac{P}{d^2} \text{ kg/mm}^2 \]  

where, \( P \) is the applied load in kg and \( d \) is the diagonal length of the indentation impression in mm. In the present case, hardness steadily increases then decreases for higher loads. The graphs are plotted for \( P \) versus hardness (Fig. 2), \( \log d \) versus \( \log P \) (Fig. 3). The plot between \( \log P \) versus \( \log d \) yields a straight line and its slope, the work hardening index, \( n \) is found to be 1.66.

\begin{table}
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According to Mayer’s law,

\[ P = k_1 d^n \]  

where \( k_1 \) is the standard hardness which is found out from the \( P \) versus \( d^n \) graph. It is known that the material takes some time to revert to elastic mode after the applied loading is removed, so a correction \( x \) is applied to the observed \( d \) value. Kick’s law may be satisfied as given below

\[ P = k_2 (d+x)^2 \]  

Simplifying Eqs (3) and (4) yields

\[ d^n = (k_2/k_1)^{1/2} d + (k_2/k_1)^{1/2} x \]  

The slope of \( d^n \) versus \( d \) yields \((k_2/k_1)^{1/2}\) and the intercept is a measure of \( x \). From the hardness value the yield strength \((\sigma_y)\) can be calculated using the relation.

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

The yield strength is calculated to be equal to 2.058 MPa. The hardness parameters are presented in Table 2.

4 Conclusion

Mixed crystals of \((\text{NH}_4)_2\text{SbF}_5 - \text{K}_2\text{SbF}_5\) is grown by slow and controlled evaporation solvent technique. It crystallizes in the orthorhombic system with lattice parameters \( a = 6.5219 \) Å, \( b = 13.7689 \) Å, \( c = 6.2914\)Å and \( \alpha = \beta = \gamma = 90^\circ \). The microhardness study shows that hardness steadily increases, then decreases for higher loads. The work hardening coefficient \( n \) is found to be less than 2, this is in good agreement with the mixed crystals of \( \text{NH}_4\text{H}_2\text{PO}_4 - \text{K}_2\text{H}_2\text{PO}_4 \) (Ref.16).

References

16 Mott B W, Micro indentation hardness testing (1956).