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# Growth and Characterization of $MgF_2$ Added $(NH_4)_2SbF_5$ Single Crystals

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**Abstract :** Single crystals of pure and $MgF_2$ added Di-Ammonium Penta Fluoro Antimonates , an electro optic crystal has been grown by slow evaporation technique. The grown crystals are subjected to single crystal X-ray diffraction, UV-Vis studies, Fourier Transform Infrared (FTIR) and Microhardness studies. Single crystal X-ray diffraction confirms the crystals belongs to Orthorhombic system.The FTIR spectrum analysis has confirmed the functional groups in the grown crystals. The optical behavior was examined by UV-Vis studies and found that the crystal is transparent in the entire visible region. Microhardness studies reveal the mechanical strength of the grown crystals. The addition of $MgF_2$ makes the surface of the crystal more softer than that of the pure $(NH_4)_2SbF_5$ crystal.

**Key Words :** Di Ammonium Penta Fluoro Antimonates, Super ionic crystals, EDAX, Micro Hardness, DC Conductivity.

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## 1. Introduction

Trivalent Antimony Fluoride complexes represent an extensive class of inorganic compounds, among which many substances exhibits unusual electro physical [1-3], Optical [4] and other

properties which stimulated their thorough investigation by different physico chemical methods [5]. It has also been reported that a number of fluorides have high ionic conductivity. These compounds are of considerable interest due to the assumption that the presence of liable cations $NH_4^+$ in a crystal lattice, which is likely to lead to higher values of conductivity than in the cations of heavy alkali metals[6]. The ionic conduction of several Ammonium fluoro antimonates are reported earlier [7-9]. Some of the Ammonium fluoro antimonates such as $(NH_4)_2SbF_5$ and $(NH_4)_3Sb_4F_{15}$ are classified as super ionic conductors [1,10]. The specific conductivity of $(NH_4)_2SbF_5$ is in the order of $10^{-2}$ S /m [11]The antimony fluro complexes are the promising compounds for producing different purpose materials which include Piezoelectric [12-13] and biologically active compounds [14]. The growth, dielectric, and microhardness studies of sodium and ammonium are reported earlier. [15-18]. Motivated by this, pure and $MgF_2$ added $(NH_4)_2SbF_5$ crystals have been crystallized and characterized in the present work and the results are reported.

## 2. Experimental Studies

Crystals of pure and magnesium fluoride added $(NH_4)_2SbF_5$ are grown by solution growth employing slow evaporation technique at room temperature. Appropriate proportions of Ammonium fluoride ($NH_4F$), Antimony tri oxide ($Sb_2O_3$) , and Hydrofluoric acid (HF)are mixed together to prepare the solution. The proposed chemical reaction is

$$2NH_4F + 0.5\ Sb_2O_3 + 3HF \rightarrow (NH_4)_2SbF_5$$

The homogenous saturated solution was kept in PVC containers for slow evaporation. For the growth of doped crystals 2 mole % of Magnesium Fluoride ($MgF_2$) was added to the above said solution. Single crystals with good transparency are obtained in a period of one month and are shown in Figure 1.

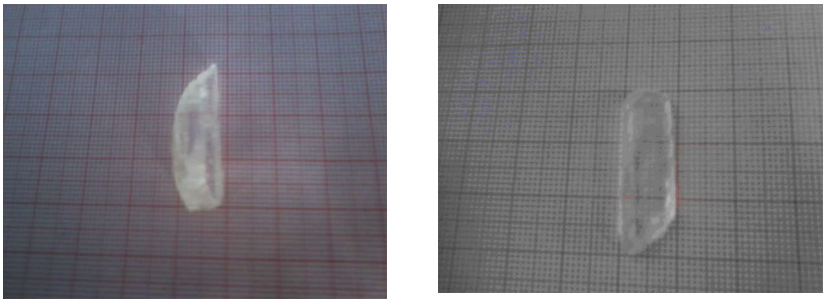

Figure 1. Photograph of as grown pure and $MgF_2$ added $(NH_4)_2SbF_5$ single crystals.

## 3. Results and Discussions

### 3.1 Single Crystal X-ray Diffraction Analysis

Single crystal X-ray diffraction studies has been carried out to confirm the crystallinity and to find the lattice parameters of the grown crystals. Single crystal of pure and $MgF_2$ doped $(NH_4)_2SbF_5$ were subjected to single crystal x-ray diffraction studies using BRUKER NONIUS CAD4 diffractometer to obtain the unit cell parameters. The obtained results shows that the lattice parameters for pure $(NH_4)_2SbF_5$ crystals are a = 6 .50 A°, b = 14.21 A°, c = 6.8 A°, $\alpha = \beta = \gamma = 90°$ and Volume = 628 $A^3$ °. and for $MgF_2$ added $(NH_4)_2SbF_5$ crystals a = 6.48 A°, b = 14.13 A°, c = 6.74 A°, $\alpha = \beta = \gamma = 90°$ and Volume = 618 $A^3$ °. The results confirm that the $MgF_2$ doped $(NH_4)_2SbF_5$ crystals crystallizes in the same orthogonal structure as that of pure $(NH_4)_2SbF_5$ .The incorporation of $MgF_2$ into the lattice of the crystal has resulted in changing the lattice parametesr of doped $(NH_4)_2SbF_5$ without changing its basic structure.

### 3.2Fourier Transform Infrared Analysis

Infrared spectroscopy is effectively used to determine the functional groups present in the crystals. The FTIR spectrum was recorded using Bruker IFS spectrometer. Figure 2a.shows the IR spectra of pure and $MgF_2$ added $(NH_4)_2SbF_5$ crystals in the range 400 - 4000 $cm^{-1}$ . The broad band lying at 3118 $cm^{-1}$ is due to the NH stretching of Ammonium. Strong absorption band at 1401 $cm^{-1}$ in the spectra is due to O H stretching vibration. Absorption peak at 566.45 $cm^{-1}$ is due to symmetric $NH_2$ bending vibrations. The peak at 1109 $cm^{-1}$ is due to the $NH_2$ rocking vibrations. The sharp peak at 457.99 $cm^{-1}$ is due to the Sb -F vibrations . The FTIR spectrum of $MgF_2$ doped $(NH_4)_2SbF_5$ is shown in Figure 2b. The spectrum is similar to that of pure $(NH_4)_2SbF_5$, but there is shift in the peak values suggesting the wide range of interactions for the groupings. The addition of the peaks at 3725.38, 3501.53, 2466.61, 1224.96, 906.13 $cm^{1}$ in the doped samples were observed when compared to the pure $(NH_4)_2SbF_5$.

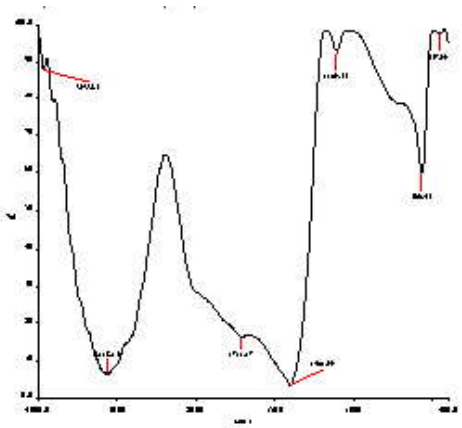

Figure 2a.FTIR spectra of pure $(NH_4)_2SbF_5$ Single crystals

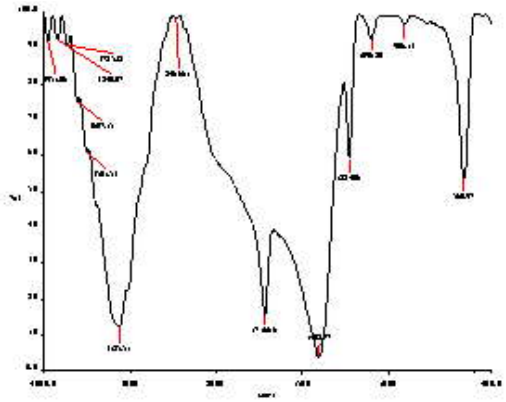

Figure 2b. FTIR spectra of $MgF_2$ doped $(NH_4)_2SbF_5$ single crystals

## 3.3 Energy Dispersive Analysis

Energy dispersive x-ray analysis is a useful tool for elemental analysis of the grown crystals. EDAX analysis was carried out using JEOL-6360 Scanning Electron Microscope. The recorded spectrum is shown in Figure 3. The presence of $Mg^{2+}$ in the grown crystal was confirmed from EDAX spectrum.

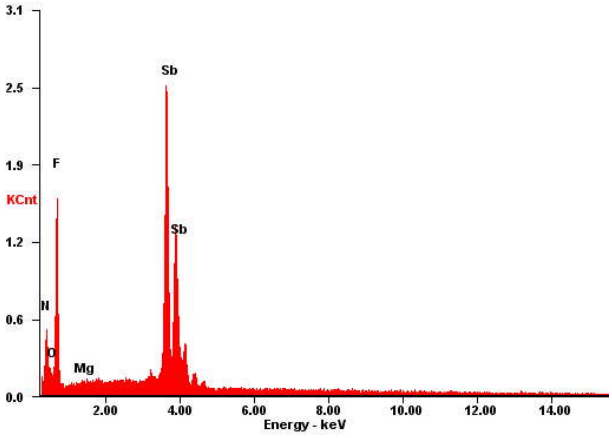


Figure 3. EDAX spectra for $MgF_2$ doped $(NH_4)_2SbF_5$ single crystals

## 3.4 UV-Vis Spectral Analysis

The UV Visible study of the grown crystals was carried out by Shimadzu UV 1600 Spectrometer. The UV-Vis Spectrum gives limited information about the structure of the molecule because

the absorption of UV and Visible light involves promotion of the electron in σ and π orbital from the ground state of higher energy states [19].

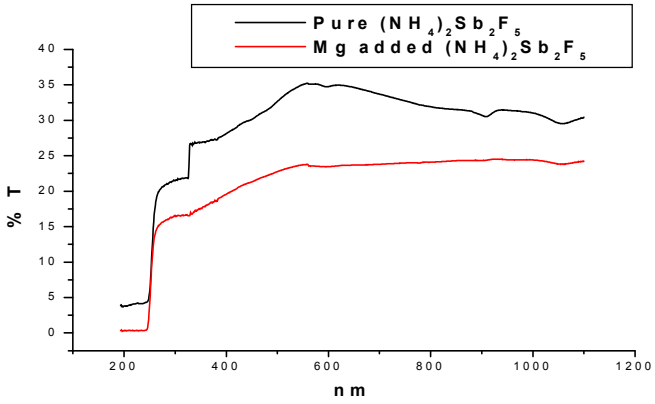


Figure 4. Transmission spectra of pure and Sr added $(NH_4)_2SbF_5$ crystals

Figure 4 shows the transmission curve, in which the lower cut off wavelength is obtained at 250 nm for pure and 260 nm for doped crystals. It is inferred from the spectra that both pure and doped $(NH_4)_2SbF_5$ crystals have large transmission window in the entire visible region. The wide transmission in the entire visible region enables it to be a potential candidate for opto electronics applications.

## 3.5 Microhardness studies

Hardness is defined as the resistance offered by a material to external mechanical action endeavoring to scratch, indent or any other way affects its structure. Microhardness measurements were done using Vicker's Hardness Indenter using Leitz Weitzier Hardness Tester. The indentation time was fixed as 10s.Vicker's Hardness Number (Hv) is calculated using the relation

$$H v = 1.8554 \ P \ / \ d^2 \quad Kg\ mm^{-2}$$

Where P is the load applied and d is the diagonal length of the indented impressions. A plot between the load p and hardness number Hv is shown inFigure 5, which indicates that the hardness number increases with increasing load. On further increasing the load beyond 50 gm, the Hv value starts decrease , indicating the starting of fracture on the surface of the crystal. Hardness number is found to be increasing with the doping concentration of $Mg^{2+}$ in the lattice of the crystal.

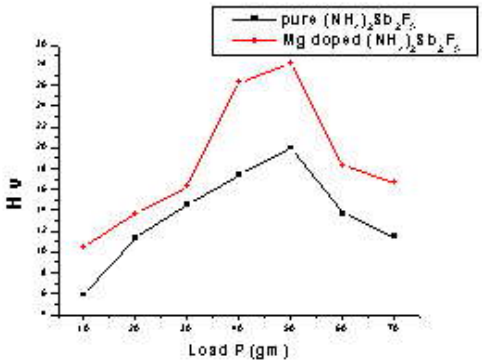


Figure 5. load Vs Hv for pure and Mg added $(NH_4)_2SbF_5$ crystals

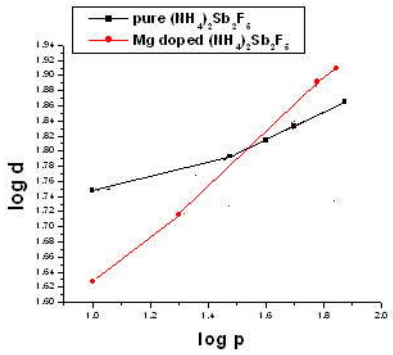


Figure 6. log P Vs log d for pure and Mg added $(NH_4)_2SbF_5$ crystals

The Figure 6. shows the plot between log P and log d for both the crystals. The slope of the straight line gives the work hardening coefficient (n). The hardness coefficient for pure $(NH_4)_2SbF_5$ is 1.344 and that of $MgF_2$ added crystal is found to be 3.419. According to Onitsch 's law [20], the pure $(NH_4)_2SbF_5$ is a hard crystal and the addition of $MgF_2$ makes the crystal surface more softer than that of the pure crystal.

## 3.6 DC Conductivity studies

The DC Conductivity of pure and $MgF_2$ added $(NH_4)_2SbF_5$ crystals are calculated and the values of DC Conductivity against temperature are plotted in Figure 7. It is observed that for both the crystals , the conductivity increases with increase in temperature. As the defect concentration increases with increase in temperature, the conductivity also increases. The conductivity values of $Mg^{2+}$ added crystals are lower than that of the pure $(NH_4)_2SbF_5$ crystals.

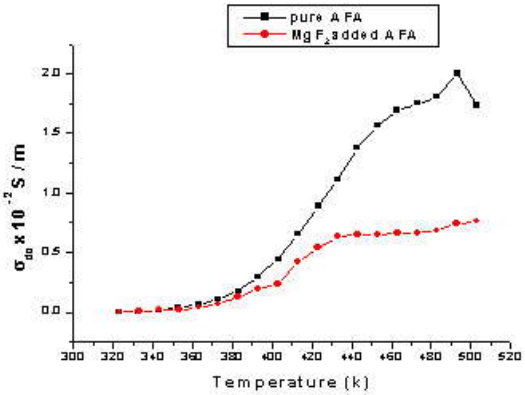


Figure 7 .Variation of DC conductivity (x $10^2$ S/ m) with temperature for pure and Mg added $(NH_4)_2SbF_5$ single crystals

The lower value of conductivity in $Mg^{2+}$ is due to the reduction of dislocations and defects on the crystal due to the presence of $Mg^{2+}$ ions in the crystal.

## 4. Conclusion

Pure and $MgF_2$ added Di- Ammonium Penta Fluoro Antimonates single crystals were grown by slow evaporation method at room temperature. X-ray diffraction studies confirm that both the crystals belong to orthorhombic system. The transmission spectra are determined by UV-Vis studies. FTIR spectra is discussed to confirm the various functional groups in the grown crystals. Microhardness studies shows that the hardness increases with increase in load and the addition of $MgF_2$ makes the crystal softer than pure crystal. DC conductivity studies reveals that the conductivity increases with increase in temperature and the conductivity is lower for the $Mg^{2+}$ added crystals due to the absence of defects.

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