

Growth, Spectral, Optical, Thermal, Mechanical and Dielectric properties of CdCl₂ added (Na)₂ SbF₅ Single Crystals

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Abstract

Single crystals of pure and CdCl₂ added sodium penta fluoro antimonates, an electro optical crystal has been grown by slow evaporation technique. The grown crystals are subjected to single crystal X-ray diffraction, Fourier Transform Infrared (FTIR) studies, EDAX, UV-Vis studies and microhardness studies. Single crystal X-ray diffraction confirms that the crystal belongs to Orthorhombic system. The FTIR spectrum analysis has confirmed the functional groups in the grown crystal. The optical behaviour was examined by UV-Vis studies and found that the crystal is transparent in the entire visible region. Microhardness studies reveals the mechanical strength of the grown Crystal. The decomposition point of the sample was identified by TG/DTA studies. The samples was measured and Dielectric properties were measured at different frequencies and temperature.

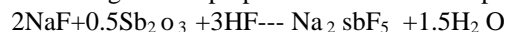
Keywords: Inorganic compounds; doping; Single Crystal; growth; XRD; Microhardness.

1. INTRODUCTION

Tivalent Antimony Fluoride complexes represent an extensive class of inorganic compounds, among which many substances exhibit unusual electro optical, physical and other properties [1,2]. It has also been reported that a number of Fluoride Compounds have high ionic conductivity [3,4]. These compounds are of considerable interest due to the assumption that the presence of liable cations Na²⁺ in a crystal lattice, which is likely to higher values of conductivity than in cations of heavy alkali metals [5]. The ionic conduction of some sodium fluoro antimonate such as Na₂ SbF₅ and K₂ SbF₅ are classified as super ionic conductors [6,7]. The growth, dielectric and microhardness studies of Sodium and Ammonium [8,9] are reported earlier. Pure and CdCl₂ added Na₂ SbF₅ Crystals have been crystallized and characterized and the results are reported.

2. EXPERIMENTAL STUDIES

Crystals of pure and Cadmium Chloride added Na₂ SbF₅ have been grown by slow evaporation technique at room temperature. Appropriate proportion of Sodium Fluoride (NaF) Antimony trioxide (Sb₂O₃), and Hydrofluoric acid (HF) are mixed together to prepare the solution. The proposed chemical reaction is



The homogeneous saturated solution was kept in PVC containers for slow evaporation. For the growth of doped crystals 3mole% of Cadmium Chloride (CdCl₂) was added to the above said solution. Single Crystals with good transparency are obtained in the period of one month.

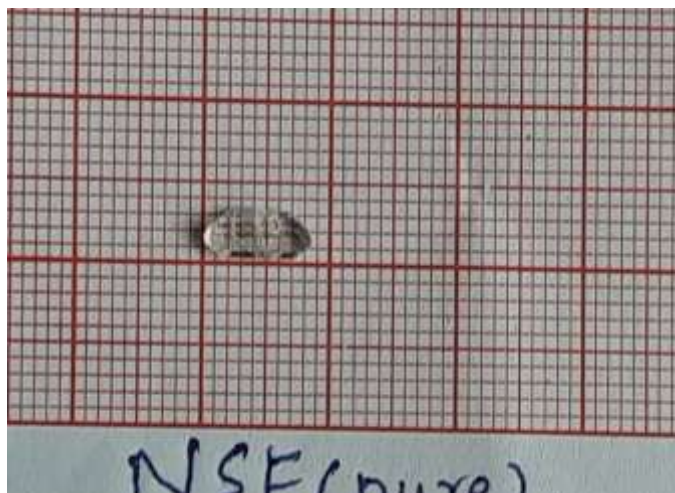


Figure:(1a). NSF (pure) Crystal

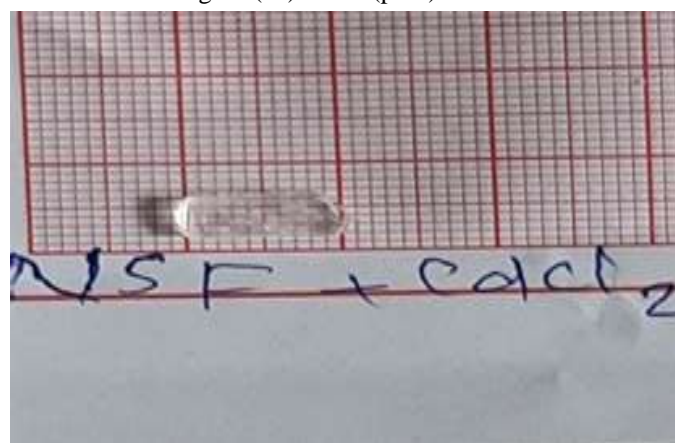


Figure :(1b). NSF+Cdcl2 added crystal

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. The lattice parameters for pure Na₂ sbF₅ crystals are a= 5.453Å°, b=8.006Å°, c=11.133Å°, α=β=γ=90° , and Volume=486.1Å⁰and for Cdcl2 added Na₂ sbF₅ crystals are a=5.4248Å°,b=8.045Å°,c=11.173Å°.α=β=γ=90°, and Volume=487.6Å⁰. The findings show that it crystallises in the same orthorhombic .

3.2.Fourier Transform Infrared Analysis

Infrared spectroscopy is effectively used to determine the functional groups present in the crystals. The FTIR spectrum was recorded using Perkin Elmer Spectrometer using KBr technique. figure 2a and 2b shows the IR Spectra of pure and Cdcl2 added Na₂ sbF₅ crystals in the range from 4000cm⁻¹ - 400cm⁻¹. Strong absorption band at 3780 cm⁻¹ and 3402 cm⁻¹ spectra are due to O-H stretching vibration. The peak occur at 1608 cm⁻¹ Corresponds to the bending of O-H bond. The sharp peak at 1355 ,1283 ,1112 cm⁻¹ may be due to the symmetric stretching of Sb-O bond. The very sharp peak at 546 cm⁻¹ confirm the presence of Sb-F stretching vibration. The spectrum is similar to that of pure Na₂ sbF₅ but there is assume that the shift in the peak values suggesting 3562 cm⁻¹ and 3402cm⁻¹ wide in range of interactions for the groupings. The addition of the peaks at 1377 cm⁻¹ and 1256 cm⁻¹ the doped samples were observed when compared to the pure Na₂ sbF₅ .

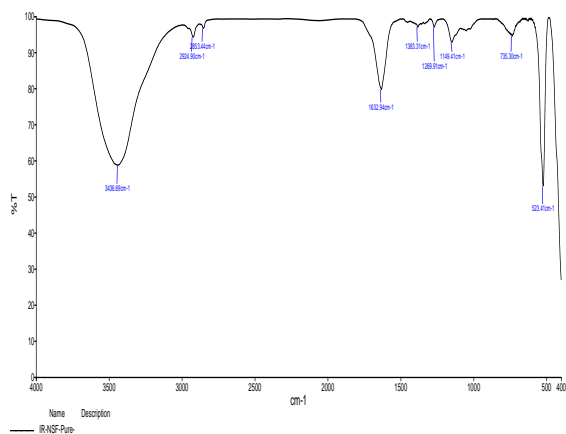


Figure2a: FTIR Spectrum of pure Na₂SbF₅

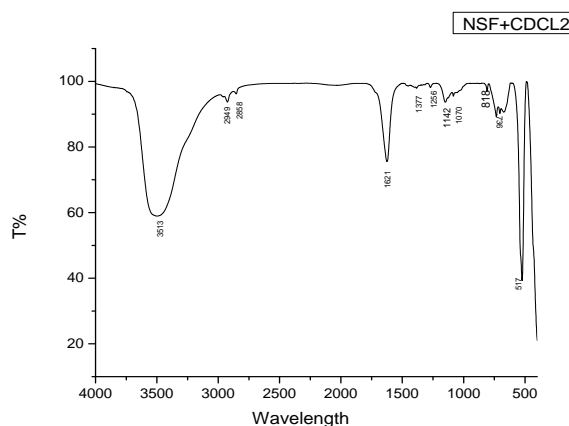


Figure 2b:FTIR Spectrum of Na₂ SbF₅ doped with Cadmium Chloride

3.3 Energy Dispersive Analysis

Energy dispersive X-ray analysis is a useful tool for elemental analysis of the grown Crystals.EDS analysis were carried out using Scanning Electron microscope.The recorded spectrum is shown in figure 3.The presence of Sb,Na,Cd,F,cl₂ in the are confirmed from EDX spectrum grown crystals

Element	Line Type	Wt%	Atomic %
F	K series	34.32	60.39
Na	K series	17.38	25.27
Cl	K series	1.54	1.45
Cd	L series	1.88	0.56
Sb	L series	44.88	12.32
Total:		100	100

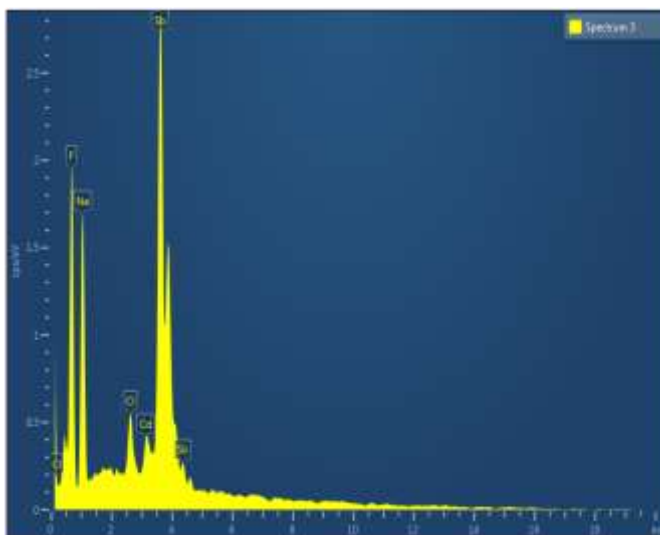


Figure 3: EDX Spectrum for CdCl₂ doped Na₂SbF₅ single crystal

3.4 UV-V is spectral Analysis

The UV visible study of the grown crystals was carried out by Perkin Elmer Lambda 35 UV-Vis spectrometer in the Wavelength range of 100-1200nm. UV-Vis spectrum gives limited information about the structure of the molecule because the the absorption of UV and visible light involves promotion of the electron in sigma and pi orbital from the ground state of higher energy states.

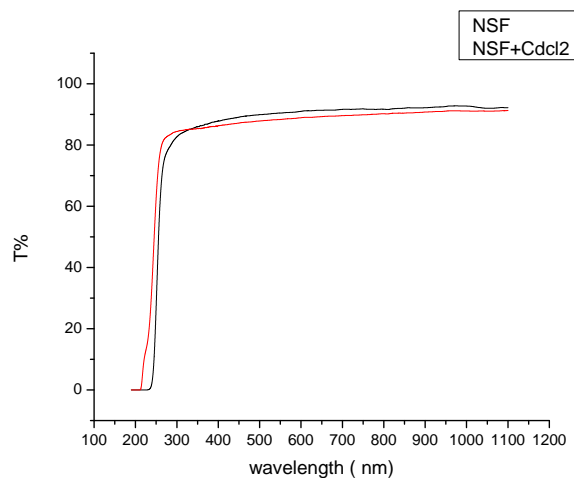


Figure 4 shows the transmission curve in which the lower cut off wavelength is obtained at 250 nm for pure and 260 nm for doped crystals. It is Inferred from the spectra that both pure and doped Na₂SbF₅ crystals have large transmission window in the entire visible region.

3.5. THERMAL ANALYSIS

TG/DTA thermal curves for sodium penta fluoro antimonate crystal doped with CdCl₂ crystal were recorded using TG/DTA thermal analysis in the temperature range 0-7000C and it is shown in the fig.5. It is clear from the TG that the sample is thermally stable upto 2960 c. The sample undergoes endothermic transition at 3460C and it corresponds to melting point of the sample. At this temperature, there is a slight weight loss of about 5 weight % and it may be due to the absorbed water molecules. It may be noted here that the endothermic transition at 2960 C is not decomposition point because there is no heavy weight loss of the sample. The sharp endothermic peak shows the good crystalline perfection of the sample. When the temperature is increased above the melting point, there is a gradual and significant weight loss (75%) occurs in the range of temperature 270-6500 C and this is due to the decomposition and the release of gaseous particles such as fluorine and other ions from the lattice of the crystal. The DTA curve also shows the same kind of thermal transition in the sample.

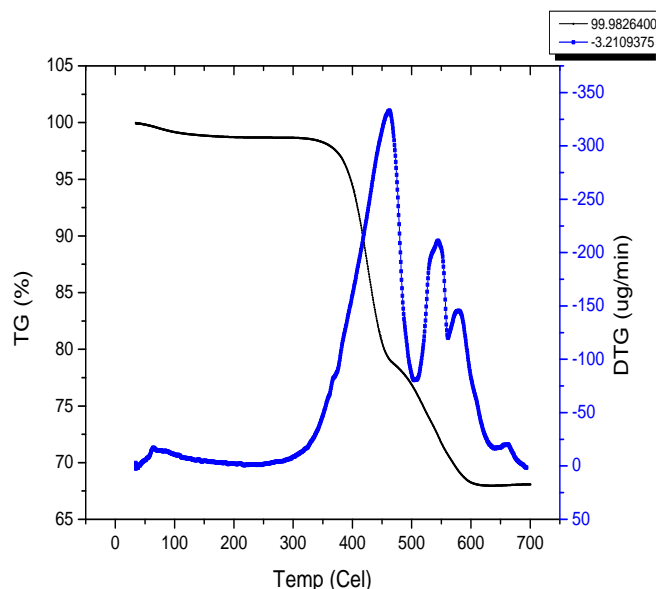


Figure:5 TG/DTA thermal curves for sodium penta fluoroantimonite crystal added CdCl₂ crystal

3.6. 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 (16) were done using Vickers hardness indenter using Leitzweitzier Hardness tester . The indentation time was fixed at 10s. Vickers hardness number (Hv) is calculated using the relation $Hv = 1.8554 P/d^2$ Kg/mm. 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 in figure 6a. which indicates that the hardness number increases with increasing the load exhibits reverse indentation size effect(RISE). Hardness number is found to be increasing with the doped concentration of CdCl₂ in the lattice of the crystal. Figure 6b. indicates that the log p increases also diagonal value is also increasese

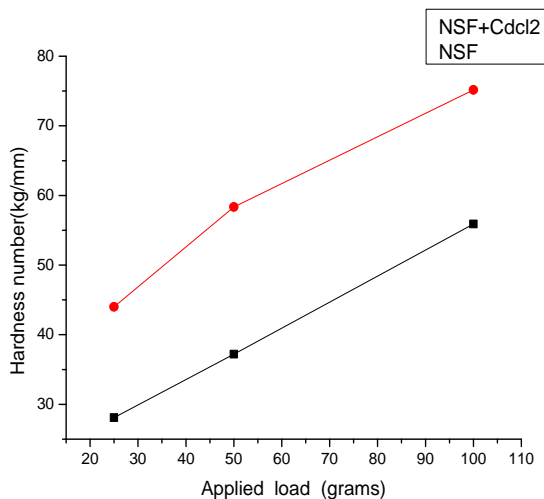


Fig :6a. Variation of hardness number with applied load

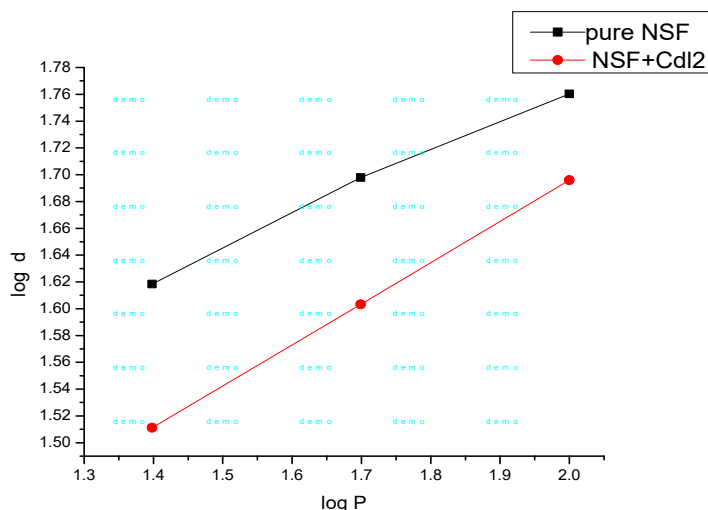


Fig.:6b. Variation of log P with log d and Cdcl₂ added Na₂ sbF₅ Crystal

3.7. DIELECTRIC STUDIES

Every material has a unique set of electrical characteristics that are dependent on its dielectric or insulation properties. Accurate measurements of these properties can provide valuable information to ensure an intended application or maintain a proper manufacturing process. The electrical parameters such as dielectric constant, dielectric loss, ac conductivity and activation energy etc were calculated at different temperature and at different frequencies study of dielectric response in crystals is one of the basic electrical properties which give the information also the electric field distribution within the solid. Crystals with high transparency and defect free are selected and used for the dielectric measurements. The extended portion of the crystal is removed completely and the opposite faces are polished and coated with good quality graphite to obtain a good ohmic contact. The dielectric constant (ϵ_r) is calculated using the relation $\epsilon_r = \frac{Cd}{\epsilon_0 A}$ where C is the capacitance, d is the thickness of the sample, A is the area of the electrode contact and (ϵ_0) is the absolute permittivity of the free space. The dielectric loss of the sample was directly measured using the LCR meter for different frequencies at 500C and 1000C and the results are shown in figures 7a and 7b. shows the variation of dielectric constant and dielectric loss factor with temperature at different frequencies of 100HZ, 1000HZ, 10KHZ, 100KHZ, and 1MHZ. It is seen from the plots that the dielectric constant is relatively high values of dielectric constant is relatively high in lower frequency region and then decreases with the applied frequency. The high values of dielectric at low frequencies may be due to the presence of combinations of all four polarizations namely space charge, orientational, electronic and ionic polarizations. The low value of dielectric constant at high frequencies occurs due to the loss of these polarizations at low temperature. Increase of dielectric constant with temperature may be due to the thermal excitation of and about their lattice point and blocking of charge carriers at the electrodes [13,14].

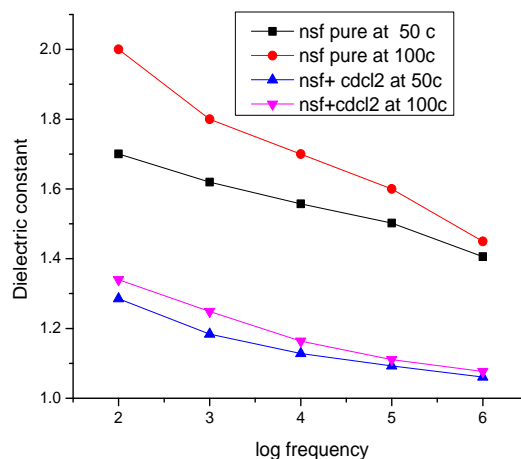


Figure:7a Variation of Dielectric constant with frequency For pure and Cdcl₂ added NSF crystal

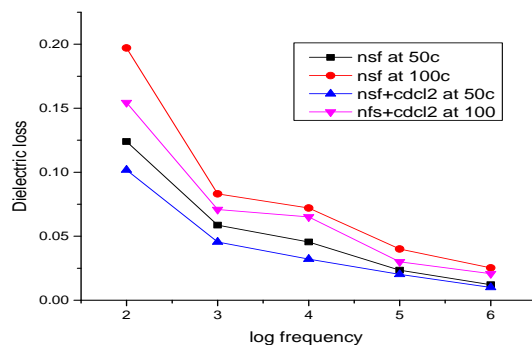


Figure:7b Variation of Dielectric loss with frequency for pure and Cdcl₂ added NSF crystal

CONCLUSION

Pure and CdCl₂ added Na₂SbF₅ single crystals were grown by slow evaporation method using deionized water as solvent at room temperature. Single crystal X-ray diffraction studies confirm that both crystals belong to Orthorhombic system. The transmission spectra are determined by UV-Vis studies. FTIR Spectra discussed to confirm the various functional groups in the grown crystals. EDAX Studies represent the presence of CdCl₂ in the grown crystals. Microhardness studies show that the hardness increases with increase in load. The thermal stability of CdCl₂ doped NSF crystal is found to be at 2960 °C. Dielectric constant and dielectric loss factor of the samples have been measured at different frequencies and temperatures and these values are observed to be decreasing with increase of frequency and increasing with increase of temperature.

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