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Structural, Optical, Mechanical and Electrial Studies of Copper Chloride Doped Sodium Fluoro Antimonate Crystals

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Abstract: Single crystals of copper chloride doped sodium fluoro antimonate were grown by solution method with slow evaporation technique. The solubility of the samples in water has been measured at different temperatures. The mechanical properties such as hardness, yield strength and stiffness constant of pure and copper chloride doped sodium fluoro antimonate crystals have been determined at different applied loads. EDAX spectrum has been recorded to identify the elements presents in the sample. The etch patterns of the copper chloride doped sample have been photographed and analyzed. By XRD studies, it is understood that both undoped sodium fluoro antimonate (SFA) and copper chloride doped sodium fluoro antimonate crystals crystallize in monoclinic structure. The thermal stability of the samples is observed to be more than 200 ^{o}C. The functional groups of the sample have been identified by FTIR studies. Also the samples have been subjected to dielectric studies to understand electrical processes that are taking place in the samples.

1. Introduction

Antimony fluoride complexes are the inorganic compounds which exhibit interesting superionic, electrical and optical properties and it has been reported that a number of these complexes have high ionic conductivity [1-3]. These complexes may produce different purpose materials which include piezoelectric, ferroelectric and biologically active materials [4-6]. Ammonium penta fluoro diantimonate has shown superionic conductivity and it is reported that the phase transitions are at 257 K and 398 K and these successive phase transitions are due to the reorientations of NH_4^+ and $[SbF_5]^{2-}$ groups [7]. The potassium fluoro antimonates such as $KSbF_4$ and $K_3Sb_4F_{15}$ are also observed to be showing high ionic conductivity [8]. Growth and microhardness studies of $NaSbF_4$, $NaSbF_5$, $NaSb_2F_7$ and $Na_3Sb_2F_9$ have been reported in the literature and microhardness and correction to the diagonal length of the indentation impression of $Na_2Sb_2F_8$ crystals have been reported by Benet Charles *et al*. [9,10]. Many attempts have been made to find new ultraviolet (UV) and deep ultraviolet (DUV) nonlinear optical crystals. Compared with oxide crystals, fluoride complex crystals have larger band gap, therefore they are suitable for DUV harmonic generation. However, they have small second harmonic coefficients, which is unfavorable for obtaining high power output at the harmonic frequencies [11]. Some of the antimony fluoride compounds can be prepared and studied are $MSbF_4$, M_2SbF_5, MSb_2F_7, MSb_3F_{10}, MSb_4F_{13}, $M_2Sb_3F_{11}$ and $M_3Sb_4F_{15}$ (where M = Na, K, NH_4, Tl, Cs, Rb) [12]. Single crystals of undoped sodium fluoro antimonate (Na_3Sb4F_{15}) were recently grown and various studies have been carried out by Kumuthini *et al.*[13]. In this work, crystals of undoped and copper chloride doped Na_3Sb4F_{15} were grown by solution method and the grown crystals were subjected to different studies and the results are discussed.

2. Experimental

2.1 Crystal growth

Sodium fluoride, antimony trioxide, hydrofluoric acid and copper chloride were used as the starting materials for the preparation of pure and copper chloride doped $Na_3Sb_4F_{15}$ samples. The saturated aqueous solutions of pure and 3 mole% of copper chloride added samples were prepared and taken in the growth vessels and they were kept in a constant temperature bath at 305 K for the growth crystals. The crystals were grown by slow evaporation and the seed immersion technique was followed to obtain the big-sized crystals. The seed crystals were prepared by spontaneous nucleation. Single crystals of the samples were harvested after a growth period of 35 days and they are shown in the figure 1.

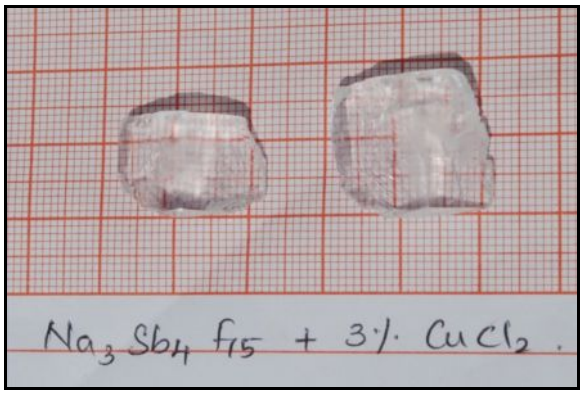

Fig.1: Harvested crystals of 3 mole % of copper chloride doped sodium fluoro antimonate

2.2 Instrumentation

TG/DTA thermal curves of the samples were recorded using a Perkin Elmer thermal analyzer in nitrogen atmosphere at a heating range of 5 ^oC to 700 ^oC. Single crystal XRD data of the samples were obtained to find the lattice dimensions using ENRAF NIUS CAD-4 X-ray diffractometer with MoK_α (λ=0.71069 Å) radiation. The microhardness studies for the grown crystals were carried out using a SHIMADZU HMV-2000 microhardness tester fitted with a Vickers diamond pyramid intender. Dielectric studies of the sample have been carried out at different frequencies and temperatures using a HIOKI 3532 LCR Hitester with a conventional two terminal sample holder. Etching studies of the grown crystal were performed using a metallurgical-optical microscope with polarizing facility with the halogen lamp as the source. Energy Dispersive X-Ray Spectroscopy (EDAX) is a chemical microanalysis technique, which detects X-rays emitted from the sample during bombardment by an electron beam to find the elemental composition and EDAX spectrum was recorded using a SEM- EDAX detector (Model: Oxford Instruments, INCA Penta FETx3). Fourier Transform Infrared (FTIR) technique is most useful for identifying functional groups of compounds. It can be applied for the analysis of solids, liquids and gases and it is based on the principle of Michelson Interferometer with a sensitive infrared detector and a digital minicomputer and which provides higher resolution and higher accuracy. FTIR spectra of the grown samples were recorded in KBr matrix using Perkin- Elmer RXI spectrometer in the wave number range 4000 cm^{-1} to 400 cm^{-1}.

3. Results and Discussion

3.1 Measurement of solubility

Thermodynamically, solubility means that the chemical potential of the pure solid is equal to the chemical potential of the same solute in the saturated solution. The growth rate of a crystal depends on its solubility and temperature. The solubility data of a material governs the amount of material which is available for the growth and hence defines the total size limit. Solvent and solubility factor define super saturation which is the driving force for the rate of crystal growth. Hence for a material to grow as a crystal, determination of its solubility in a particular solvent is an essential criterion. Solubility of the grown crystals was measured by gravimetrical method [13] in the temperature range 30-60 °C. The measured values of solubility are presented

in the figure 2. The results indicate that the solubility increases with increase of temperature for pure and copper chloride doped sodium fluoro antimonate (Na_3 Sb4 F_{15}) crystals and hence the samples have positive temperature coefficient of solubility. Solubility values are found to be more for copper chloride doped sample and it is clear that the solvent is able to accommodate a marginally increased amount of solute for the saturation at the same temperature for copper chloride added sample. The increase in solubility for the copper chloride added sodium fluoro antimonate ($Na_3Sb_4F_{15}$) crystal may lead to change of thermodynamic parameters such as surface concentration of growth species and the surface energy and hence it may be responsible for the change in the growth rate and morphology of the doped crystals compared to undoped crystals.

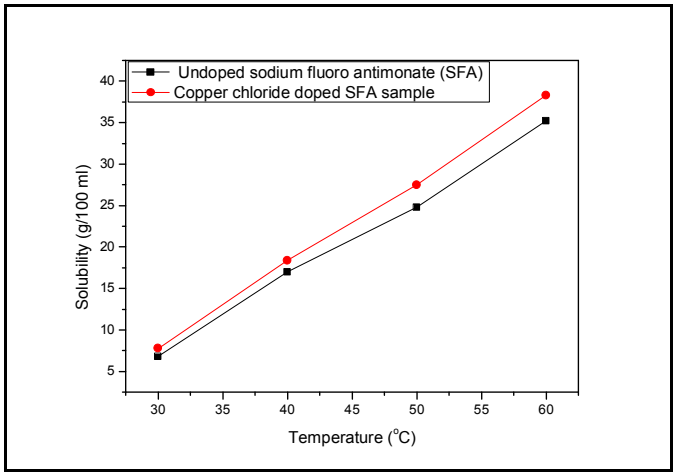

Fig.2: Solubility curves of pure and copper chloride doped $Na_3Sb_4F_{15}$ samples

3.2 XRD studies

Single crystal XRD data of pure and copper chloride doped sodium fluoro antimonate crystals were collected from a single crystal X-ray diffractometer with graphite monochormated MoK_a radiation and the obtained data are presented in the table 1. From the data, it is observed that the grown crystals crystallize in monoclinic system. The unit cell parameters of copper chloride doped sample are observed to be varying slightly compared to those of undoped sample. The changes in the lattice parameters are due to incorporation of dopant in the lattice of sodium fluoro antimonate crystal. The presence of dopants in the doped crystal may produce lattice strain which leads to change of unit cell parameters.

Table 1: Unit cell parameters for undoped and copper chloride doped sodium fluoro antimonate crystals

Sample	Unit cell parameters	Volume (Å)^3
Undoped sodium fluoro antimonate crystal (SFA)	a = 8.131(2) Å b = 5.494(1) Å c = 8.652(3) Å α = 90 °, β= 94.37(2)° γ=90°	385.41(2)
Sodium fluoro antimonate doped with 3 mole% of copper chloride	a = 8.208(13) Å b = 5.515(4) Å c = 8.736(9) Å α = 90 °, β=94.88(2) ° γ= 90°	394.03(6)

3.3 FTIR studies

FTIR studies involve the examination of stretching, bending, twisting and rotating vibrational modes of atoms in a molecule and hence to identify the functional groups of samples. The FT-IR spectrum of the sample were recorded using a Perkin-Elmer FT-IR spectrometer and it is shown in the figure 3. The broad vibrational

band observed around 3420 cm^{-1} is attributed to asymmetric OH stretching mode of adsorbed water molecule in the sample. The medium broad band noticed around1632 cm^{-1} is assigned to the bending vibration of water molecules. The assignments for peaks/bands are given in accordance with the data in the literature [14]. The FT–IR assignments for the absorption peaks/bands of the sample are provided in the table 2.

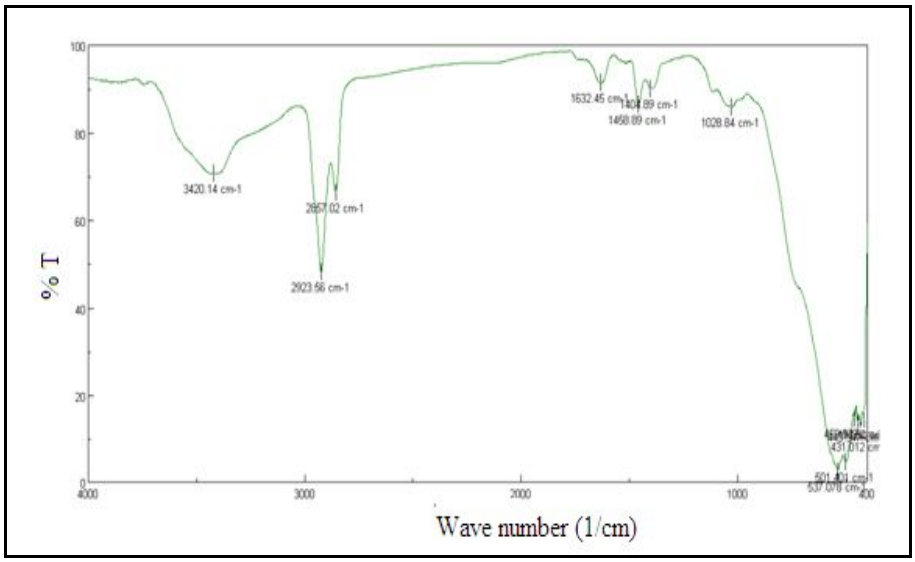

Fig.3: FTIR spectrum of copper chloride doped sodium fluoro antimonate crystal

Table 2: FTIR assignments for copper chloride doped sodium fluoro antimonite crystal

Wave number (cm^{-1})	**Assignments**
3420.14	O-H stretching mode of adsorbed water molecule
2923.56	Combination band
1632.45	OH bending mode
1028.84	Sb-F vibration
501.40	Sb-F bending

3.4. Hardness testing

Hardness testing is the simplest and the least expensive method for mechanical characterization of materials which is imperative for device fabrication. Hardness testing also provides information regarding other mechanical properties like tensile strength, yield strength and work hardening coefficient. Transparent crystals free from cracks were selected for microhardness measurements. Microhardness analyses were carried out using Shimadzu Vickers microhardness tester fitted with a diamond indenter attached to an incident light microscope. The well polished crystal was placed on the platform of the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. Microhardness number was determined using the relation $H_v = 1.8544\ P/d^2$. The variation of hardness number with the applied load for the samples is shown in the figure 4. The results show that hardness number increases gradually upto a certain load and then it decreases. The increasing part of the curve is due to the reverse indentation size effect and the decreasing part of the curve is due the direct indentation size effect. Yield strength of the material can be found out using the relation, yield strength (σ_y) = (H_v / 3) and the stiffness constant (C_{11}) for different loads was calculated the formula $C_{11} = H_v^{7/4}$ where H_v is the microhardness of the material [15] and the evaluated values are given in the table 3. From results, it is observed that yield strength and stiffness constant of samples show the same behavior as that of hardness number. Due to incorporation of copper chloride in the host sodium fluoro antimonate crystals, the mechanical properties such as hardness, yield strength and stiffness constant are observed to be increased.

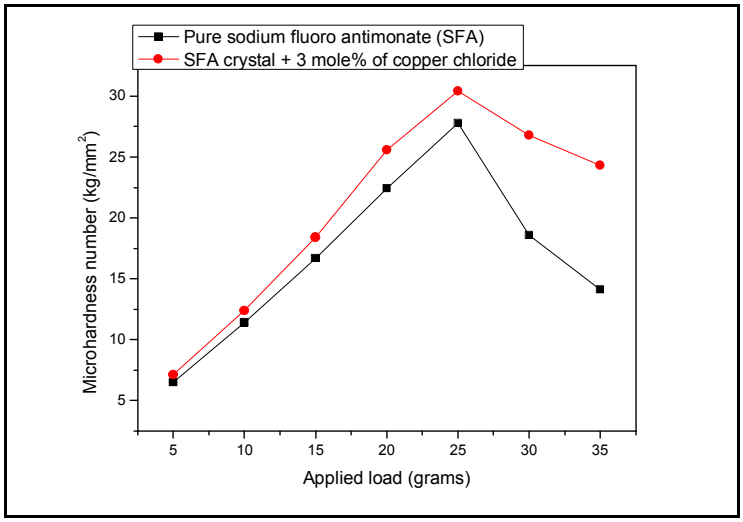

Fig.4: Variation of hardness number with applied load for pure and copper chloride doped sodium fluoro antimonate crystals

Table 3: Values of yield strength and stiffness constant for pure and copper chloride doped sodium fluoro antimonate crystals

Applied load (g)	Pure sodium fluoro antimonate(SFA)		SFA crystal + copper chloride	
	Yield strength x 10^6 (pascal)	Stiffness constant x 10^{14} (pascal)	Yield strength x 10^6 (pascal)	Stiffness constant x 10^{14} (pascal)
5	21.23	0.45	23.25	0.53
10	37.24	1.21	40.50	1.41
15	54.55	2.36	60.10	2.36
20	73.17	3.95	83.62	5
25	90.81	5.77	93.52	6.75
30	60.76	2.85	87.54	5.41
35	45.73	1.76	79.40	4.56

3.5 Measurement of dielectric properties

The dielectric constant, dielectric loss and electrical conductivity are the basic electrical properties of insulators. The dielectric constant is a physical measure of the electric polarizability of a material. The amount of power loss in a dielectric material when subjected to an electric field is known as dielectric loss. A low value of dielectric loss is desired for a dielectric material for device applications. Conductivity in a solid is due to the mobility of electrons or ion imperfections which are charged. 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 $\varepsilon_r = (C\ d)/(\varepsilon_0\ A)$ 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 permittivity of the free space. The dielectric loss of the sample was directly measured using the LCR meter. Figures 5 and 6 show the variations of dielectric constant and loss factor with frequency at different temperatures like 30 ^oC, 80 ^oC and 150 ^oC. It is seen from the plots that the dielectric constant is relatively high in the lower frequency region and then decreases with the applied frequency. The high values of dielectric constant at low frequencies may be due to the presence of combination of polarization effects. The low value of dielectric constant at high frequencies occurs due to the loss of the polarizations at low temperature. Increase of dielectric constant with temperatures may be due to the thermal excitation of atoms about their lattice point and blocking of charge carriers at the electrodes[16]. The obtained results indicate that the dielectric constant and loss factor are observed to be increased when sodium fluoro antimonate crystals are doped with copper chloride.

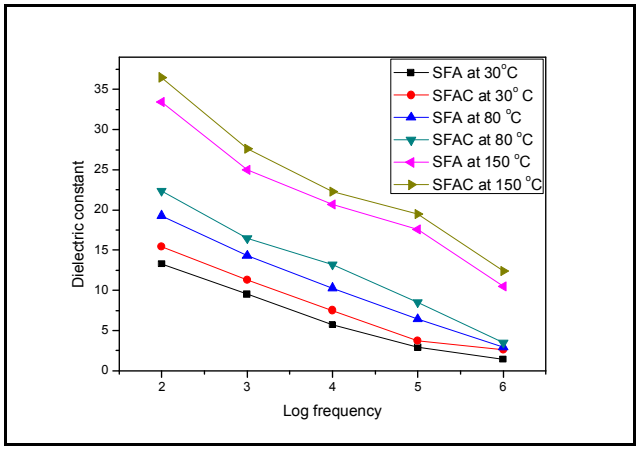

Fig.5: Variation of dielectric constant with frequency at different temperatures for pure sodium fluoro antimonate (SFA) and copper chloride doped sodium fluoro antimonate (SFAC) crystals

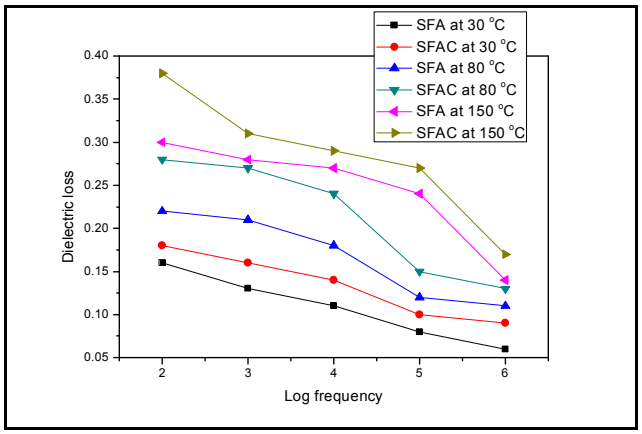

Fig.6: Variation of dielectric loss with frequency at different temperatures for pure sodium fluoro antimonate (SFA) and copper chloride doped sodium fluoro antimonate (SFAC) crystals

3.6 Etching studies

A single crystal of 3 mole% copper chloride doped sodium fluoro antimonate was etched in distilled water for 5 s and 15 s. Leitz optical microscope was used to study the etched faces. The etched samples were dried using a tissue paper and surface features were analyzed using the optical microscope. The sample is magnified by the objective which has magnification from 10 to 150 times. The magnified image is viewed through the eyepieces which have magnification from 8 times to 20 times. The etching patterns of the sample are presented in the figures 7 (a) and 7 (b). The results show that when the sample is etched for 5 seconds, it reveals the etch pits. But when the sample is etched with water for 15 seconds, the etch pits are reduced. The black dots in the etch patterns seem to be the presence of dopant material.

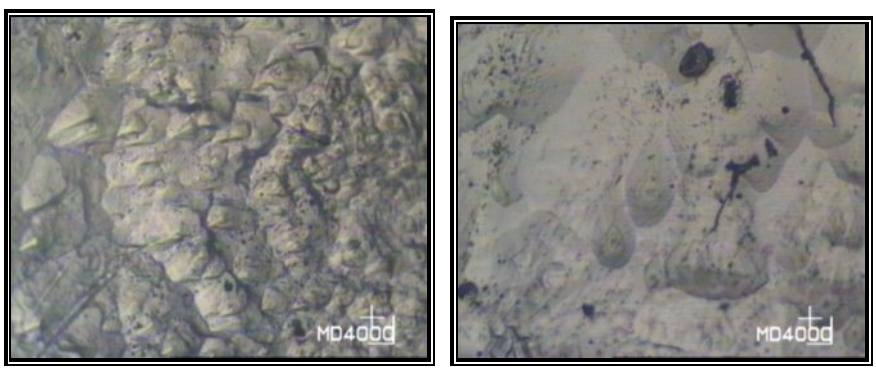

Fig.7(a) **Fig.7 (b)**

Fig.7: Etch patterns of the copper chloride doped SFA sample:(a) etched for 5 seconds and (b) etched for 15 seconds

3.7 EDAX studies

EDAX spectrum has been recorded to identify the elements present in the sample. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sample and spectrum are compared with known characteristic X-ray energy values to determine the presence of the elements in the sample [17]. The recorded EDAX spectrum of copper chloride doped SFA crystal is shown in the figure 8. The results show that the elements such as F, Na, Cl, Sb, Cu and O are present in the sample. The weight percentage of the elements in the sample is provided in the table 4.

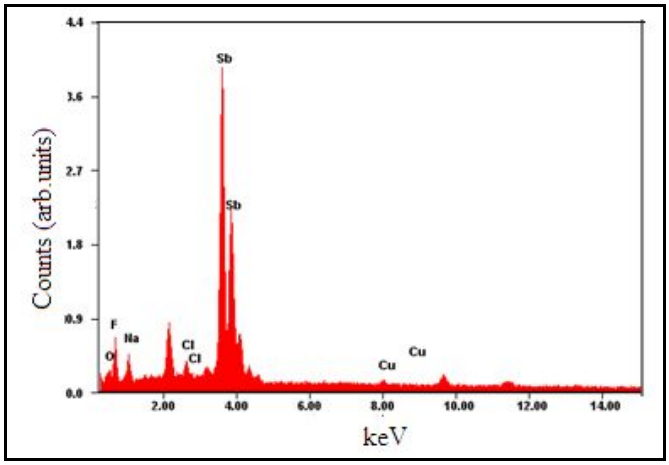

Fig. 8: EDAX spectrum of copper chloride doped SFA crystal

Table 4: Weight percentage of elements in copper chloride doped SFA crystal

Element	Weight (%)
Oxygen	2.34
Fluorine	19.69
Sodium	8.09
Chlorine	1.18
Antimony	67.35
Copper	1.35

3.8 TG/DTA studies

Thermal studies like TG/DTA were carried out to find out the weight change, energy change and various endothermic and exothermic transitions in the samples with the change of temperature. The recorded TG/DTA thermal curves for pure and copper chloride doped SFA crystals are presented in the figures 9 and 10. It is noticed from the results that the pure SFA sample is thermally stable upto 249 ^{o}C and copper chloride doped SFA crystal is thermally stable upto 255 ^{o}C. Since there are no weight loss below 200 ^{o}C, the samples have no water of crystallization. It is to be mentioned here that the OH stretching mode noticed in the FTIR spectrum may be due the adsorbed water molecules on the samples. The values of decomposition point/melting point of the pure and copper chloride doped SFA crystals are 259 ^{o}C and 264 ^{o}C respectively. Hence the decomposition/melting point of copper chloride doped SFA crystal is observed to be more than that of undoped SFA crystal. When the temperature is increased above the melting point, there is a gradual and significant weight loss (75%) occurs in the range of temperature 270-650^{o}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 crystals. The DTA curves also show the same kind of thermal transitions in the samples.

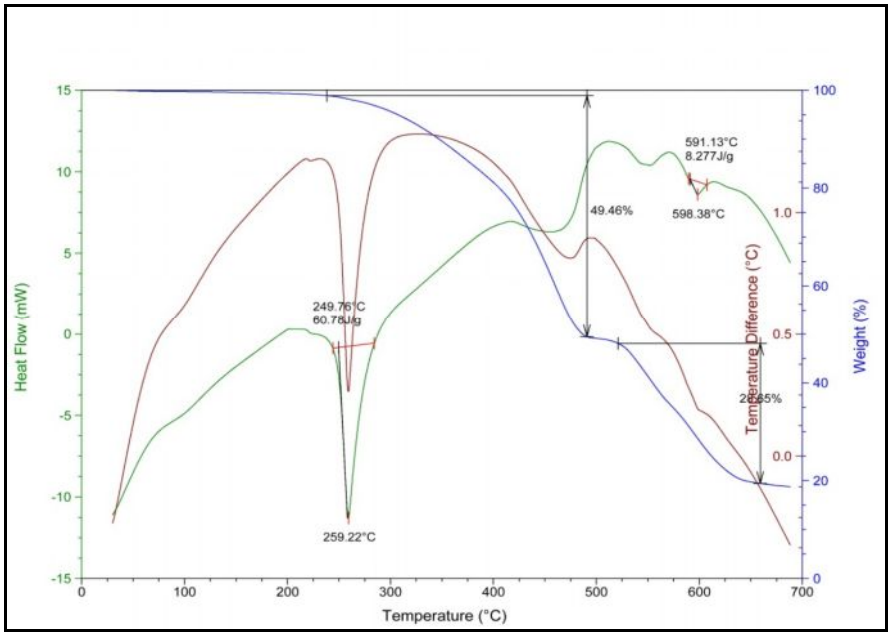

Fig.9: TG/DTA thermal curves for pure sodium fluoro antimonate crystal

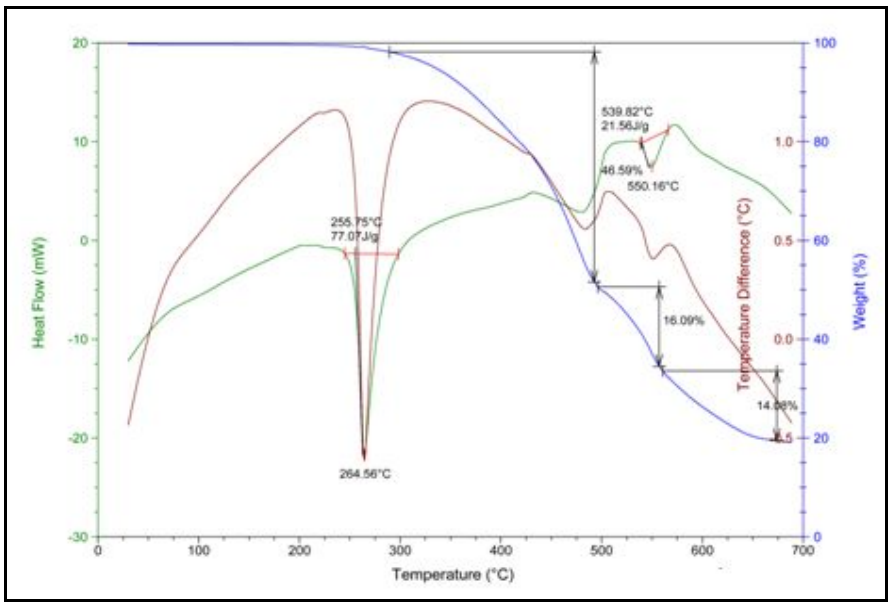

Fig.10: TG/DTA thermal curves for copper chloride doped sodium fluoro antimonite crystal

4.Conclusions

Single crystals of undoped sodium fluoro antimonate (SFA) and copper chloride doped sodium fluoro antimonate were grown by slow evaporation technique. The solubiltiy of the samples was determined at different temperatures and found that both the samples have postive temperature coefficient of solubility. The vibrational frequencies of the sample have been found by FTIR analysis. The results show that the thermal stability of copper chloride doped SFA crystal is more than that of undoped SFA crystal. Etch pit patterns have been analyzed. Dielectric constant and dielectric loss factor of the samples have been measured at different frequencies and temperatures and these values are observed to be decresing with increase of frequency and increasing with incresae of temperatrue. The unit cell parameters have been evaluated by the single crystal XRD methods. The elements present in the sample have been identified by EDAX method.

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