Growth And Studies Of Nickel Chloride Doped Sodium Fluoro Antimonate Crystals

R.Kumuthini, P.Selvarajan, S.Selvaraj

***Abstract*— Undoped and Nickel chloride doped sodium fluoro antimonite (SFA) crystals were grown by slow evaporation technique at room temperature. The solubility of the samples in water has been measured at different temperatures. The values of lattice parameters of the samples were obtained by X-ray diffraction (XRD) studies. The microhardness was measured for the samples at different applied loads. EDAX spectrum has been recorded for nickel chloride doped SFA crystal to identify the elements presents in the sample. The decomposition point of the sample was identified by TG/DTA studies. Laser damage threshold (LDT) value of the samples was measured and dielectric properties were measured at different frequencies and temperatures. Second harmonic generation (SHG) efficiency of the samples was measured using Kurtz powder technique.**

***Index Terms*— Inorganic crystal; doping; single crystal; solution growth; characterization; NLO; XRD**

I. INTRODUCTION

Crystals of antimony fluoride complexes such as ammonium fluoro antimonate, sodium fluoro antimonite have a lot of applications like ferroelectric, piezoelectric, NLO applications. It has been reported that a number of these complexes have high ionic conductivity [1-5]. 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 [6]. The potassium fluoro antimonate such as $KSbF_4$ and $K_3Sb_4F_{15}$ are also observed to be showing high ionic conductivity [7]. 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*. [8, 9]. 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 [10]. In this work, single crystals of undoped sodium fluoro antimonate ($Na_3Sb_4F_{15}$) and nickel chloride doped $Na_3Sb_4F_{15}$ were grown and the grown samples were subjected to various characterization studies.

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II. EXPERIMENTAL WORK

A. *Growth of sample crystals*

The AR grade chemicals such as sodium fluoride, antimony trioxide, hydrofluoric acid and nickel chloride were purchased commercially and used as the starting materials for the growth of undoped and nickel chloride doped $Na_3Sb_4F_{15}$ samples. Sodium fluoride, antimony trioxide, hydrofluoric acid were mixed in 2:3:12 molar ratio and using double distilled water as the solvent the saturated solution was prepared. The saturated aqueous solution was stirred well using a magnetic stirrer for 2 h and filtered using a Whatmann filter paper. Similarly, saturated solution of nickel chloride (2 mole%) added $Na_3Sb_4F_{15}$ sample was prepared. The prepared solutions were taken in the growth vessels and kept in a constant temperature bath. Due to slow evaporation, the sample crystals were grown in a period of 30 days.

B. *Characterization techniques*

Single crystal XRD data of the samples were obtained using ENRAF CAD-4 X-ray diffractometer with MoK_α (λ=0.71069 Å) radiation. The powder XRD pattern of the sample was recorded on a microprocessor controlled X-ray diffractometer (SIEFERT XRD 3000P) using nickel filtered CuK_α radiation. TG/DTA thermal curves of the sample were recorded using a Perkin Elmer thermal analyzer in nitrogen atmosphere at a heating range of 5^{o}C to 700^{o}C. 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 samples have been carried out at different frequencies and temperatures using a HIOKI 3532 LCR Hitester with a conventional two terminal sample holder. 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). To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystal using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm. Laser damage threshold (LDT) studies were carried out for the samples using a Nd:YAG laser with the wavelength of 1064 nm, 18 ns pulse width. The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200).

III. Results and Discussion

A. *Solubility measurement by gravimetrical method*

Solubility is a measure of the chemical potential of solid in the saturated solution. The growth rate of a crystal depends on its solubility and temperature. Solvent and solubility factor define supersaturation 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 [11] in the temperature range 30-60°C. The variation of solubility with the temperature for the grown crystals is presented in the figure 1. The results indicate that the solubility increases with increase of temperature for both the samples. It is observed that when nickel chloride is added as the dopant, the solubility increases which indicates that the solvent is able to accommodate an increased amount of solute for the saturation at the same temperature for pure sample compared to nickel chloride added sample.

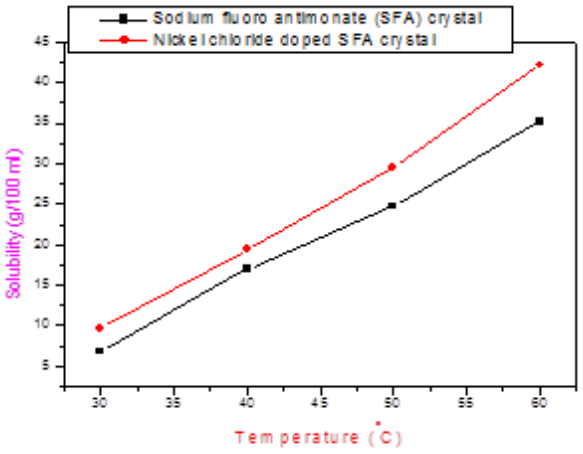

Fig.1: Solubility curves of undoped and nickel chloride doped $Na_3Sb_4F_{15}$ samples

B. *Structural studies*

The grown crystals of nickel chloride doped $Na_3Sb_4F_{15}$ subjected to single crystal XRD studies using a single crystal X-ray diffractometer with graphite monochromated MoK_a radiation and the obtained data are presented in the table 1. From the data, it is observed that the grown doped crystal crystallizes in monoclinic system. The obtained data are observed to be almost the same values compared to those of undoped $Na_3Sb_4F_{15}$ as reported in the literature [12]. The slight changes in the lattice parameters are due to incorporation of dopant in the lattice of sodium fluoro antimonate crystal. The powder XRD pattern of nickel chloride doped $Na_3Sb_4F_{15}$ crystal is shown in figure 2. The sharp reflection peaks indicate the good crystallinity of the sample. Using the INDEXING software package, the diffraction peaks were indexed. The unit cell parameters of the sample have been determined using the UNITCELL software package. The obtained values from powder XRD pattern are found to be almost the same as those obtained by single crystal XRD studies.

Table 1: Unit cell parameters for nickel chloride doped sodium fluoro antimonate ($Na_3Sb_4F_{15}$) crystal

Sample	Unit cell parameters	Volume (Å)^3
Nickel chloride doped sodium fluoro antimonate crystal	a = 8.092(6) Å b = 5.526(2) Å c = 8.702(3) Å α= 90°, β= 95.21(4)° ϒ=90°	387.3(2)

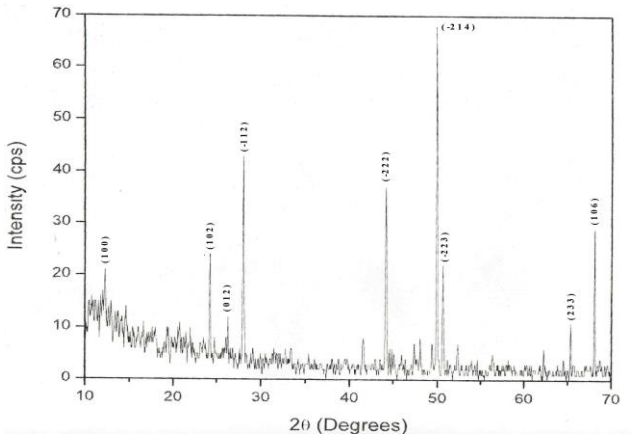

Fig.2: Powder XRD pattern of nickel chloride doped $Na_3Sb_4F_{15}$ crystal

C. *Measurement of dielectric constant and dielectric loss*

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 temperatures and at different frequencies. The dielectric constant and the dielectric loss of the samples have been measured using an LCR meter for different frequencies at 80 °C and at 40 °C and the results are shown in figures 3 and 4. The values of dielectric constant and dielectric loss decrease with increase in frequency. In general the variations in dielectric constant with frequency suggest the presence of higher space charge polarization of the material in the low frequency region and the decrease in polarization leads to the reduction in dielectric constant. The space charge polarization depends on the purity and perfection of the material and its influence is noticeable in the low frequency region. At higher frequencies, the values of dielectric constant and loss are low because molecules of larger relaxation times may not be able to respond to these higher frequencies. The lower value of dielectric constant at high frequencies may be due to the loss of polarizations gradually and is important for these materials in the construction of photonic and NLO devices. It is also noticed that the values of dielectric loss decrease with increase in frequency for the samples and the low value of dielectric loss indicates that the grown crystals are of good quality dielectrics[13,14]. It suggests that the dielectric loss strongly depends on the frequency of the applied field, which is similar to the dielectric constant in the ionic system. The results show that the values of dielectric properties like dielectric constant and loss factor of the samples are more at 80 °C compared to those values at 40 °C

and this indicates the normal dielectric behavior of the samples.

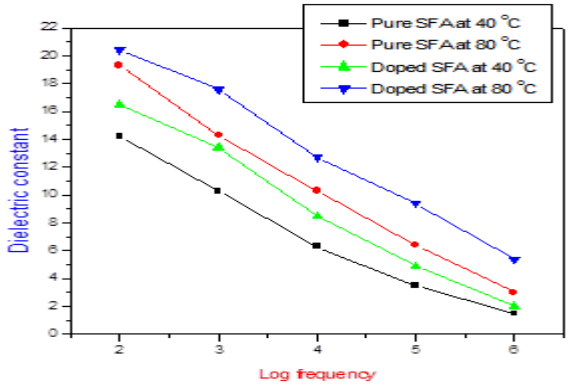

Fig.3: Variation of dielectric constant with frequency for pure and nickel chloride doped sodium fluoro antimonite (SFA) crystals

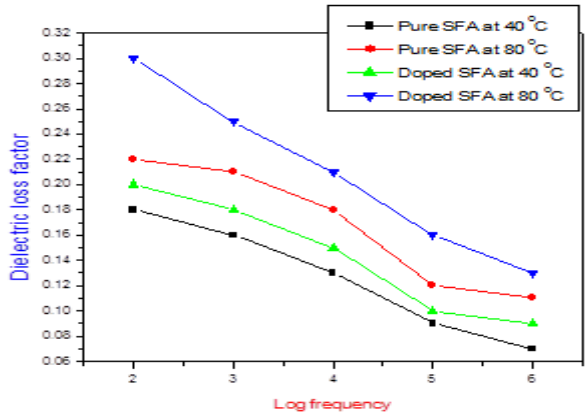

Fig.4: Variation of dielectric loss with frequency for pure and nickel chloride doped sodium fluoro antimonite (SFA) crystals

D. SHG studies

The analysis of second-order nonlinearity like second harmonic generation (SHG) of the grown crystals was performed by Kurtz powder method. The single crystals were powdered and were irradiated by an incident radiation (1064 nm) of pulse width 8 ns from a Q-switched quanta RAY GCR Nd:YAG laser. KDP was used for calibrating the SHG intensity. The output power of the crystal was measured using a power meter and the NLO property of the crystal was confirmed from the estimation of green radiation of the crystal. The obtained data of SHG efficiency of the grown crystals are summarized in table 2.

Table 2: Relative SHG efficiency of pure and nickel chloride doped SFA samples

Sample	Relative SHG efficiency
Pure SFA crystal	0.84
SFA crystal + 2 mole % of Nickel chloride	1.02

E. LDT studies

Laser damage threshold (LDT) values for the sample crystals using a Nd:YAG laser with the wavelength of 1064 nm. The LDT measurement involves the interaction of high power laser radiation with the matter followed by various physical, chemical, optical, thermal and other processes that are taking place in the material. LDT value is the maximum permissible power that can withstand in a particular crystal and it is determined using the formula $P = E/\pi r^2$ where E is the energy in mJ, is the pulse width, r is radius of the spot in mm[15]. The obtained values of LDT of the undoped and nickel chloride doped SFA crystals are 0.53 GW/cm^2 and 0.61 GW/cm^2.

F. Measurement of hardness

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 5. 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. The hardness values are observed to be increasing when nickel chloride is added as the dopant into sodium fluoro antimonite crystals.

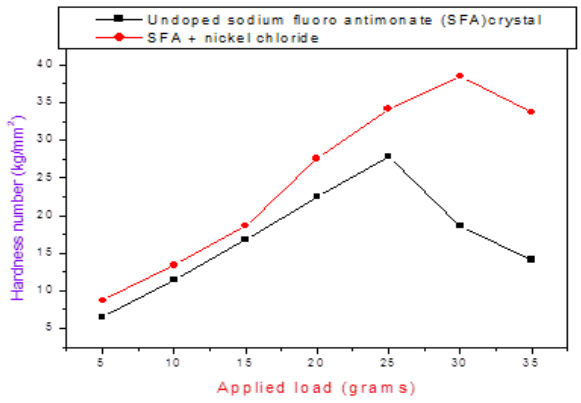

Fig.5: Variation of hardness number with applied load for nickel chloride doped sodium fluoro antimonate ($Na_3Sb_4F_{15}$) crystals

G. EDAX spectral 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. The recorded EDAX spectrum of nickel chloride doped sodium fluoro antimonate ($Na_3Sb_4F_{15}$) crystals are shown in the figure 6. The results show that the elements such as F, Na, Cl, Sb, Ni and O are

present in the sample. The weight percentage of the elements in the sample is provided in the table 3.

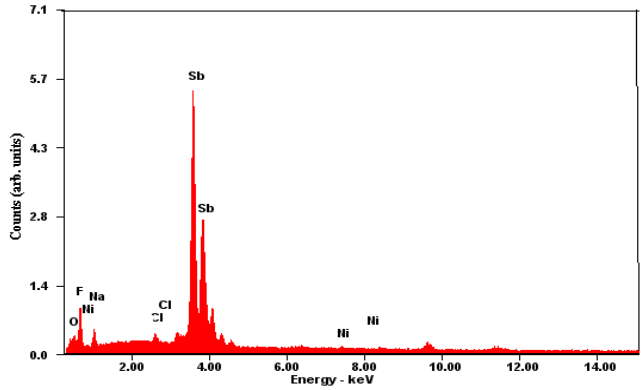

Fig.6: EDAX spectrum of nickel chloride doped SFA crystal

Table 3: Weight percentage of elements in nickel chloride doped sodium fluoro antimonate ($Na_3Sb_4F_{15}$) crystals

Element	Weight (%)
Oxygen	2.48
Fluorine	21.52
Sodium	6.94
Chlorine	2.04
Antimony	61.33
Nickel	4.45

H. Measurement of thermal stability and weight change by TG/DTA studies

TG/DTA studies were carried out to find out the weight change and thermal stability of the samples. The recorded TG/DTA thermal curves for nickel chloride doped sodium fluoro antimonate crystal is presented in the figure 7. It is noticed from the results that the nickel chloride doped $Na_3Sb_4F_{15}$ crystal is thermally stable upto 220 ^oC. Since there is no weight loss below 200^oC, the sample has no water of crystallization [12]. The value of decomposition point/melting point of the nickel chloride doped $Na_3Sb_4F_{15}$ crystal is 260 ^oC. When the temperature is increased above the melting point, there is a gradual and significant weight loss occurs in the range of temperature 280-650^oC and this is due to the decomposition and the release of gaseous particles such as fluorine, chlorine and other ions from the lattice of the crystals.

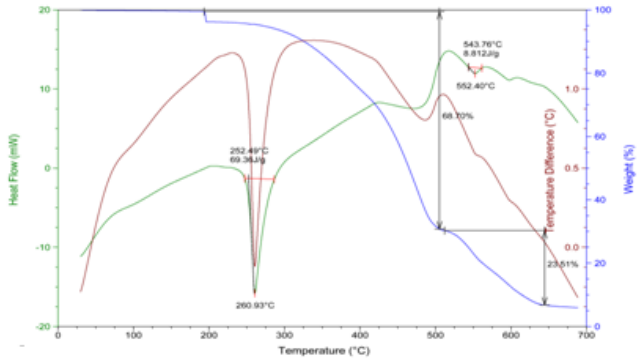

Fig.7: TG/DTA curves of nickel chloride doped SFA crystal

IV. Conclusions

Undoped and nickel chloride doped sodium fluoro antimonite (SFA) crystals were grown by solution method. The solubiltiy of nickel chloride doped SFA sample is found to be more than that of undoped SFA sample. The grown crystals are found to be crystallzing in monoclinic structure. 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 temperatrue. The different elements in the doped SFA sample have been identified by EDAX analysis. Hardness was found to be more for nickel chloride doped sample compared to undoped sample. SHG studies indicate that the grown crystals are second-order NLO materials. LDT value of nickel chloride doped SFA crystal is found to be more than that of undoped SFA crystal. The thermal stability of the nickel chloride doped SFA crystal is found to be 220 ^oC.

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