STUDY ON GROWTH, STRUCTURAL, THERMAL, MECHANICAL, OPTICAL AND DIELECTRIC PROPERTIES OF L-PROLIN DOPED NSH CRYSTALS

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Abstract - The single crystal of L-Prolin doped Nickel Sulphate Hexa Hydrate (NSH) was grown from slow evaporation technique for different molar concentrations, viz., (0.2 to 1 mole% in steps of 0.2). The crystallinty of the grown single crystals was estimated by powder X-ray diffraction studies. Thermal stability of the crystals is tested using TG/DTA. The mechanical strength of the crystals has been measured by Vicker's micro hardness. Optical transparency of grown crystal has been analyzed by UV-Vis-NIR spectral studies. The dielectric study is carried out for both pure and doped NSH crystals.

Key words: Crystal growth, X-ray diffraction, Thermal properties, Mechanical properties, Optical properties and Dielectrics.

I. INTRODUCTION

Crystal growth and characterization is one of the important research area in science and technology. Developments in technology have stimulated the importance of discovering new materials and modifying the already known materials. Growth of single crystals and their structural and physical characterization come under the scientific research on crystalline materials. Single crystals are important materials for electronic, optical devices and laser crystals. In recent years several studies dealing with organic inorganic and semi organic molecules and materials called nonlinear optics (NLO) are being reported due to the increasing need for photonic applications. The nonlinear responses induced in various molecules in solution and solids are of great interest in many fields of research [1-3]. Crystalline semi-organic salts of amino acids have recently attracted considerable interest among researchers. The amino acid group materials have been mixed with inorganic salts to form adducts or complexes in order to improve their mechanical, thermal and NLO properties [4-8]. In the present investigation the single crystal of pure Nickel Sulphate Hexa Hydrate and L-Prolin doped Nickel Sulphate Hexa Hydrate was grown by slow evaporation method. Nickel sulphate hexa hydrate (NSH) crystals are widely used for UV light filters and UV sensors [9-11]; however they possess moisture regaining property. Recently reported crystals are Rubidium Nickel Sulphate Hexahydrate (RNSH), Ammonium Nickel Sulphate Hexahydrate (ANSH), Iron Nickel Sulphate Hexahydrate (FNSH), Potassium Nickel Sulphate Hexahydrate (KNSH), etc. [12-15]. The grown crystals were characterized by powder X-ray diffraction, thermal, mechanical studies. The optical transparency and optical constants were assessed employing UV–visible NIR studies in the range of 200–1100nm. The wide optical band gap of the grown crystal has been found. The title compound has good dielectric behavior and the results indicate an increase electrical parameter viz. σ_{ac}, ε_r and tan δ with the increase of temperature.

II. CRYSTAL GROWTH

Crystal growth is a major stage of a crystallization process and consists of new atoms, ions, or polymer strings into the characteristic arrangement of a crystalline Bravais Lattice .The title compound was prepared by dissolving analar grade Nickel Sulphate Hexa Hydrate (NSH) by means of doping it with L-Prolin in different but definite molecular ratios. We have grown pure and L-prolin doped crystals by the slow evaporation method at room temperature. NSH crystal was doped with L-Prolin in six NSH:L–Prolin molecular ratios, viz. 1:0.000, 1:0.002, 1:0.004, 1:0.006, 1:0.008 and 1:0.010.Approximate molar ratio of materials was taken using digital balance and dissolved in double distilled water. The solution of pH value 7 was stirred with magnetic stirrer and allowed to evaporate without disturbance. Optically good quality NSH single crystals have been grown within a period of 7 to 14 days. Initially very small crystals appeared then grew bigger in size. Out off grown crystals, best crystals were selected for further studies and are shown in Figure1.

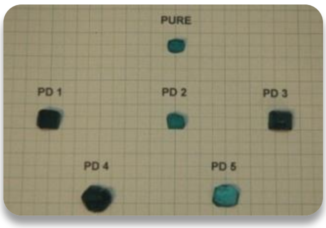


Fig1. *Photograph of the grown Pure and Doped NSH crystals.*

III. CHARACTERIZATIONS

X-ray power diffraction (PXRD) is a rapid analytical technique primarily used for identification of a crystalline material and can provide information of unit cell dimension. The analysed material is finely ground, homogenized and average bulk composition is determined. PXRD data were collected from powdered sample for pure and doped NSH crystals using diffractrometer. The reflections were indexed. Analysis of the X-ray peaks was done by available methods and lattice parameters were determined [13- 18].

The thermal analyses are used to find out weight loss (TGS) melting and decomposition point (DTA) of the grown crystals. Thermo gravimetric analyses was carried out for the pure NSH crystal using a Perkin Elmer thermal analyzer at a heating rate of 10 C/min in the nitrogen atmosphere heated from 40- 950 C to understand the thermal stability

The mechanical stability of the grown crystals were analysed by the Vicker"s microhardness test which was performed using the Vivker's microhardness tester. The well-polished, flat faced crystals were used. The hardness test was performed for the loads varying from 25g to 100g and the stability of the crystals towards the external stresses was observed.

A transmission spectrum is very important for NLO materials, because a nonlinear optical material can be of practical use if it wide optical transparency window. The UV-Vis-NIR absorption spectra were recorded in the wavelength range 200-1100nm for the all six crystals grown by using Double beam spectrophotometer 2202.

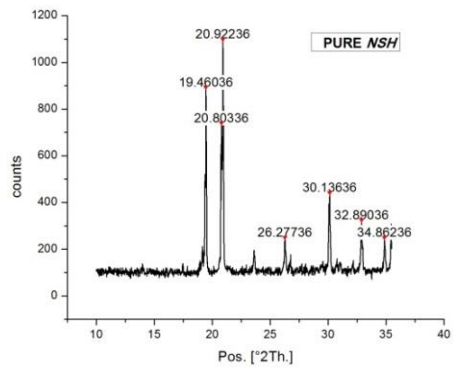
The dielectric constant of the material can be measured using two probe method. The samples were cut and polished, opposite faces of the crystals were coated with good quality graphite to obtain a good ohmic contact with the electrodes. The capacitance and dielectric loss measurements were carried out for various temperatures ranging from 40^0C to 75^0C [19,20,21] using an Agilent 4284ALCR meter for various frequencies 20Hz,100Hz,1KHz,10KHz,100KHz,1MHz.

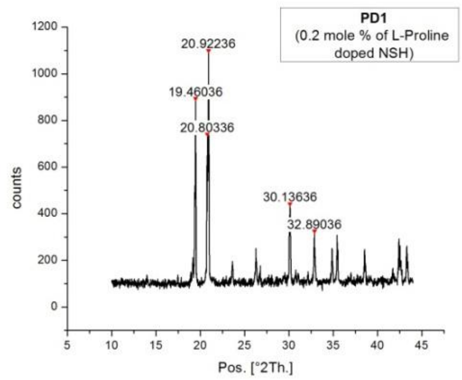
The dimension of the crystal was measured using a microscope. Air capacitances were also measured for the dimensions equal to that of the crystals [22, 23, 24].

IV. RESULTS AND DISCUSSION

4.1 POWDER XRD

X-ray diffraction studies of solution grown NSH crystals was carried on XPERT-PRO using X-ray CuKα radiation (1.54059340) was used. The samples were scanned in the 2ϴ range of 10^0-70^0 X-ray diffractogram is shown in figure2. The technique is based on observing the scattered intensity when X-ray beam is incident on a sample. It is a function of incident and scattered angle, polarization, and wavelength or energy[10]. The incident beam will be scattered at all scattering centers, which lay on lattice planes. The angle between incident beam and the lattice planes is called ϴ. The angle between incident and scattered beam is 2ϴ.The angle 2ϴ of maximum intensity is called the Bragg angle. The figure2 shows the powder X-ray diffraction pattern, the d - spacing of lattice planes depend on the size of the elementary cell and determine the position of the peaks. The intensity of each peak is caused by the crystallographic structure, the position of the atoms within the elementary cell and their thermal vibration. The presence of prominent Bragg's peak 2ϴ angle confirms the perfect crystal line structure. The diffraction data almost matches with JCPDS data for pure NSH crystals. Table1 indicates the unit cell parameters satisfy the condition for Tetragonal system i.e., a=b≠c and α=β=γ=90^0 from the above data and it may be concluded that the grown crystals of NSH have tetragonal system with very slight changes in the peak positions, slight change in the relative intensities, cell volume and lattice parameters and these slight changes are due to the doping of L-prolin in NHS crystal.





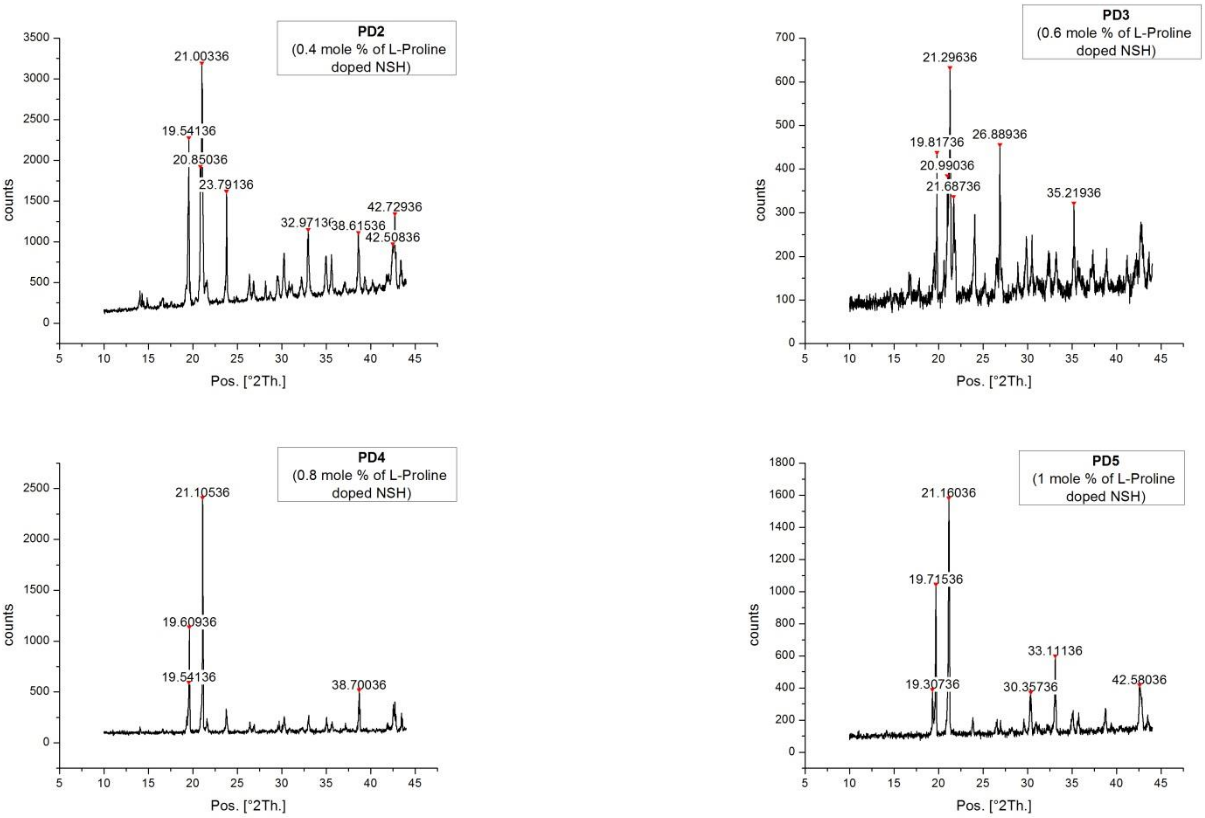


Fig2. *Indexed Powder XRD pattern of pure and doped NSH crystal*

Table 1 – Calculated Lattice parameter for pure and doped NSH single crystals.

Samples	Crystal system	Unit cell parameters			Volume
		a=b	c		
Pure NSH	Tetragonal	6.782	18.266	α=β=γ=90^0	840.130
PD1(0.2 mole % of L-Proline doped NSH)		6.789	18.253		841.506
PD2(0.4 mole % of L- Proline doped NSH)		6.763	18.251		834.721
PD3(0.6 mole % of L- Proline doped NSH)		6.783	18.279		841.089
PD4(0.8 mole % of L- Proline doped NSH)		6.791	18.016		830.849
PD5(1 mole % of L- Proline doped NSH)		6.777	18.276		836.411

4.2 THERMAL STUDIES

Thermo gravimetric (TG) and differential thermal analyses (DTA) of the L-prolin doped NSH single crystal were carried out using Perkin Elmer Diamond TG/DTA instrument. A platinum crucible was used for heating the sample and analyses were carried out in an atmosphere of nitrogen at a heating rate of 10^{0}C/min in the temperature range of 30-400^{0}C. The whole experiment was performed in nitrogen atmosphere. Mass of a substance is measured as function of time or temperature while the substance is subjected to controlled temperature program. It is found that the material is stable up to 85^{0}C. The decomposition process starts at 85^{0}C and this continues to 170^{0}C. This is due to removal of entrapped lattice water. Measurement of the temperature difference between the sample and inert reference material while heating both. An endothermic peak (around 130^{0}C for NSH crystals) corresponding to the elimination of the water molecules. Thermal decomposition reactions are usually endothermic.TG/DTA curve for pure and doped NSH crystals is shown in Figure3.

Fig3. *TGDTA curve of Pure NSH and PD5(1 mole % of L-Proline doped NSH)*

4.3 MECANICAL STUDIES

Hardness is the resistance offered by a solid to the movement of dislocation. Vicker's micro-hardness test was carried out at room temperature on all grown crystals. Hardness number (Hv) was calculated using the relation Hv=1.852 P/d 2 Kg/mm^2. It is found that the hardness number increases with the increasing load. The working hardening coefficients (n), were determined from the slopes of Log p vs. Log d plots. The values of n are found to be greater than two. According to Onitsch[23] and Hanneman[24] (n) should lie between 1.0 to 1.6 are hard materials and above these values for soft material. The n values observed in the present study indicate that all the crystals grown belong to soft material category. This has been shown in Figure4 and Table2.

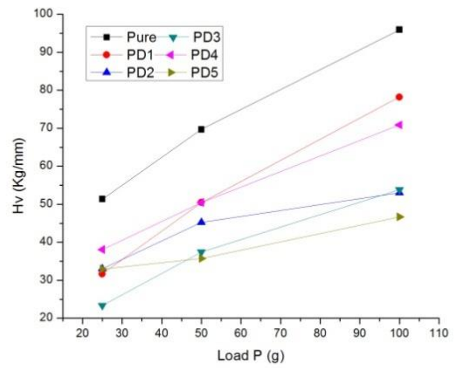


Fig4. *Plot for hardness number (H_v) vs. (Load P)*

Table2. Work hardening coefficient (n)

Samples	Microhardness (Hv) for the loads of			Work hardening coefficient (n)
	25gm	50gm	100gm	
Pure NSH	51.35	69.65	95.9	3.63975
PD1(0.2 mole % of L-Proline doped NSH)	30.55	39.15	60.15	5.74864
PD2(0.4 mole % of L- Proline doped NSH)	53.7	65	86.65	3.00839
PD3(0.6 mole % of L- Proline doped NSH)	21.05	27.4	45.7	4.97124
PD4(0.8 mole % of L- Proline doped NSH)	55.35	69.5	92.15	3.61273
PD5(1 mole % of L- Proline doped NSH)	51.35	69.65	95.9	2.64086

4.4 OPTICAL STUDIES

The optical transmission range and the transparency cut off limits are important for NLO materials. The UV-Vis-NIR spectroscopy of the pure and doped NSH crystals was performed by using Double Beam Spectrophotometer. The crystals have a good optical transmission in the entire visible region and the lower cut off wavelength is observed. The band gap energies were calculated and presented in Table3 and Figures5-6 showed the UV absorbance and True plots. The single crystals are mainly used for optical applications. Thus the study of optical transmission range of grown crystal is important. The optical transmission spectrum was recorded using Double Beam spectrophotometer in the wavelength region 200 – 1100nm. The UV Vis NIR absorption spectra are observed in the present study. Efficient non-linear optical crystals have an optical transparency lower cut-off wavelengths between 200-400nm [14]. The lower cut off region lies in the range 384 nm. The low absorption in the visible and NIR regions along with low cut off wavelengths confirm the suitability of the grown crystals for NLO applications. The grown crystals has good transmission in UV as well as in visible regions.

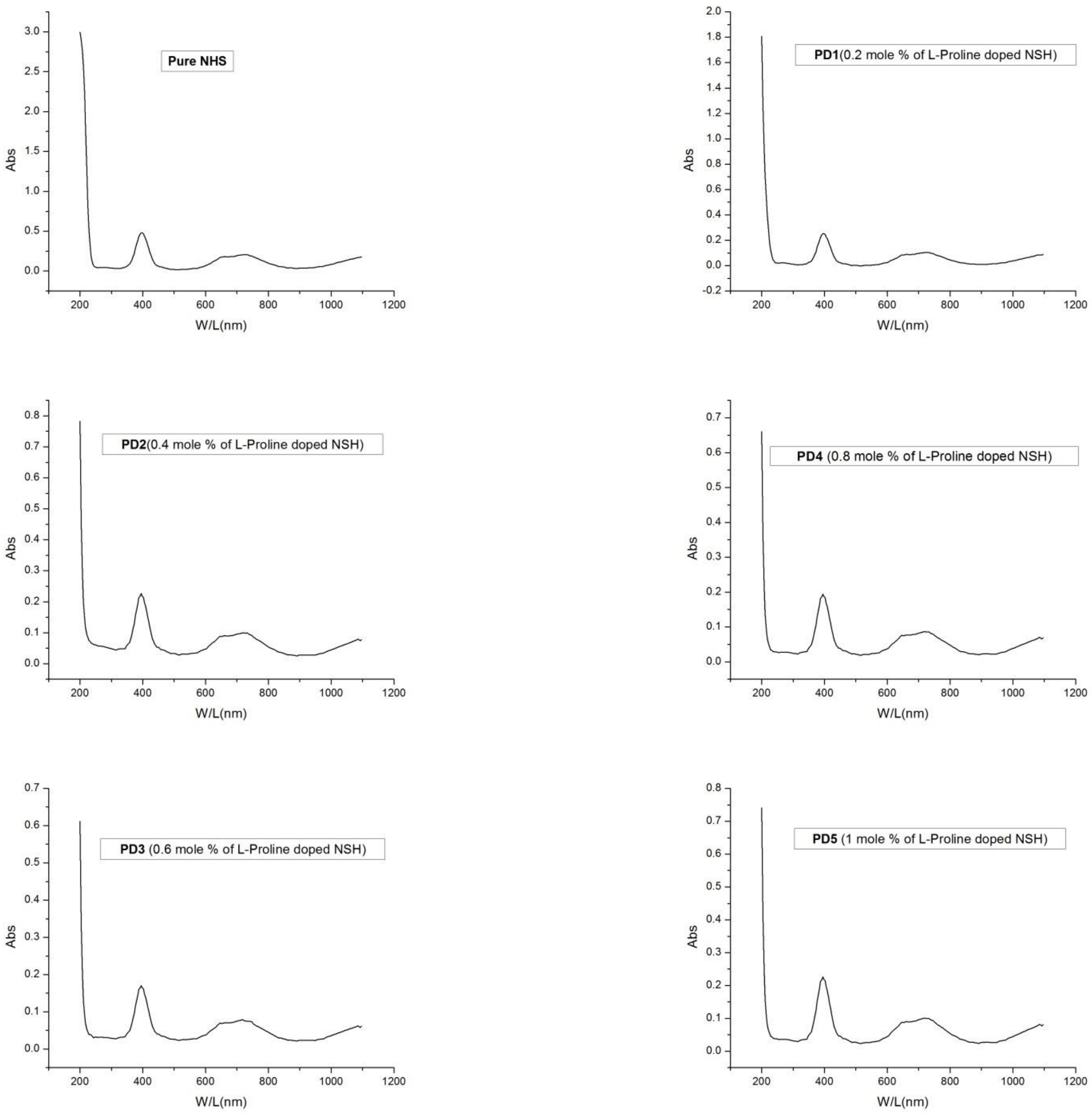


Fig5. *UV-Vis-NIR spectroscopy of the pure and doped NSH crystals*

Table 3 - Results of Band Gap Energy.

S.No.	Samples	Band gap energy E_g(eV)
1	Pure NSH	5.02
2	PD1(0.2 mole % of L-Proline doped NSH)	5.36
3	PD2(0.4 mole % of L- Proline doped NSH)	5.38
4	PD3(0.6 mole % of L- Proline doped NSH)	5.46
5	PD4(0.8 mole % of L- Proline doped NSH)	5.49
6	PD5(1 mole % of L- Proline doped NSH)	5.53

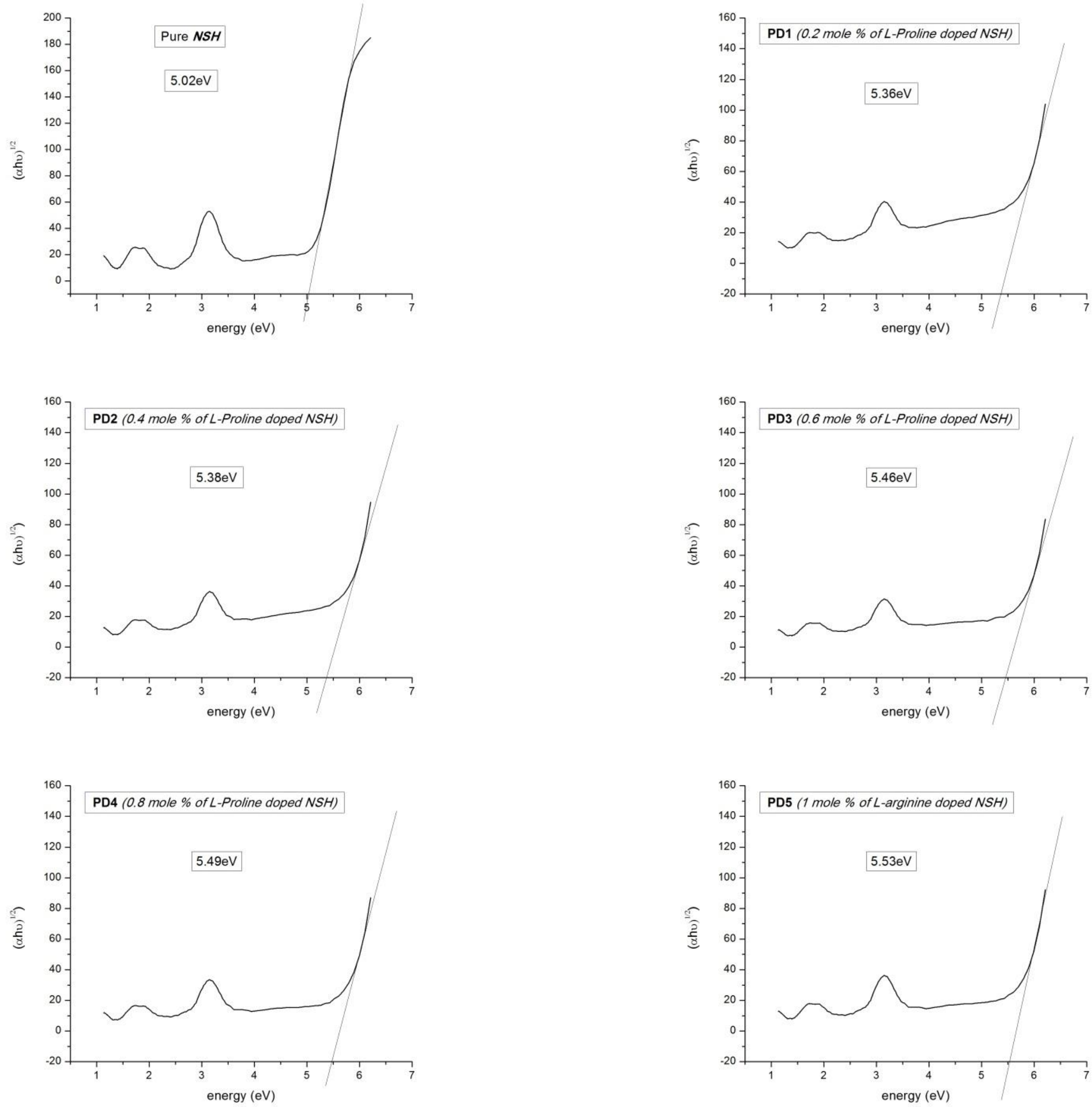


Fig6. *Plot of energy versus* $(\alpha h\upsilon)^2$

4.4 ELECRICAL STUDIES

The AC electrical conductivity (σ) was calculated using the relation.

$$\boxed{\sigma = \varepsilon_0\, \varepsilon_r\, \omega \tan \delta}$$

Where ε_0 is the permittivity of free space (8.85×10^{-12} $C^2 N^{-1} m^{-2}$) and ω is the angular frequency (ω = 2πf; f is the frequency) [11].

The dielectric constant (ε_r) of the crystal was calculated using this relation

$$\varepsilon_r = \left(\frac{A_{air}}{A_{crys}}\right)\left(\frac{C_{crys} - C_{air}\left(1 - \frac{A_{crys}}{A_{air}}\right)}{C_{air}}\right)$$

Where A_{cry} is the area of the crystal touching the electrode and A_{air} is the area of the electrode. The dielectric losses were measured for all the grown crystals by a method adopted by previous authors [12, 13]. The ε_r, tanδ and σ_{ac} values obtained in the present study with different frequencies are shown in Figures 7-9.The ε_r, tanδ and σ_{ac}

values obtained at 50^0C with all the frequencies are provided in Table4. All the electrical parameters are found to increase with the increase in temperature. This is normal dielectric behavior. This can be understood on the basis that the mechanism of polarization is similar to the conduction process. The electronic exchange of the number of ions in the crystal gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization.

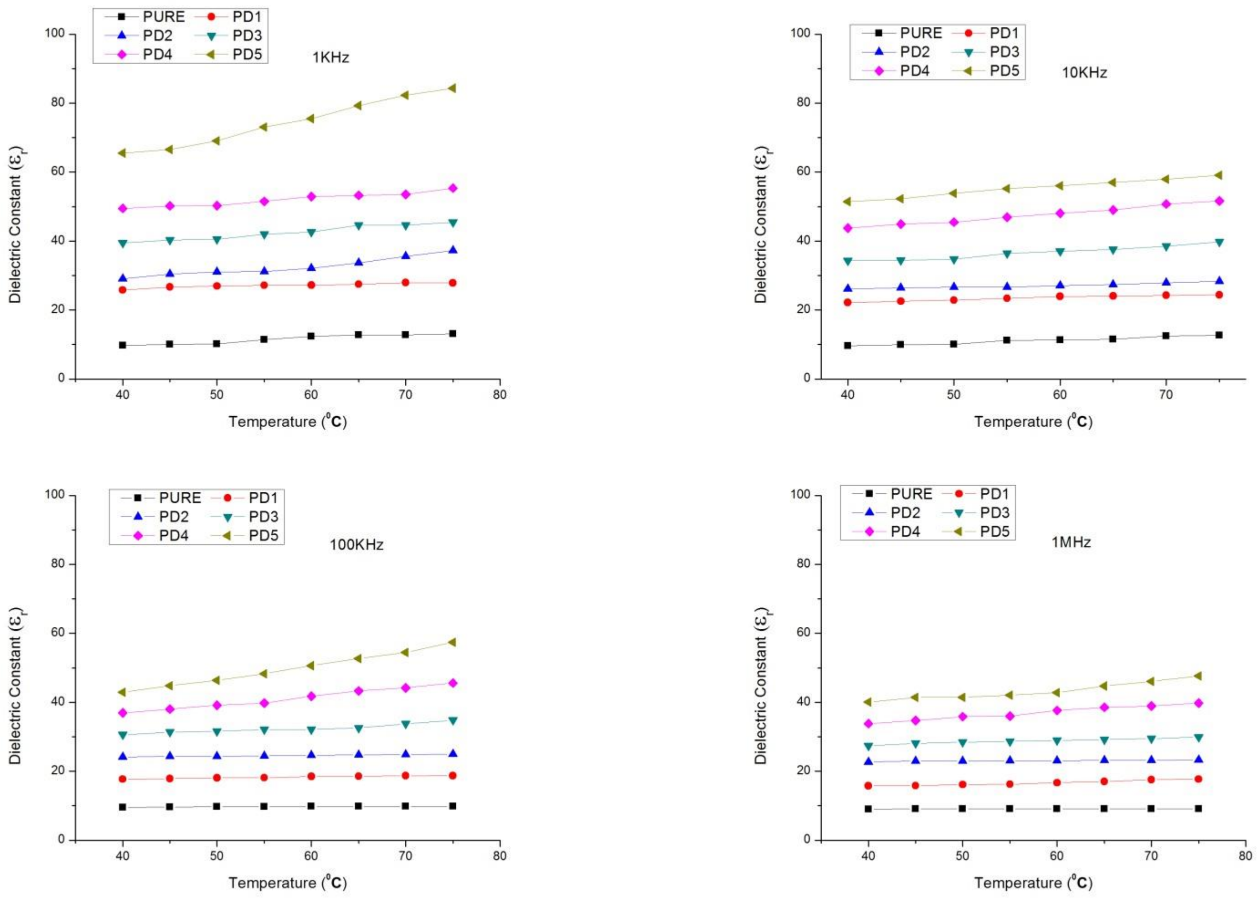


Fig7. *The dielectric constants for pure and doped NSH*

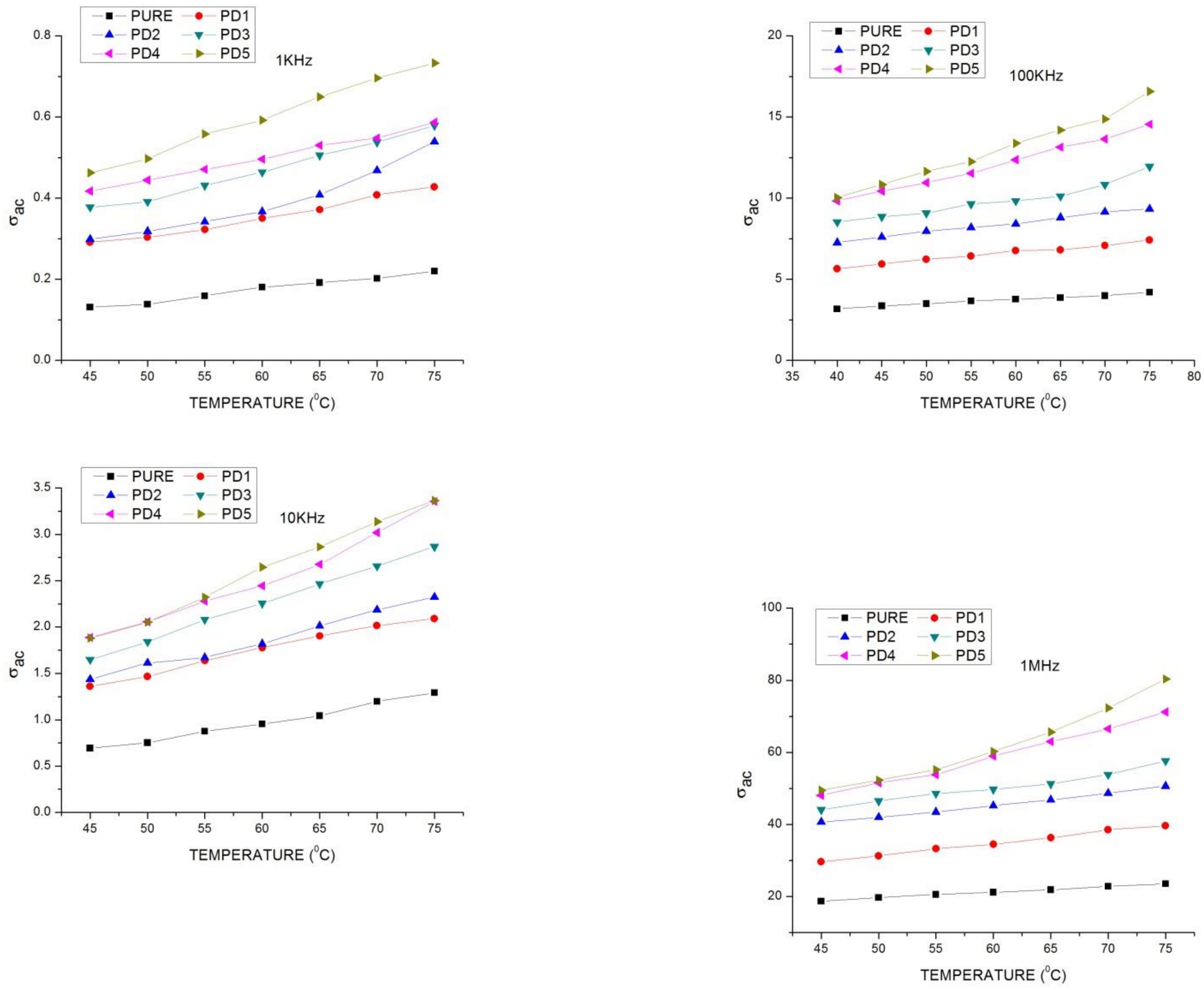
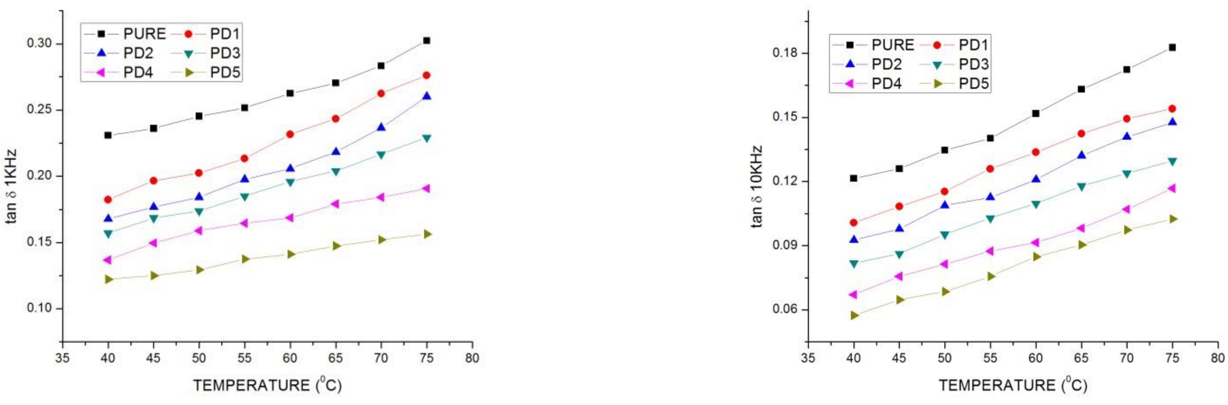
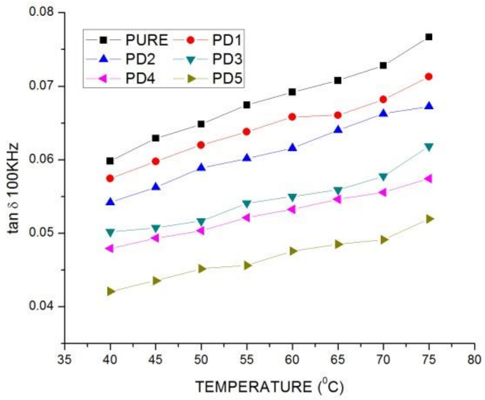


Fig8. *The AC electrical conductivities (x10^{-6}mho/m) for pure and doped NSH crystal*





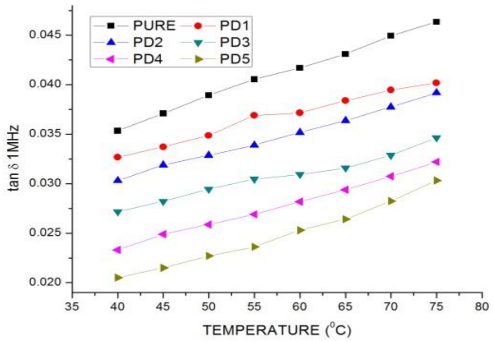


Fig9. *The dielectric loss factors for pure and doped NSH crystals*

Table 4 – The ε_r, tanδ and σ_{ac} ($x10^{-6}$ mho/m) values at 50^{0}C for pure and doped NSH.

Samples	Parameter	With a frequency of			
		1KHz	10KHz	100KHz	1MHz
Pure NSH	ε_r	12.980	10.157	10.040	9.705
	Tanδ	0.245	0.135	0.065	0.039
	$\sigma_{ac(x10^{-6}\ mho/m)}$	0.138	0.752	3.495	19.687
NSH+ PD1	ε_r	26.951	22.860	18.089	16.132
	Tanδ	0.203	0.115	0.062	0.035
	$\sigma_{ac(x10^{-6}\ mho/m)}$	0.303	1.466	6.231	31.266
NSH+ PD2	ε_r	31.084	26.667	24.359	22.980
	Tanδ	0.184	0.109	0.059	0.033
	$\sigma_{ac(x10^{-6}\ mho/m)}$	0.318	1.612	7.971	41.991
NSH+ PD3	ε_r	40.510	34.698	31.597	28.415
	Tanδ	0.174	0.095	0.052	0.029
	$\sigma_{ac(x10^{-6}\ mho/m)}$	0.391	1.840	9.069	46.509
NSH+ PD4	ε_r	50.297	45.477	39.159	35.837
	Tanδ	0.159	0.081	0.050	0.026
	$\sigma_{ac(x10^{-6}\ mho/m)}$	0.444	2.056	10.955	51.540
NSH+ PD5	ε_r	69.104	53.824	46.390	41.437
	Tanδ	0.129	0.069	0.045	0.023
	$\sigma_{ac(x10^{-6}\ mho/m)}$	0.497	2.052	11.646	52.277

V. CONCLUSION

Optical quality crystals can be successfully grown by slow evaporation method. The grown crystals were characterized by PXRD, thermal, mechanical, electrical and optical (UV-Vis-NIR) measurements. The PXRD of spectra confirms the crystalline perfection of the grown crystals. Lattice parameters calculated from the XRD pattern of the pure and doped NSH crystals and determination of lattice volume indicate that the impurity molecules have entered in the crystal matrix of NSH. The thermal stability of the title crystal was determined by TG/DTA studies. The hardness values of the crystals are varied with the dopants used and belong to the category of soft materials. The dielectric constants were found to increase with increasing temperature. The increase of AC conductivity with increase of temperature has been understood as essentially due to temperature dependence. The UV-Vis-NIR spectral studies revealed that the band gap of pure NSH was altered due to doping of L-Prolin. The preset study indicates that dopant L-Prolin leads to the discovery of promising low value dielectric materials. So it is more interesting that doped crystals are useful in micro electronic industry.

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