DIELECTRIC PROPERTIES OF PURE AND NI^{2+} DOPED GLYCINE SODIUM SULFATE CRYSTALS

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Abstract

Pure and Ni^{2+} added glycine sodium sulfate (GSS) single crystals were grown by the slow evaporation technique and characterized chemically, structurally, thermally, optically, mechanically and electrically. Effect of Ni^{2+} addition as an impurity on the properties of GSS has also been investigated. All the six crystals grown exhibit normal dielectric behavior and are found to be thermally stable up to 250˚C, NLO active and mechanically soft. The Ni^{2+} addition is found to increase the dielectric parameters. The low dielectric constant values observed for pure GSS indicate that GSS is not only a promising NLO material but also a low dielectric constant value dielectric material.

Keywords: *Activation energy, Crystal growth, Dielectric crystal, Electrical properties, X-ray diffraction*

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1. INTRODUCTION

Non-linear optical (NLO) have been playing an important role in laser science and technology. The major goal of scientists is the search for new non-linear optical materials. The semi-organic non-linear optical crystal not only possesses the high optical non-linearity of a purelyorganic compound but also the favourable thermal and mechanical properties of an inorganic compound [1]. Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their non-linear optical properties. Although some of the amino acids are already reported to have NLO activity [2-4], the amino acid glycine based crystals are now a days shown greater interest for NLO applications [5,6].

Microelectronics industry needs replacement of dielectric materials in multilevel interconnect structures with new low dielectric constant (ε_r) materials, as an interlayer dielectric (ILD) which surrounds and insulates interconnect wiring. Lowering the ε_r values of the ILD decreases the RC delay, lowers power consumption and reduces “cross-talk” between nearby interconnects [7,8]. As the utility of low-ε_r value dielectric materials is in the electric circuits with water proof condition, water soluble materials in the single crystal form would also be very much interesting. Hoshino et al. [9] reported the dielectric properties of triglycinefluroberyllate.Goma et al. [10] have reported reduction in ε_r value in the case of potassium dihydrogenorthophosphate(KDP) added with 0.6 mol% urea which illustrates that urea doping to KDP reduces the ε_r value. Meena and Mahadevan [7] have found that single crystals of L-arginine acetate and L-arginine oxalate are promising low-ε_r value dielectric materials.

In the present study, we have reported the electrical properties of pure and Ni^{2+} doped GSS crystals.

2. EXPERIMENTAL

2.1. Crystal Growth

Analytical reagent (AR) grade α-glycine and sodium sulfate (Na_2SO_4) were mixed in the ratio of 1:1 in deionized water. The solution was stirred continuously and the saturated solution was allowed to cool to room temperature. Good quality single crystals of GSS have been collected within 30 days. GSS was added with $NiSO_4$. $7H_2O$ in five different molar ratios, *viz*. 1:0.002, 1:0.004, 1:0.006, 1:0.008, and 1:0.010 and the five different Ni^{2+} doped GSS crystals were grown in a period of about 30 days similarly under identical conditions with the pure GSS crystal growth.

2.2. Characterization

The capacitance (C_{crys}) and dielectric loss factor (tanδ) measurements were carried out to an accuracy of ±2% for all the six crystals grown by the conventional parallel plate capacitor method using an LCR meter (Agilant 4284A) at various temperatures ranging from 40-120˚C with five different frequencies, *viz*. 100Hz, 1kHz, 10kHz, 100kHz and 1MHz in a way similar to that followed by Mahadevan and his co-workers [11-13]. The temperature was controlled to an accuracy of ±1˚C. The observations were made while cooling the sample. The dimensions of the crystal were measured using a traveling microscope. Air capacitance (C_{air}) was also measured. Since the variation of air capacitance with temperature was found to be negligible, air capacitance was measured only at the lower temperature considered. The crystals were shaped and polished and the opposite faces were coated with graphite to form a good conductive surface layer (ohmic contact). The sample was mounted between the silver electrodes and annealed at 120˚C for about 30 min to homogenize the sample before taking the readings.

As the crystal area was smaller than the plate area of the cell, the real part of the dielectric constant ($\varepsilon' = \varepsilon_r$) of the crystal was calculated using Mahadevan's formula [7, 10, 14-16],

$$\varepsilon' = \left[\frac{A_{air}}{A_{crys}}\right] \left[\frac{C_{crys} - C_{air}\left(1 - \frac{A_{crys}}{A_{air}}\right)}{C_{air}}\right], \quad \text{.............................(1)}$$

Where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode. The imaginary part of the dielectric constant (ε'') was calculated using the relation[17],

$$\varepsilon'' = \varepsilon' \tan\delta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

The AC electrical conductivity (σ_{ac}) was calculated using the relation,

$$\sigma_{ac} = \varepsilon_0 \varepsilon' \omega \tan\delta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where ε_0 is thepermittivity of free space ($8.85\times10^{-12}\ C^2N^{-1}m^{-2}$) and ω is the angular frequency ($\omega=2\pi f$; f=100Hz-1MHz in the present study).

3. RESULTSAND DISCUSSION

3.1 General Features

Fig-1 shows a photograph of the pure and Ni^{2+} added single crystals grown in the present study. The grown crystals are transparent and colorless. Morphology of the Ni^{2+} doped GSS crystals is observed to be similar to that of the pure GSS crystal. Also, significant coloration has not been observed due to Ni^{2+} doping.

The single crystals grown in the present study are represented as: Pure GSS → the undoped GSS crystal; GN1, GN2, GN3, GN4 and GN5→ 0.2, 0.4, 0.6, 0.8 and 1.0 mol% Ni^{2+} doped GSS crystals respectively.

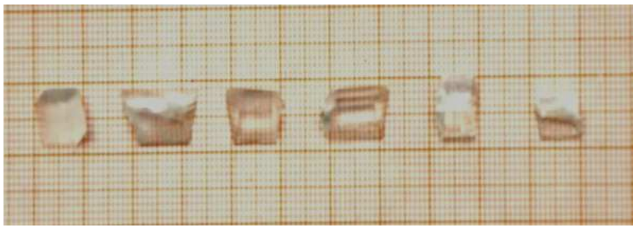


Fig-1: Photograph showing the pure and Ni^{2+} doped GSS crystals (From left: Pure GSS, GN1, GN2, GN3, GN4 and GN5)

Single crystal X-Ray diffraction analysis reveals that pure and Ni^{2+} doped GSS crystallize in the monoclinic system and belongs to the $P2_1$ space group. Thermal studies show that the GSS crystal is stable up to 250˚C and it is mechanically soft. It is a good NLO material.

3.2. Electrical Properties

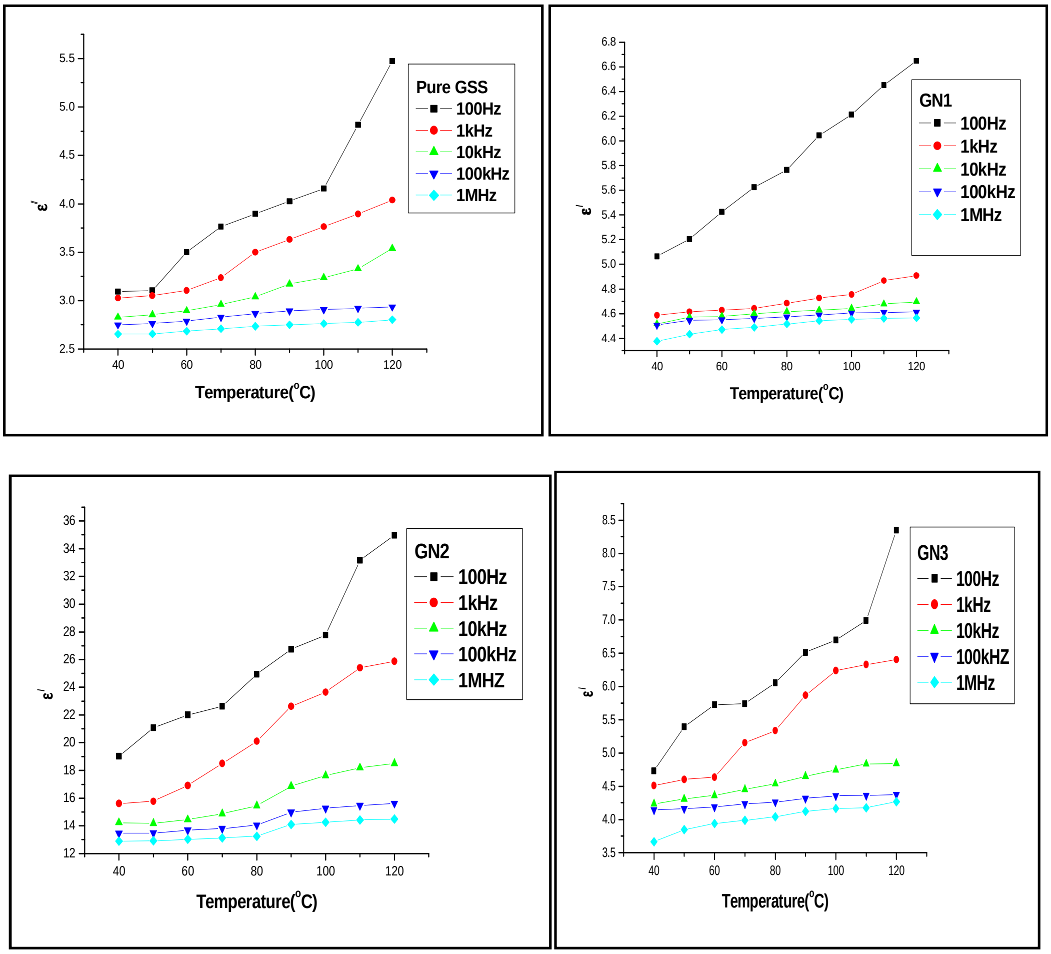
The dielectric parameters, *viz*. ε', ε'', $\tan\delta$ and σ_{ac} observed for the pure and Ni^{2+} doped GSS crystals grown in the present study are shown in Fig-2 to Fig-5. It can be seen that all the four dielectric parameters increase with the increase in temperature. The ε', ε'', and $\tan\delta$ values decrease whereas the σ_{ac} value increases with increase in frequency. This indicates that all the six crystals grown in the present study exhibit normal dielectric behavior in the temperature and frequency ranges considered. Also, it is observed that the dielectric parameters do not vary systematically with the impurity concentration. The $\tan\delta$ values observed in the present study are considerably low which indicates that the crystals grown are of high quality.

The high dielectric constant at low frequency is due to the presence of all types of polarizations, *viz*. electronic, ionic, orientation, space charge, etc. The space charge polarization will depend on the purity and perfection of the sample. Its influence is large at high temperature and is not noticeable in the low frequency region. In normal dielectric behavior, the dielectric constant decreases with increasing frequency and reaches a constant value, depending on the fact that beyond a certain frequency of the electric field, the dipole does not follow the alternating field. The crystals with high dielectric constant lead to power dissipation. The material having low dielectric constant will have less number of dipoles per unit volume. As a result it will have minimum losses as compared to the material having high dielectric constant. Therefore the grown crystals may be used for high speed electro-optic modulations.

Variation of dielectric constant with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. The variation at low temperature is mainly due to the crystal expansion and electronic and ionic polarizations. The variation at high temperature is mainly due to the thermally generated charge carriers and impurity dipoles. Varotsos [18] has shown that out of the contribution from electronic and ionic polarizations, the electronic polarizability practically remains constant. The increase of dielectric constant with the increase of temperature is essentially due to the temperature variation of ionic polarizability. Thus the major contribution to the observed dielectric constant of the crystals grown in the present study can be from electronic and ionic polarizations.

Electrical conductivity of GSS crystals may be determined by the proton transport within the framework of hydrogen bonds. Conductivity mechanism in ice containing the hydrogen bonds and the conductivity associated with the incorporation of impurities into the crystal lattice can be combined to understand the conductivity mechanism in pure and impurity added crystals. The proton conduction can be accounted for by motion of protons accompanied by an excess of positive charge (D defects). Electric polarization may be modified by migration of these defects. However, migration of these defects may not change the charge at an electrode [19].

The motion of defects occurs by some kind of rotation in the bond with defects. When the temperature of the crystal is increased, there is a possibility of weakening of the hydrogen bonding system due to rotation of the carboxyl ions in the glycine molecules. The increase of conductivity with the increase of temperature observed for the pure and Ni^{2+} added GSS crystals in the present study can be understood as due to the temperature dependence of the proton transport.



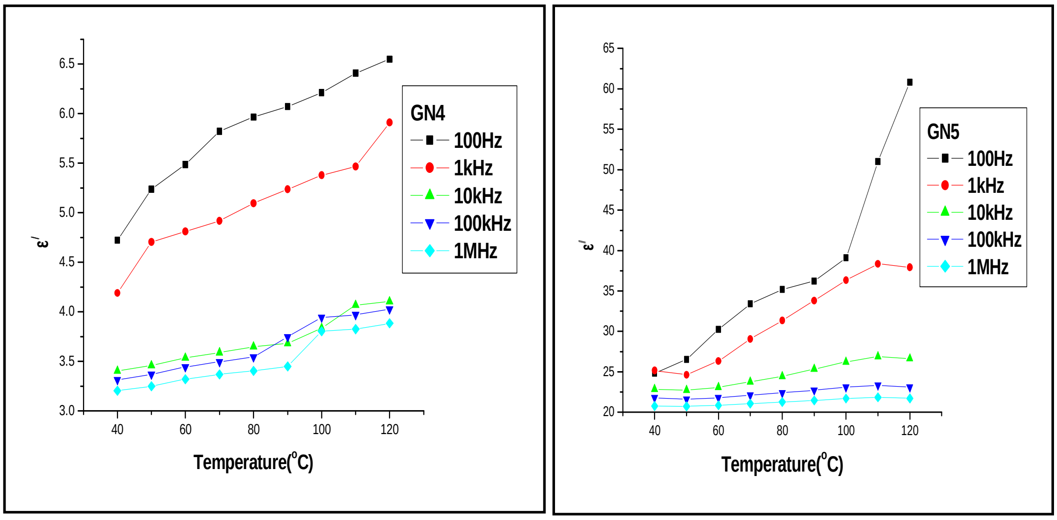
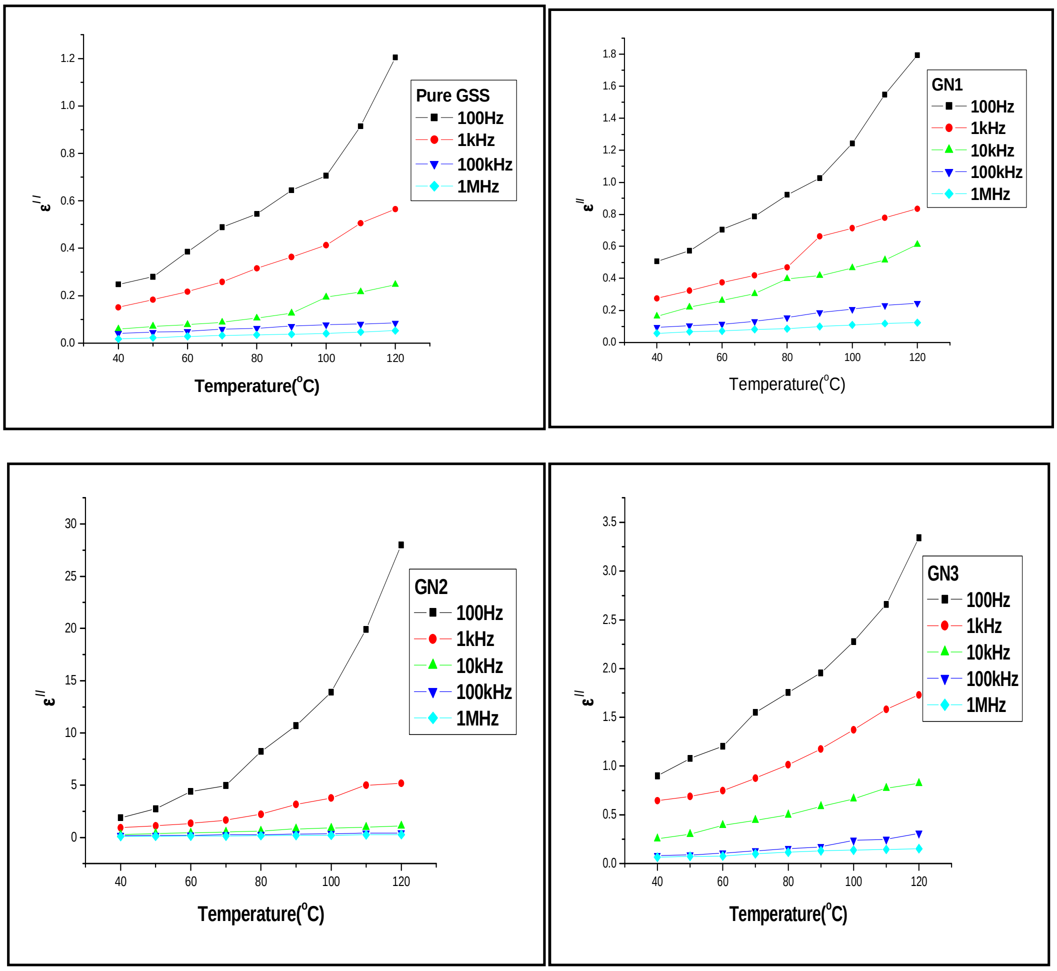


Fig-2: The real part of the dielectric constant (ε′) values for the pure and Ni^{2+} doped GSS crystals



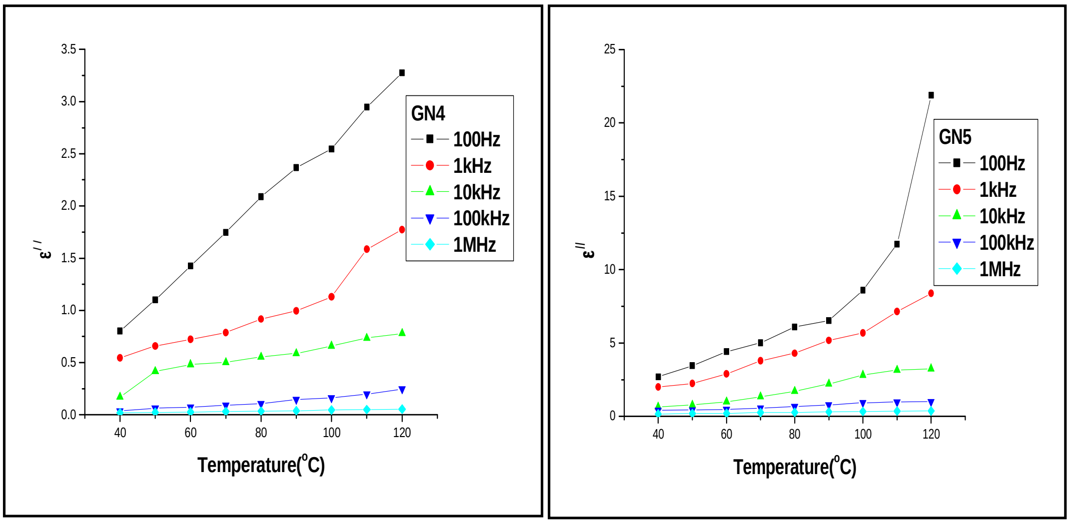
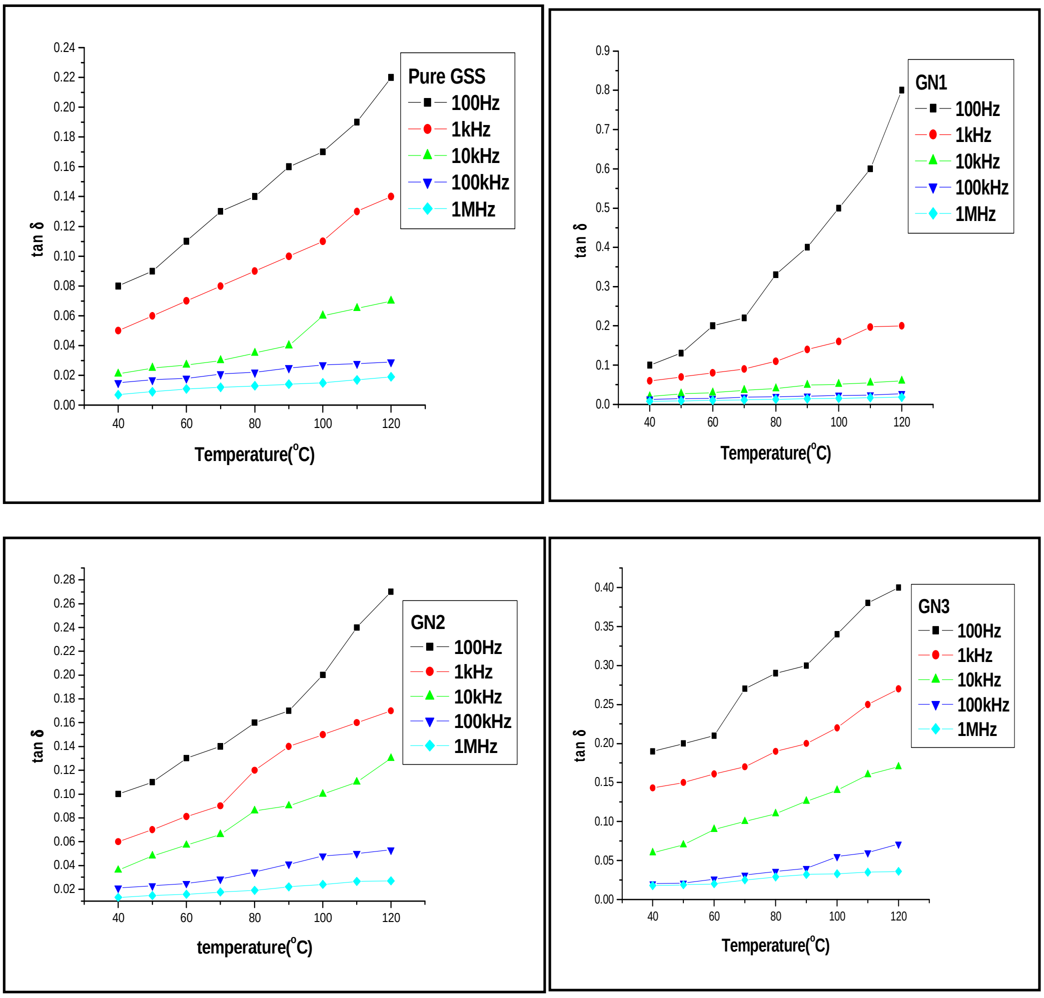


Fig-3: The imaginary part of the dielectric constant (ε'') values for the pure and Ni^{2+} doped GSS crystals



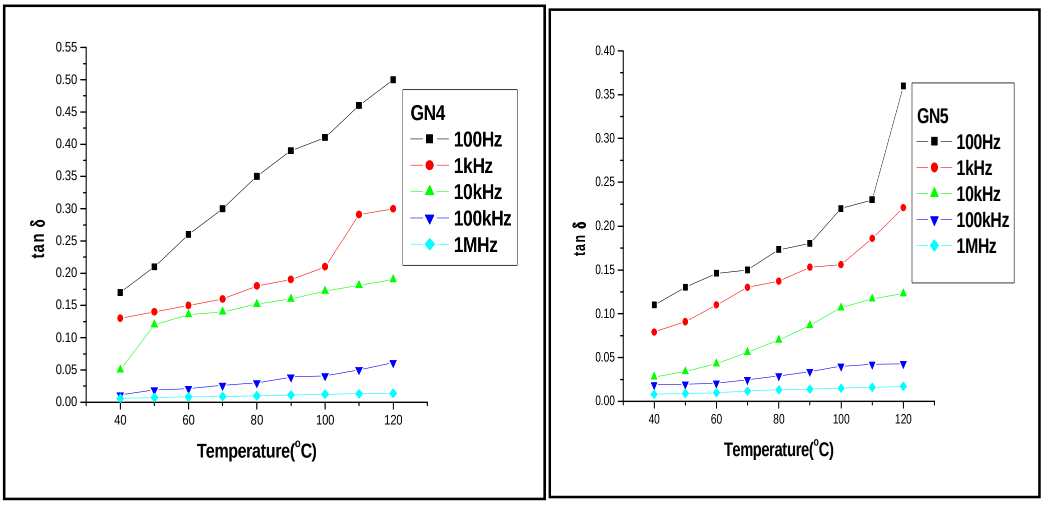
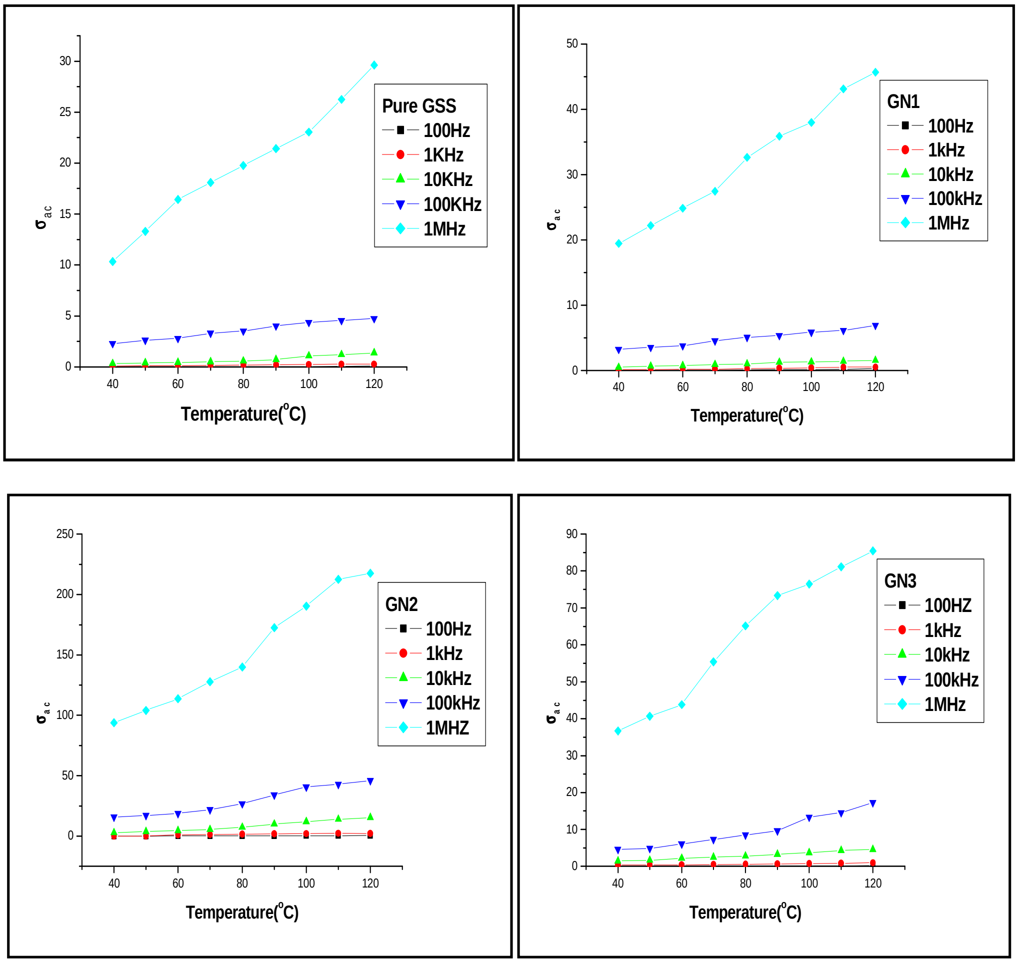


Fig-4: The dielectric loss factors (tan δ) for the pure and Ni^{2+} doped GSS crystals



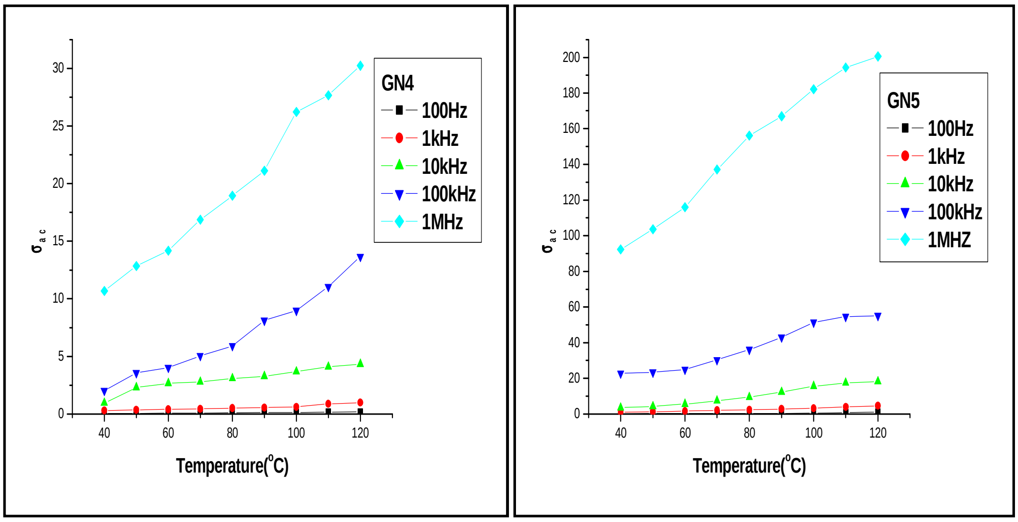
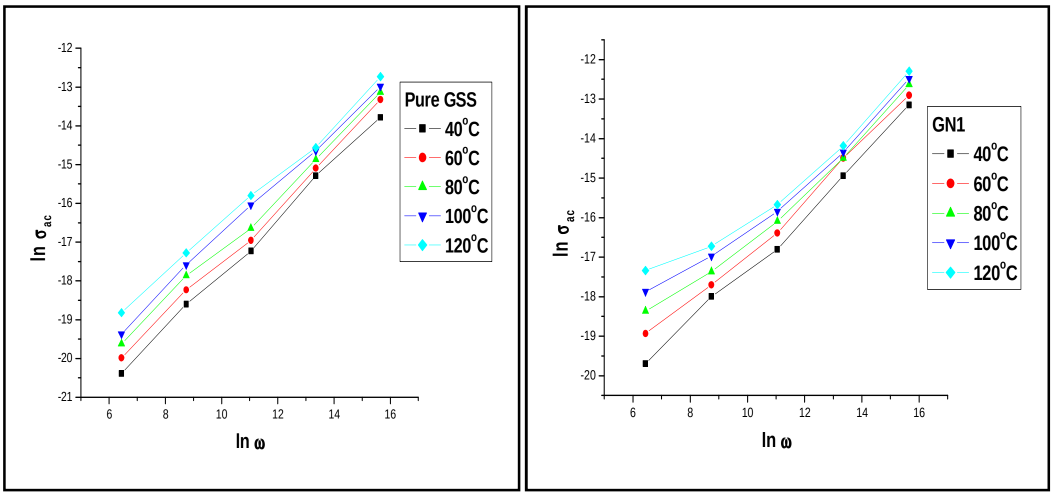


Fig-5: The AC electrical conductivities (σ_{ac})($\times 10^{-7}$ mho/m) for the pure and Ni^{2+} doped GSS crystals

In order to understand the frequency dependence of the electrical conductivity observed in the present study, an attempt has been made to fit the observed data into the empirical formula of the frequency dependence given by the AC power law [17,20]:

$$\sigma_{ac} = B\,\omega^{m}\ ,\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where B and m are parameters which depend on both the temperature and material of the crystal, B has the electrical conductivity units and m is a dimensionless constant. The logarithmic representation of equation (4) shown in Fig-6 gives a straight line with a slope equal to m and an intercept equal to ln B on the vertical axis at ln ω = 0.0. The values of m and B were determined from Fig-6 for all the six crystals at the designated temperatures (40, 60, 80 100 and 120˚C).



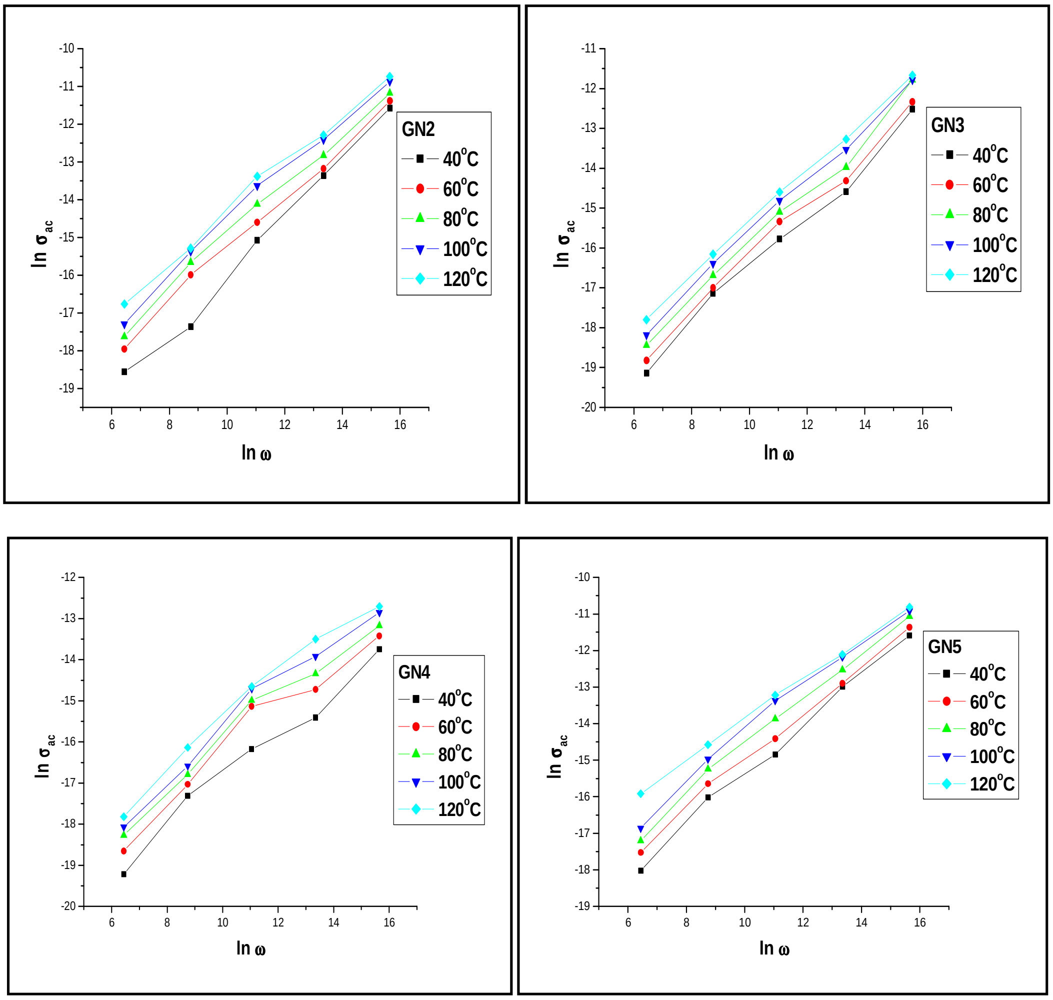


Fig-6: Variation of lnσ_{ac} with respect of ln ω for the pure and Ni^{2+} doped GSS crystals

Fig-7 shows the temperature dependence of m values. The m value observed in the present study is within the range 0.55-0.82. It has been reported in the literature [17,20] that values of m ranges between 0 and 1. When m=0, the electrical conduction is frequency dependent or DC conduction, but for m≤1, the conduction is frequency independent or AC conduction. Results obtained in the present study indicate that the conduction phenomenon in the studied crystals is AC conduction which is due to the hopping of charges (possibly the protons).

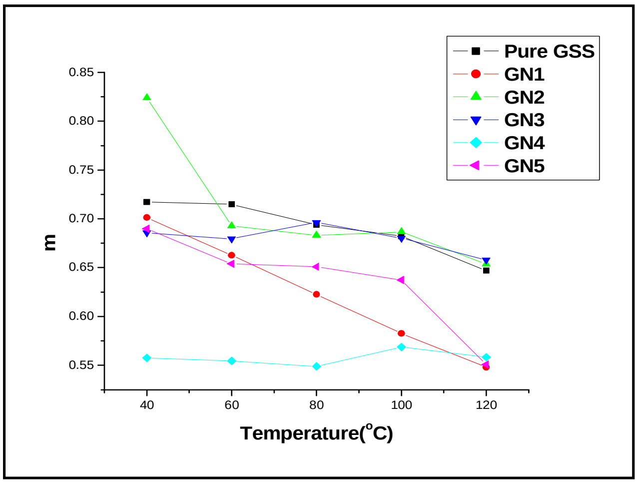


Fig-7: Temperature dependence of m values for the pure and Ni^{2+} doped GSS crystals

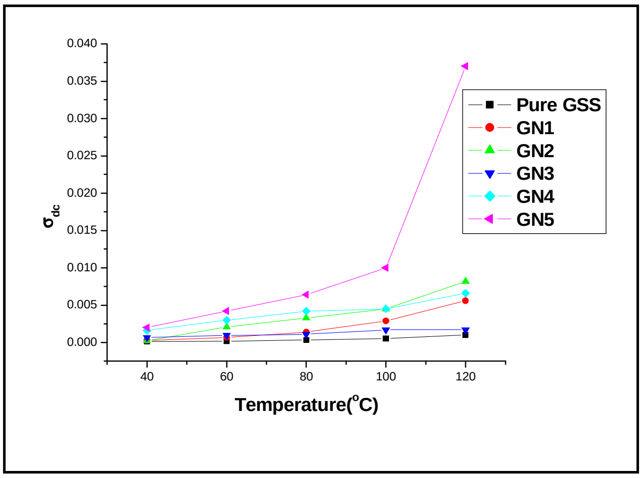


Fig-8: Temperature dependence of B ($=\sigma_{dc}$) ($\times10^{-9}$ mho/m) values for the pure and Ni^{2+}doped GSS crystals

Fig-8 shows the temperature dependence of B values. As the B values are with units of electrical conductivity and are obtained for zero frequency, it may be considered as the DC electrical conductivity. The AC electrical conductivity (σ_{ac}) values observed for 1kHz frequency and the above DC electrical conductivity (σ_{dc}=B) values were fitted into the Arrhenius type relations:

$\sigma_{ac}= \sigma_{0AC}\exp(-E_{ac}/kT)$, ……………..……..(5)

and$\sigma_{dc} = \sigma_{0DC}\exp(-E_{dc}/kT)$, ……………………(6)

Where E_{ac} and E_{dc} are respectively the AC and DC activation energies, k is the Boltzmann's constant , T is the absolute temperature and σ_{0AC} and σ_{0DC} are constants depending on the material of the crystals. The logarithmic representations of equations (5) and (6) are respectively shown in Figs-9 and 10. The plots in both the cases are observed to be very nearly linear. The activation energies were determined from the above plots for all the six crystals considered.

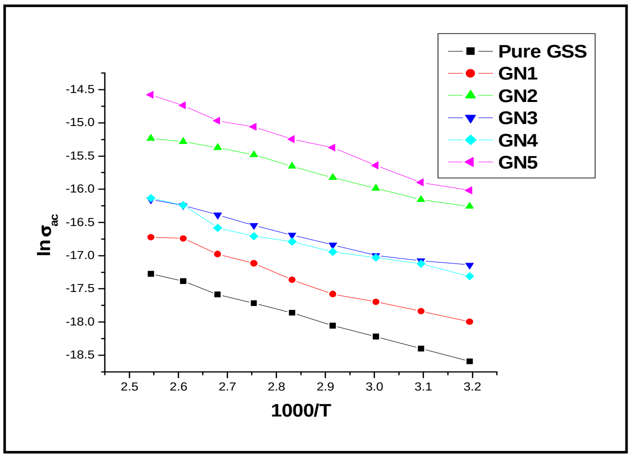


Fig-9: The lnσ_{ac} versus 1000/T plots for 1kHz frequency for the pure and Ni^{2+} doped GSS crystals

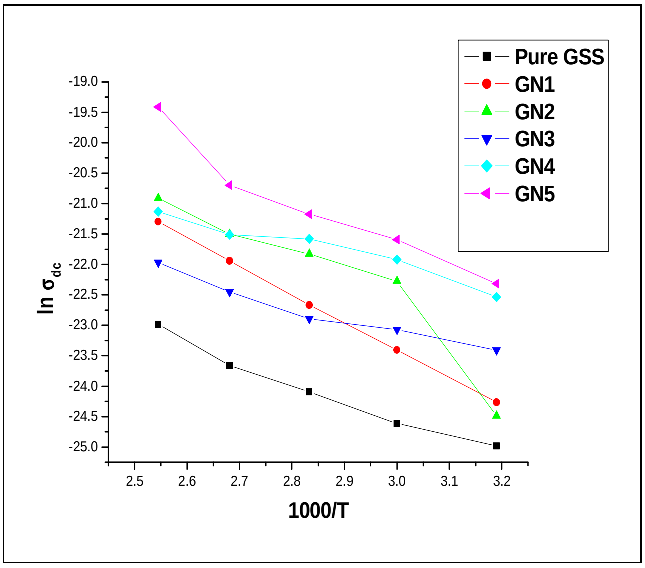


Fig-10: The lnσ_{dc} versus 1000/T plots for the pure and Ni^{2+} doped GSS crystals

The ε', ε'', tan δ and σ_{ac} values with 1kHz frequency at 40˚C, σ_{dc} values at 40˚C, E_{ac} values with 1kHz frequency and E_{dc} values observed for all the six crystals grown in the present study are provided in Table-1. The σ_{dc} values are observed to be significantly less than the σ_{ac}values. Also, the E_{dc} values are significantly more than the E_{ac}values. This is a normal behavior of dielectric crystals.

Table-1: The ε′, ε″, tan δ and σ_{ac} values with 1kHz frequency at 40˚C, σ_{dc} values at 40˚C, E_{ac} values with 1kHz frequency and E_{dc} values

Crystal	ε′	ε″	tan δ	σ_{ac}(×10^{-7}) (mho/m)	σ_{dc}(×10^{-9}) (mho/m)	E_{ac}(eV)	E_{dc}(eV)
Pure GSS	3.026	0.151	0.050	0.084	0.014	0.176	0.262
GN1	4.587	0.275	0.060	0.153	0.028	0.181	0.396
GN2	15.62	0.937	0.060	0.087	0.023	0.147	0.434
GN3	4.510	0.645	0.143	0.359	0.068	0.140	0.185
GN4	4.191	0.545	0.130	0.303	0.163	0.149	0.174
GN5	25.16	1.988	0.079	1.105	0.203	0.193	0.355

It can be seen that all the electrical parameters considered do not vary systematically with the impurity concentration in the solution used for the growth of single crystals. The Ni^{2+} ions are expected to replace the Na^{+} ions and also to some extent expected to occupy the interstitial positions. This may create a disturbance in the hydrogen bonding system at random. As the conduction in these crystals is protonic and mainly due to the hydrogen bonding system, the random disturbance in the hydrogen bonding system may cause the electrical parameters vary nonlinearly with the impurity concentration.

The ε′ values observed for the pure GSS crystals are significantly less than that observed for the Ni^{2+} doped GSS crystals. Also, it is less than that for silica. Silica has ε_r (= ε′) ≈4.0, in part as a result of the Si-O bonds. Several innovative developments have been made for the developments of new low-ε_r value materials to replace silica. However, there is still a need for new low-ε_r value dielectric materials [7, 8].

The low-ε′ values observed for the pure GSS single crystals at near ambient temperatures with a frequency of 1kHz indicate that the GSS crystal is not only a potential NLO material but also a promising low-ε_r value dielectric material, expected to be useful in the microelectronics industry.

CONCLUSIONS

Pure and Ni^{2+} doped α-glycine sodium sulfate (GSS) single crystals have been successfully grown by the free evaporation method and characterized. The GSS crystal is found to be thermally stable up to 250˚C and mechanically soft. All the six crystals grown are found to exhibit normal dielectric behavior. Analysis of the AC electrical conductivity data indicates that the conductivity in pure and Ni^{2+} doped GSS crystals is due to the proton transport.

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