

Effect of Ni²⁺ Ion on the Properties of Glycine Sodium Sulphate and Glycine Potassium Sulphate Crystals – A Comparative Study

A.Karolin¹, K.Jaya Kumari²

Assistant Professor, Department of Physics, Nanjil Catholic College of Arts and Science, Kaliyakkavilai,
Tamilnadu, India¹

Associate Professor, Department of Physics, Sree Ayyappa College for Women, Chunkankadai, Tamilnadu, India²

ABSTRACT: Single crystals of glycine sodium sulphate (GSS) and glycine potassium sulphate (GPS) have been grown by the free evaporation method and characterized chemically, structurally, optically and mechanically. Effect of Ni²⁺ addition as an impurity on the properties of GSS and GPS has also been investigated. The grown single crystals have been analysed by X-ray diffraction, Fourier transform infrared and UV-Vis-NIR spectral studies. Mechanical behaviour has been assessed by Vickers micro hardness measurements. Its nonlinear optical property has been tested by Kurtz and Perry technique.

KEYWORDS: Crystal growth, Slow evaporation technique, X-ray diffraction, micro hardness, nonlinear optical property

I.INTRODUCTION

The inorganic salt of amino acids has been promising materials owing to the non-linear optical properties exhibited by them [1-3]. Organic crystals can have very large nonlinear susceptibilities relative to inorganic crystals but exhibit low damage threshold and poor processibility. Ionic salt materials offer an important and extremely flexible approach for the development of new materials applicable over a very broad range of frequencies. In contrast, purely inorganic NLO materials typically have excellent mechanical and thermal properties but often possess relatively modest optical nonlinearities due to their lack of extended π electron delocalization.

Furthermore, inorganic crystals grown from high temperature melts typically have lower damage thresholds and more optical inhomogenities throughout their bulk due to impurities, internal stress and defects resulting from the extremely non-equilibrium growth conditions. In order to keep the merits and shortcomings, some new varieties of NLO crystals such as semiorganic crystals have been developed. The semiorganic (organic-inorganic) NLO crystals not only possess the high optical non-linearity of a purely organic compound but also the favourable thermal and mechanical properties of an inorganic compound.

Semi-organic compounds based on amino acids mixed with inorganic complexes have been found useful for second harmonic generation (SHG) process [4,5]. The purpose is to achieve the construction of useful devices such as; frequency doublers, active optical interconnect and switches. These devices have great applications in telecommunications and signal processing [6]. Glycine is a simple and effective amino acid with a zwitterionic structure. Its complexes with inorganic materials have attracted the attention of many researchers [7]. In the present investigation, α -glycine has been combined with sodium sulphate to form a new nonlinear optical material glycine sodium sulphate (GSS). Similarly, α -glycine has also been combined with potassium sulphate to form a compound glycine potassium sulphate (GPS). The effect of Ni²⁺ ion on the properties of GSS and GPS has also been

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studied in five different molar concentrations (0.2, 0.4, 0.6, 0.8 and 1.0 mole %) and the molar concentration 1.0 mole % is taken for the comparative study. The results are discussed herein.

II. MATERIALS AND METHODS

Analytical reagent (AR) grade α -glycine, sodium sulphate (Na_2SO_4) and nickel sulphate heptahydrate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) were used along with double distilled water (as a solvent) for the growth of single crystals by the free evaporation method. Sodium sulphate and α -glycine mixed in 1:1 molar ratio were dissolved in double distilled water and stirred for two hours to obtain a homogeneous solution. The solution was filtered and kept in a dust free environment. Transparent and colorless single crystals of glycine sodium sulfate (GSS) were formed at room temperature in a period of about 30 days as per the reaction

$$\text{Na}_2\text{SO}_4 + \text{CH}_3\text{NH}_2\text{COOH} \rightarrow \text{Na}_2[\text{CH}_3\text{NH}_2\text{COOH}]\text{SO}_4.$$

Glycine Potassium Sulphate crystals were also grown according to the reaction

$$\text{K}_2\text{SO}_4 + \text{CH}_2\text{NH}_2\text{COOH} \rightarrow \text{K}_2[\text{CH}_2\text{NH}_2\text{COOH}]\text{SO}_4.$$

GSS and GPS were added with $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in different molar ratios and the crystals were grown under identical conditions with the pure GSS and GPS crystal growth.

Single crystal X-ray diffraction (SXRD) analysis was performed and lattice parameters were determined for the pure and Ni^{2+} added GSS and GPS crystals using a BRUKER KAPPA APEX II diffractometer with CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$). X-ray powder diffraction (PXRD) analysis was carried out for all the crystals grown using an automated X-ray powder diffractometer (PANalytical) in the 2θ range $10-70^\circ$ with CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$). The reflection data were indexed following the procedures of Lipson and Steeple [8].

Fourier transform infrared (FTIR) spectra were recorded by the KBr pellet method for Ni^{2+} added GSS and GPS crystals grown in the wavenumber range $400-4000 \text{ cm}^{-1}$ by using a SHIMADZU spectrometer.

The UV-Vis-NIR absorption spectra were recorded in the wavelength range 190-1100nm for all the crystals grown by using a Lambda-35 spectrophotometer.

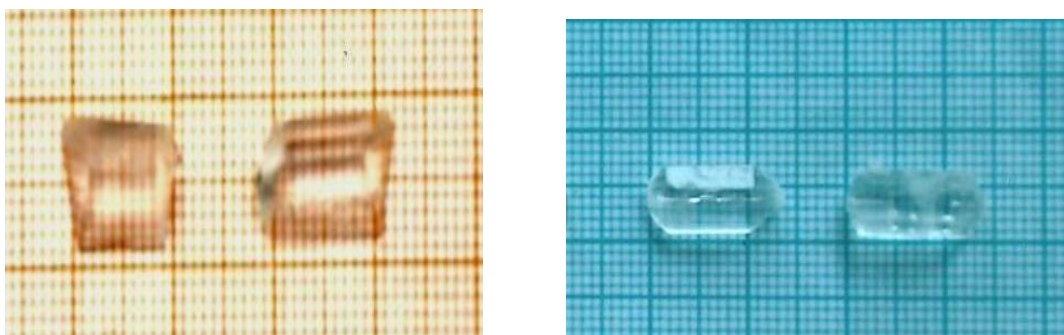
The NLO property of the grown crystals was tested by passing the output of Nd:YAG Quanta ray laser (with fundamental radiation of wavelength 1064nm) through the crystalline powder sample (Kurtz and Perry method[9]). The SHG output from the sample was compared with that from KDP.

Vickers hardness measurements were carried out on all the grown crystals by making indentations on the large area faces using a SHIMADZU HMV2 micro hardness tester.

III. RESULTS AND DISCUSSION

Single crystals grown in the present study are represented as: Pure GSS and GPS \rightarrow the undoped GSS and GPS crystals respectively; GN1, GP1 \rightarrow 1.0 mol% Ni^{2+} doped GSS and GPS crystals respectively.

Figure 1 shows a photograph of the pure and Ni^{2+} added single crystals grown in the present study. The grown crystals are transparent and colourless.



**Figure 1: Photograph showing the pure and Ni^{2+} doped GSS and GPS crystals
(From left: Pure GSS, GN1, Pure GPS and GP1)**

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Morphology of the Ni²⁺ doped GSS and GPS crystals is observed to be similar to that of the pure GSS and GPS crystals. Also, significant colouration has not been observed due to Ni²⁺ doping in both the cases.

The lattice parameters of pure and Ni²⁺ doped GSS crystals obtained through SXRD analysis are presented in Table 1. The study reveals that pure and Ni²⁺ doped GSS crystallize in the monoclinic system and belongs to the P2₁ space group. Pure and Ni²⁺ doped GPS crystals belong to orthorhombic system with space group Pmcn.

Crystal	a(Å)	b(Å)	c(Å)	β(Å)	V(Å ³)
Pure GSS	5.1000(2)	11.9400(2)	5.4600(2)	111.75(2)	308.8(1)
GN1	5.0900(1)	11.9901(1)	5.4700(2)	111.69(1)	310.2(1)
Pure GPS	5.7503(1)	7.4520(1)	10.0275(2)	-	429.6(1)
GP1	5.7410	7.4270(3)	10.0301(2)	-	427.7(1)

Table 1: Lattice parameters for the pure and Ni²⁺ doped GSS and GPS crystals. The e.s.d.s are in parenthesis.

The observed difference in the lattice volumes is very small to have any lattice distortion in the GSS and GPS crystals due to doping. This confirms that the dopant atoms have entered into the GSS and GPS crystal matrix but not distorted the regular structure of the crystals.

The recorded PXRD patterns of pure and Ni²⁺ doped GSS crystals are shown in Figure 2(a) and those of GPS crystals are shown in Figure 2(b).

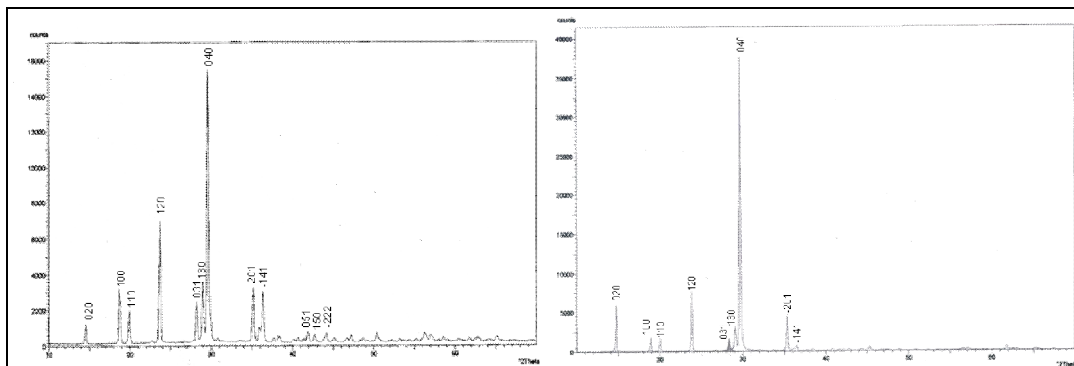


Figure 2(a): The powder X-ray diffraction patterns for pure and Ni²⁺ added GSS crystals (From Left: Pure GSS, and GN1)

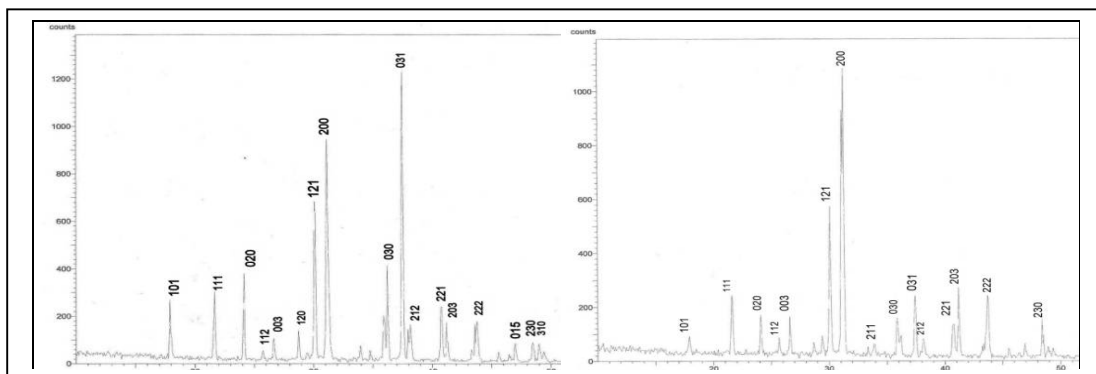


Figure 2(b): The powder X-ray diffraction patterns for pure and Ni²⁺ added GPS crystals (From Left: Pure GPS and GP1)

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Appearance of sharp and strong peaks confirms the crystalline nature of the samples. The diffraction peaks were indexed for the monoclinic (for Pure and Ni²⁺ doped GSS) and orthorhombic (for Pure and Ni²⁺ doped GPS) systems.

The FTIR spectra of pure and doped GSS and GPS crystals are shown in Figure 3(a) and 3(b) respectively. Significant difference could not be observed for the Ni²⁺ doped GSS and GPS crystals due to the lower level of dopant concentration.

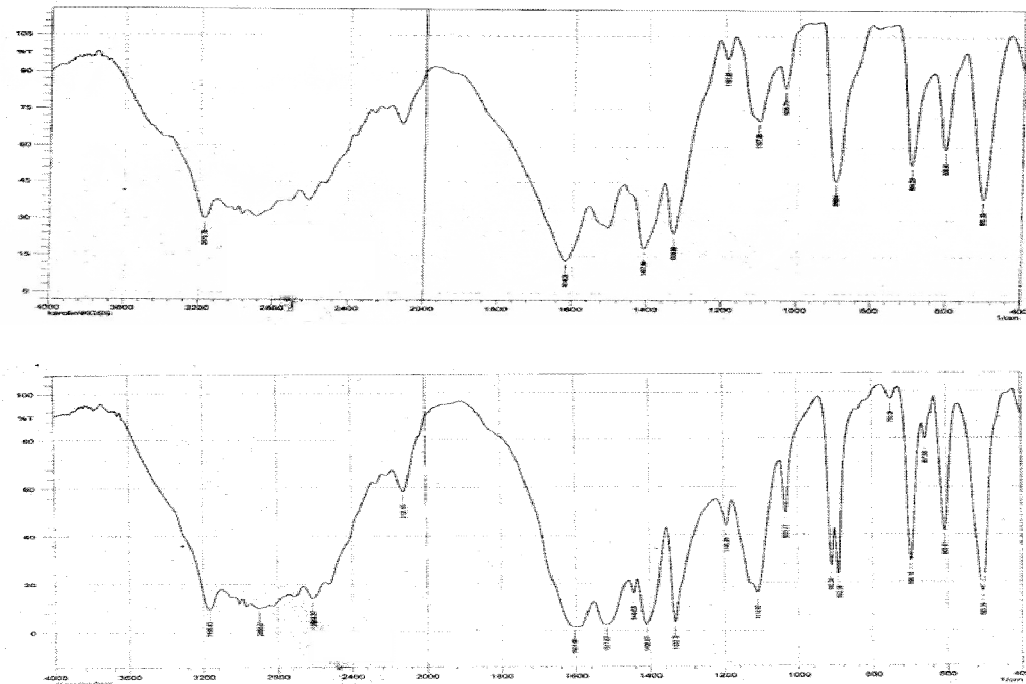


Figure 3(a): The FTIR spectra for pure and Ni²⁺ doped GSS crystals (From top: Pure GSS and GN1)

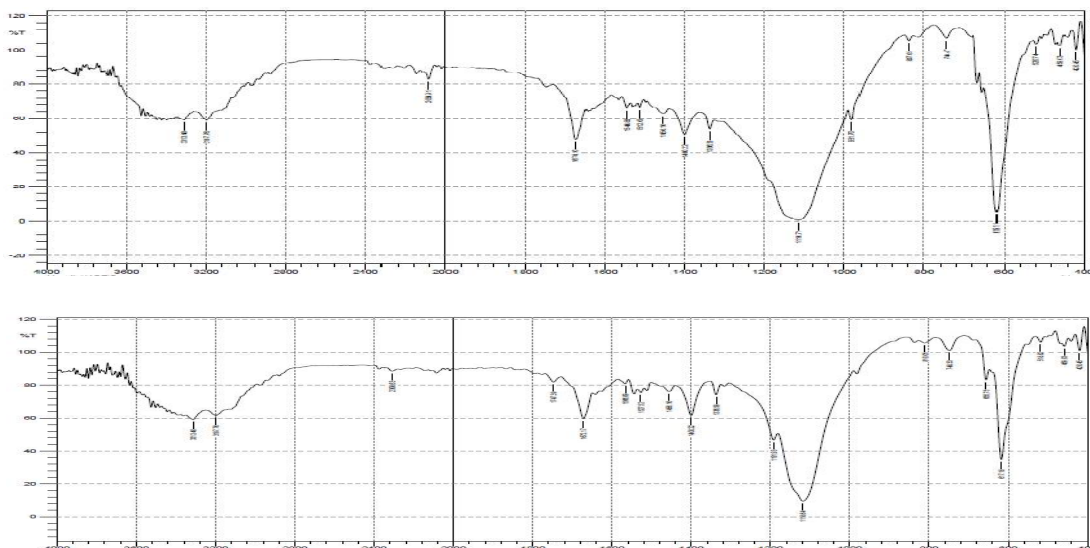


Figure 3(b): The FTIR spectra for pure and Ni²⁺ doped GPS crystals (From top: Pure GPS and GP1)

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With the help of available data on the vibrational frequencies of amino acids [10] all the molecular groups present in the grown crystals could be identified. Table 2 shows the comparison of vibrational frequencies of glycine with pure and Ni²⁺ doped GSS and GPS crystals.

FTIR wavenumbers (cm ⁻¹) for					Assignments*
Glycine [11]	Pure GSS	GN1	Pure GPS	GP1	
3175	3171	3169	3197	3197	$\gamma_{asy}NH_3^+$
2122	2122	2122	2084	-	Combination bond
1605	1616	1605	-	-	$\gamma_{asy}COO^-$
1652	-	-	1674	1672	NH ₃ ⁺ deformation
1507	-	-	1512	1527	NH ₃ ⁺ bending
1445	-	-	1456	1456	γCH_2
1413	1408	1410	1400	1400	$\gamma_{sy}COO^-$
1333	1329	1333	1336	1336	CH ₂ wagging
1110	1107	1111	1116	1118	NH ₃ ⁺ rocking, $\gamma_{sy}SO_4^{2-}$
-	750	746	744	748	SO ₄ ²⁻ bending
607	606	606	619	617	γSO_4^{2-}
504	503	503	520	518	COO ⁻ rocking

* γ . stretching vibration, γ_{asy} —asymmetric stretching vibration, γ_{sy} —symmetric stretching vibration

Table 2: Observed FTIR wavenumbers and their vibrational assignments for the pure and Ni²⁺ added GSS and GPS crystals

The UV-Vis-NIR absorption spectra observed for the pure and Ni²⁺ doped GSS and GPS crystals are shown in Figure 4(a) and 4(b) respectively. The cut off wavelength of pure GSS lies around 300nm and those of Ni²⁺ doped GSS lies around 250 nm. Pure and Ni²⁺ doped GPS crystals have cut off wavelengths nearly 325nm.

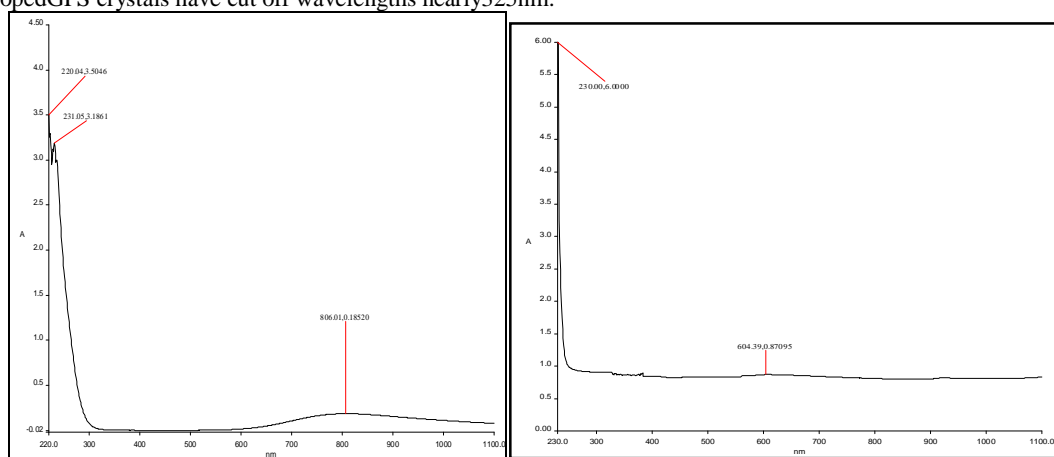


Figure 4(a): UV-Vis-NIR spectra for the pure and Ni²⁺ doped GSS crystals (From Left: Pure GSS and GN1)

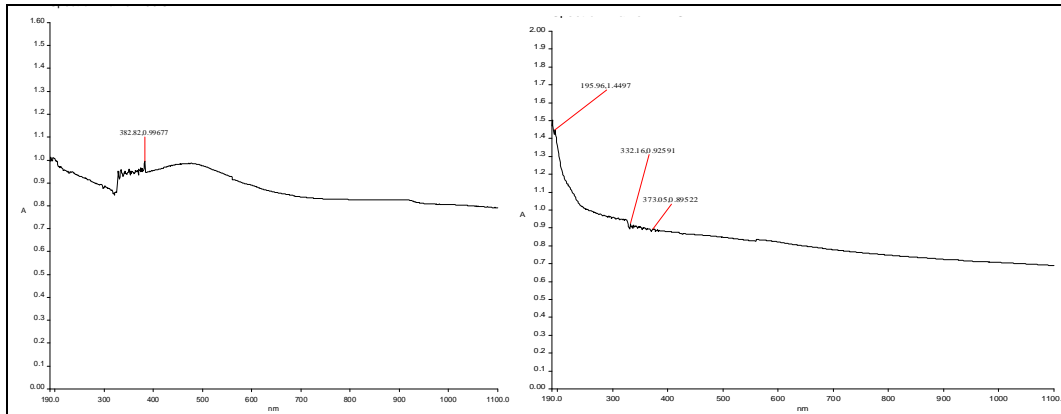


Figure 4(b): UV-Vis-NIR spectra for the pure and Ni²⁺ doped GPS crystals(From Left: Pure GPS and GP1)

It is found that the optical transparency of the GSS and GPS crystals in the UV region is increased by the addition of Ni²⁺ impurity. Efficient nonlinear optical (NLO) crystals have optical transparency lower cut-off wavelengths between 200 and 400nm. This indicates that the crystals grown in the present study can be considered as promising nonlinear optical crystals. The SHG efficiency of pure and Ni²⁺ doped GSS decreases as the dopant concentration increases (see Table 3). But, the SHG measurements made on the pure and Ni²⁺ ion doped GPS reveal that these samples do not exhibit NLO property which is endorsed by the centrosymmetric structure observed for them.

Crystal	SHG Efficiency(in KDP unit)	Absorption edge(nm)
PureGSS	0.43	296
GN1	0.18	249

Table 3: Optical absorption edges and SHG efficiencies for the pure and Ni²⁺ doped GSS crystals.

Microhardness studies on crystals provide an understanding of the plastic behaviour of the crystal [12]. The plot of Vicker’s microhardness number as a function of the applied load for the pure and Ni²⁺ doped GSS is shown in Figure 5. It is observed that the Vicker’s hardness number of the samples increases with increasing load. The hardness increases up to a load of 100gm, above which cracks start developing, which may be due to the release of internal stress generated with indentation.

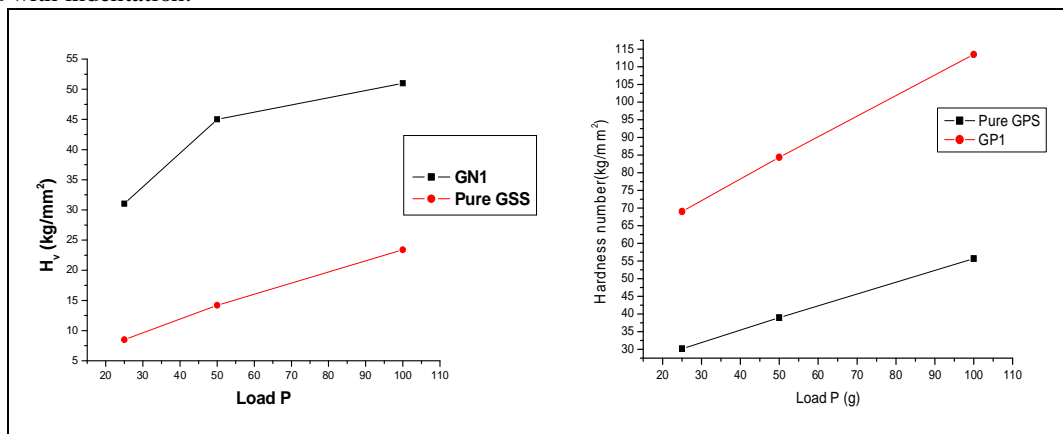


Figure 5: Hardness behaviour for the pure and Ni²⁺ doped GSS and GPS crystals(From Left: Pure GSS and GN1, Pure GPS and GP1)

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The results obtained indicate that the addition of Ni^{2+} ion increases the hardness of both the pure and Ni^{2+} ion doped GSS and GPS crystals significantly.

IV. CONCLUSION

Pure and Ni^{2+} doped glycine sodium sulphate (GSS) and glycine potassium sulphate(GPS) single crystals have been successfully grown by the free evaporation method and characterized. The observed lattice parameters and PXRD patterns indicate no lattice distortion due to Ni^{2+} doping in both the cases (GSS and GPS). It is also observed that doping with Ni^{2+} ion increased the transmittance in the UV range in both the cases. Micro hardness measurements indicate that the pure and Ni^{2+} ion doped GSS and GPS belong to soft material category and the addition of Ni^{2+} ion increases the hardness of both the crystals significantly.

REFERENCES

- [1]D.R. Askeland, P.P. Phule, "The Science and Engineering of materials" Thomson, 2003.
- [2]A.S. Haja Hameed, P. Anandan, R. Jayavel, P. Ramasamy and G. Ravi "Synthesis, growth and characterization of nonlinear optical material" J. Cryst. Growth, volume 249, pp316-320, 2003.
- [3]D. PremAnand, M.G. Mohamed, S.A. Rajasekar, S. Selvakumar, A.J. Arul Pragasam and P. Sagayaraj, "Growth and characterization of pure benzophenone and Iodine doped benzoyl glycine singlecrystals" Mater. Chem. Phys. , Volume 97,pp 501-505, 2006.
- [4]H.A. Petrosyan, H.A. Karapetyan, M.Yu. Antipin and A.M. Petrosyan J. Cryst. Growth, volume 275, pp1919-1925, 2005.
- [5]S. Haussuhl, H.A. Karapetyan, R.P. Sukiasyan and A.M. Petrosyan "Structure and properties of orthorhombic L-arginine formate" Cryst. Growth Des .volume 6pp2041- 2046, 2006
- [6]Aggarwal, M.D., Stephens, J., Batra, A.K., and Lal, R.B., "Bulkcrystal growth and characterization of semiorganic nonlinear opticalmaterials", J. Optoelectron. Adv.Mater.,**5**, pp. 555-562, 2003.
- [7]Fleck M, Becker P, Bayarjargal L, Ochrombel R, and Bohaty L, "Crystal growth, crystal structure and physical properties of polarorthorhombic tris (glycine) zinc chloride", Cryst. Res. Tech. Vol. 43,pp. 127-134, 2008.
- [8]H. Lipson and H. Steeple, "Interpretation of X-ray power Diffraction Patterns", MacMillan, New York, 1970.
- [9]S.K. Kurtz and T.T. Perry, "A powder technique for the evaluation of nonlinear optical materials" J. Appl. Crystallography volume 9 pp 3798-3813 , 1968.
- [10]R.S. Krishnan, K. Sankaranarayanan and K. Krishnan, "Raman and Infrared spectra of Amino acids" J. Indian Inst. Sci ., volume 55, 66-116, 1973.
- [11]R. Sankar, C.M. Ragahvan, R. Mohan Kumar and R. Jayavel J. Cryst.Growth, volume 309,pp30-36, 2007.
- [12]Desai C. C, and Rai J. L, "Microhardness studies of SnI_2 and SnI_4 single crystals", Bull. Mater.Sci., Vol. 5, pp. 453-457, 1983.

BIOGRAPHY

A. KAROLIN (the candidate) was born on July 15, 1973 in Kanyakumari District of Tamilnadu. She has acquired B.Sc. (1993), M.Sc. (1995), M. Phil (2003) degrees from Manonmanium Sundaranar University.

She has about 7 years of teaching experience and presently she is an Assistant Professor in the Department of Physics, Muslim Arts College, Thiruvithancode. She has about four years of research experience in the field of Crystal Growth and Characterization. She has, to her credit 8 research papers presented in various national conferences and 5 research papers published (and to be published) in various refereed international journals and proceedings.