Research Paper

Growth kinetics, Spectral and Optical properties of Glycine mixed Sodium Nitrate crystal

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Abstract

Single crystals of glycine mixed sodium nitrate (GSN) have been grown by isothermal solvent evaporation technique at ambient temperature. Crystal growth parameters such as growth rate, metastable zone width and nucleation parameters for GSN have been determined. Spectral and optical characteristics of GSN have been investigated. The optical energy gap of GSN crystal is 4.034eV. GSN crystal is optically transparent in the visible region with lower transmission cutoff at 265 nm.

Key words: spectral, optical crystal growth, glycine complex

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1. Introduction

Considerable interest in some optically nonlinear semi-organic crystals has developed in recent years due to their important role in electro-optic modulators, high density optical memories color displays, in the realization of signal processing devices involving the generation of new frequencies, signal amplification emission or oscillation etc. [1]. The basic requirement for a material to be suitable for nonlinear optical (NLO) applications is that it must have very high nonlinearity. Although many materials have high nonlinearity, their practical application is limited because of their inherent limitations. Currently the concentration is more on amino acids and their complexes because they combine the advantages of organic crystals among with that of the inorganic materials.

Glycine has the distinction of being the only amino acid which forms many addition compounds with inorganic acids and salts, besides forming metallic complexes. Most of the glycine complexes show ferro electricity at high temperature [2-4]. Glycine mixed sodium nitrate viz: glycine mixed sodium nitrate (GSN) is a nonlinear optical crystal [5]. The crystal structure of GSN [6] has been determined. It has been reported that GSN has optical nonlinearity comparable to that of KDP. However no investigation has been made on the growth kinetics, spectral and optical properties of GSN crystal. This paper presents the results and analysis of our study on GSN crystals.

2. Experimental procedure

2.1 Crystal Growth kinetics

GSN crystals were grown from aqueous solution by slow evaporation technique at ambient temperature. The starting materials were analytical grade reagents glycine and sodium nitrate. They are taken in the molar ratio of 1:1 and dissolved in double distilled water. The solution was heated on a water bath maintained at a temperature of 34oC until the volume was sufficiently reduced. Small transparent single crystals with perfect external form were obtained through spontaneous nucleation after three days of solution evaporation. In order to confirm the phase purity of GSN X-ray powder diffraction was recorded using SCINTAG powder x-ray diffractometer with Cu Kα radiation (λ =1.5418A) and index them. The sample was scanned in the 2θ values from 10° to 50° at a rate of 2°/min. The observed XRD pattern was identical with the XRD data reported [5], confirming the phase purity of the crystal. The powder XRD of GSN (figure 1) is entirely different from the XRD pattern of γ - glycine (figure 2) .

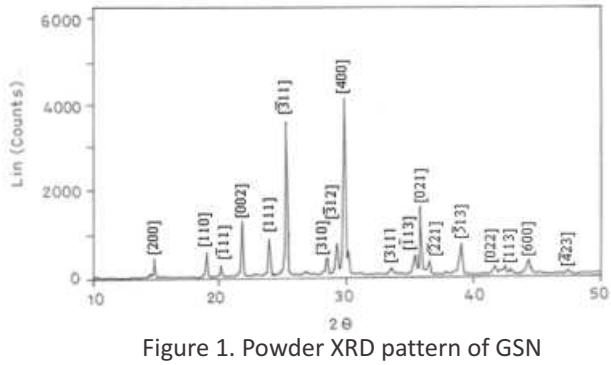

Figure 1. Powder XRD pattern of GSN

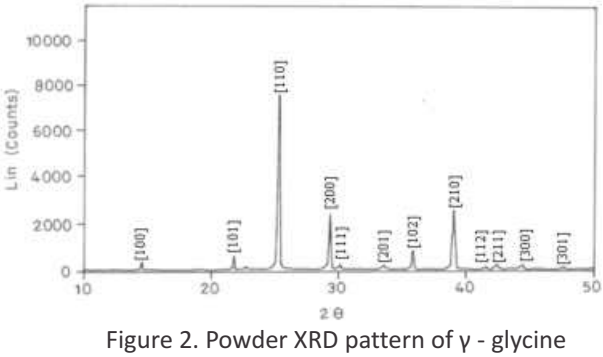

Figure 2. Powder XRD pattern of γ - glycine

Defect free crystals were selected as seeds and suspended in the mother solution maintained at constant temperature of 34°C which was allowed to evaporate in a crystal growth apparatus. Good crystals with larger dimensions were obtained within a week. The crystal faces were indexed using Enraf CAD4 diffractometer along with a four circle goniometer. GSN crystal with well developed surfaces was mounted on the goniometer and the various faces of the crystal were indexed.

In solution growth technique, the size of a crystal depends on the amount of the material available in the solution which in turn is decided by the solubility of the material in that solvent. The solubility of synthesized pure glycine and sodium nitrate mixed glycine has been determined in water. This was performed by adding water maintained at constant temperature to a known quantity of the material till the material was completely dissolved.

Good quality GSN and γ-glycine crystals were collected and finely powdered.. Two hundred milliliters of saturated GSN and γ-glycine solution was prepared in accordance to the solubility diagram and loaded in a constant temperature bath. The solutions were stirred continuously for five hours for stabilization. While stirring the solution the temperature of the bath was reduced at the rate of 5°C per hour. The temperature at which the first speck of the particle has been observed corresponds to the width of metastable zone. The experiment was repeated for saturated solutions at temperatures 35, 40, 45, 50°C.

Attempts were made to find the growth rate of the crystal along a and c-axis of the GSN crystal. For this the seed crystal was monitored continuously. The dimensions of the crystal along the a and c-axis were measured at regular time intervals.

The optical transmission of glycine mixed sodium nitrate for the wavelengths between 200 – 2500nm was recorded using Varian Cary 5E UV-VIS-NIR spectrometer. Laser Raman spectra is used to confirm the presence of functional groups in glycine mixed sodium nitrate crystals. Laser Raman spectra was recorded in the range 400-4000cm^{-1}. In order to qualitatively analyze the presence of functional groups in GSN, Fourier transform infrared (FTIR) spectrum was recorded in the range 400-4000 cm-1 using the Perkin Elmer grating Infrared spectrometer. The sample used was in pellet form in KBr phase. The characteristic absorption peaks were observed in the range from 400 to 3000cm^{-1}.

3. Results and Discussion

The morphological analysis reveals that the GSN crystal is a polyhedron with 12 developed faces. The crystal was found to be transparent and was bound by 100, 111, 11 , 00 , 1 , 11 faces, There is a pair of parallel faces, which is a pinacoid and indexed as 100. This is the most prominent face and dominates the crystal morphology. The other pinacoids are 111 and 11$\bar{1}$. They are inclined with 100 face. Different faces of the crystal in the order of prominence are as follows: 100>111>11$\bar{1}$>00$\bar{1}$>$\bar{1}$1$\bar{1}$>$\bar{1}$11. The morphology of the grown crystal is shown in Figure 3.

The variation of solubility of pure glycine and GSN with temperature between (30°C and 60°C) is shown in Figure 4.

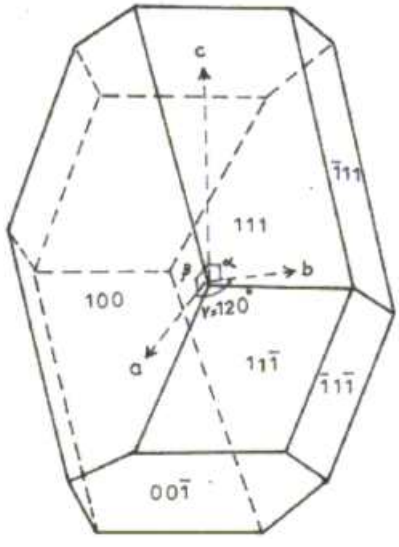

Figure 3. Morphology of Glycine mixed sodium nitrate

The solubility data could be fitted to an equation of the form S = AT2+BT+C where A,B, and C values for pure glycine and GSN

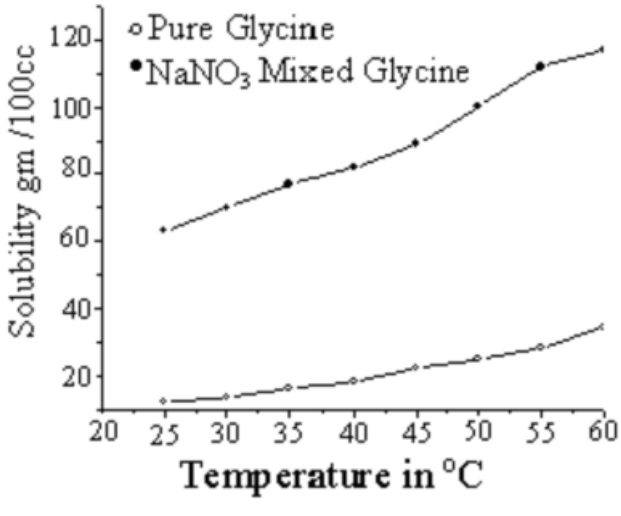

Figure 4. Solubility of glycine and Glycine mixed Sodium Nitrate

samples were given in Table 1. S and T are the solubility expressed in gm/100cm3 and temperature in degree Celsius respectively. The solubility of GSN was found to be 63gm/100cc of water and that of pure glycine is 12.5gm/100cc. GSN has a positive temperature coefficient of solubility. Therefore, slow cooling of aqueous solution of GSN could be attempted to grow bulk crystals.

Table 1: Solubility data of γ-glycine and GSN

Sample	A	B	C
Glycine	0.01002	0.23321	11.60298
GSN	0.01333	0.44762	43.89286

The metastable zone width of GSN and γ-glycine for different saturation temperatures are shown in Figure 5. The metastable zone width of γ-glycine was found to be less than that of GSN. It is obvious from the figure that the zone width for both solutions decreases as the temperature decreases.

The variation of the growth rate of the crystal with time is shown in the Figure 6. From the graph it follows that, along c-axis the crystal grows rapidly in the beginning and it grows at a lower rate after 6 hours. However the growth rate along a -axis is very less than c-axis.

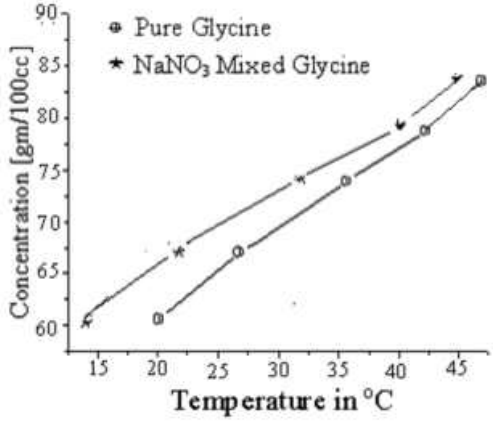

Figure 5. Metastable zone width of Glycine mixed sodium nitrate

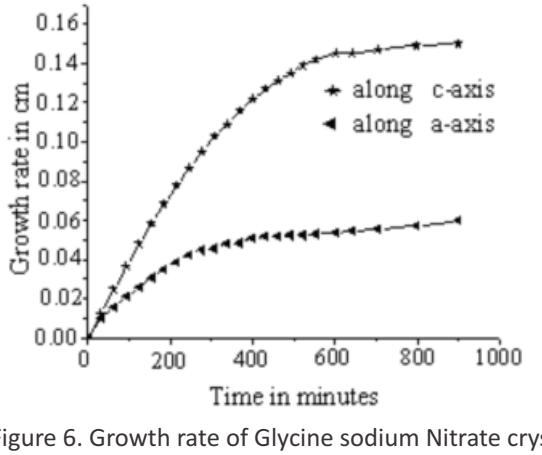

Figure 6. Growth rate of Glycine sodium Nitrate crystal.

From the UV-VIS-NIR studies we observed that the crystal is found to be transparent in the entire UV & visible spectral regions extending between 1000 and 2000nm, the absorbance is minimum, suggesting that the crystal is highly transparent and it is very much required for NLO applications. Above 2000nm slight increase in the absorbance is observed. Hence GSN crystal is optically transparent in the UV- visible region with lower transmission cutoff is observed at 265 nm. The plot of transmittance vs wavelength (nm) is shown in Figure 7.

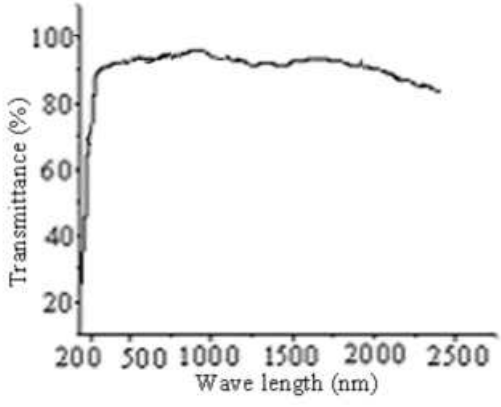

Figure7. UV VIS IR Spectra of glycine mixed sodium nitrate

Optical properties of crystalline materials give information regarding the composition nature and quality of the crystal. In a crystalline material the region of transparency to electromagnetic radiation defines the intrinsic loss mechanisms and also theoretical transmittance achievable within this region. The transparent spectral region in insulators is defined at short wavelengths by electronic transitions across the band gap and at long wavelengths by lattice vibrations. The band gap of the material Eg, sets the transmittance limit at short wavelength cut off (λ_c) is defined by $\lambda_c = hc/E_g$ in which h is Plank's constant and c is the velocity of light. The optical band gap Eg as given by Tauc's graph [7] between the product of absorption coefficient and the incident photon energy $(\alpha h\nu)^{1/2}$ with the photon energy hν at room temperature shows a linear behavior that can be considered as the proof for direct transition. Hence assuming a direct transition between valence and conduction bands, the optical energy gap (Eg) is estimated by the extrapolation of the linear portion of the curve to a point at which $(\alpha h\nu)^{1/2}$ is equal to zero [8,9]. The optical energy gap has been estimated using the Tauc's method and the optical energy band gap has been found to be 4.03eV. The variation of $(\alpha h\nu)^{1/2}$ vs energy is shown in Figure 8.

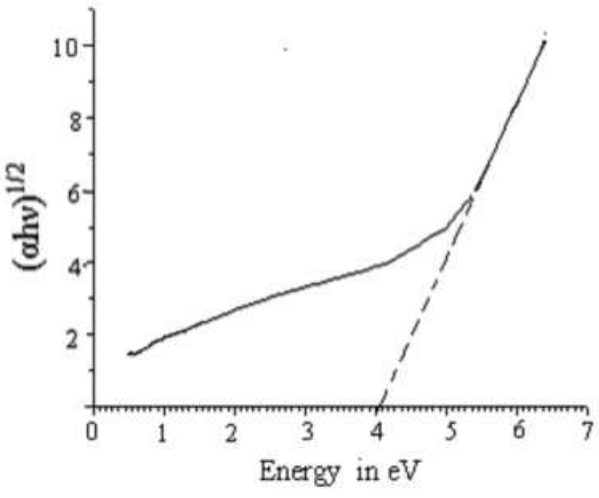

Fig. 8. Optical Energy gap of Glycine mixed sodium nitrate

In Laser Raman spectra the peaks observed at 591.9 and 683cm^{-1} are attributed to carboxylate groups while the absorption peak at 3027.8 cm^{-1} is NH stretching attributed to NH3 group. Of the remaining peaks, those at 901.5, 1334.6, and 2973.1 cm^{-1} are attributed to CH2 group while the peaks at 1057.8 and 1454 cm^{-1} are assigned to NO3 and CH groups respectively. The characteristic peaks of laser raman spectra are shown in Figure 9.

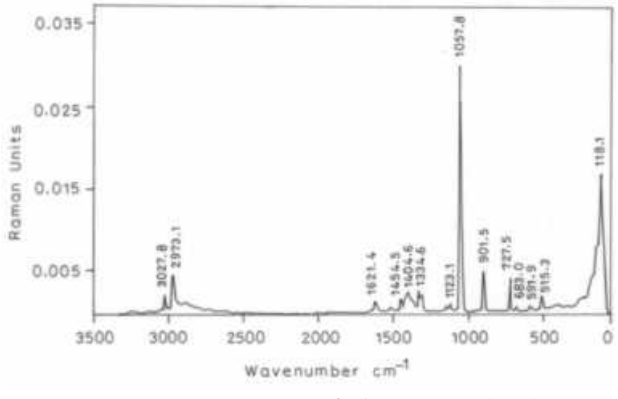

Figure 9. Laser Raman Spectra of Glycine mixed sodium nitrate

From the FTIR spectra the characteristic absorption peaks were observed in the range from 400 to 3000cm^{-1} and are shown in Figure 10.

Free glycine exists as zwitterions in which carboxyl group is present as carboxylate ion and amino group exists as ammonium ion. The absorption due to carboxyl ate group of GSN are observed at 503.4, 605.6 cm^{-1} and 887.2 cm^{-1} respectively. The symmetric and asymmetric modes of COO- are observed at 1585.4 and 1390.6 cm^{-1}. The absorption peaks due to NH_3+ group of GSN are observed at 2171.7, 2603.7, and 2754.2cm^{-1}. The asymmetric and symmetric NH bends of NH_3+ are positioned at 1124 and 1487cm^{-1} respectively. Nevertheless, from the presence of carboxylate ion it may be concluded that glycine molecules exists in zwitterionic form in GSN. The presence of NO_3- group in GSN is confirmed by the absorption peak at 1041.5cm^{-1}. Other peaks at 925.8cm^{-1}, 1326.9cm^{-1}, and 2887.2cm^{-1} are attributed to CH_2 groups from a comparison of spectra with that of glycine [10]. The position of the peaks with the proposed assignments is shown in Table 2.

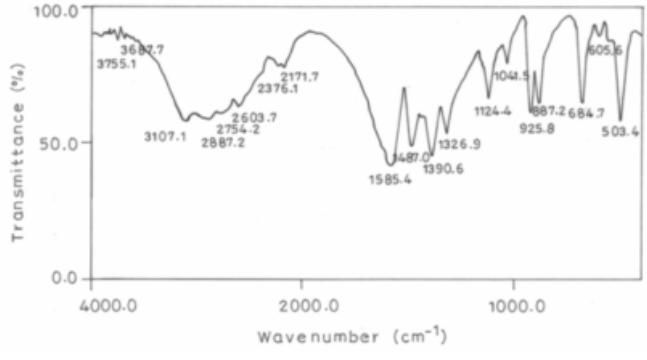

Figure10. FTIR Spectra of glycine mixed sodium Nitrate.

Table 2: Laser Raman and IR frequencies of Glycine mixed Sodium nitrate crystals (Wave number in cm)

Infrared	LaserRaman	Assignment
3755.1	-	Combination band
3687.7	-	Combination band
3107.1	3027.8	NH_3^+
2887.2	2973.1	CH_2
2754.2	-	NH_3^+
2603.7	-	NH_3^+
2171.7	-	NH_3^+
1585.4	1621.4	COO^-
1487	454.5	NH_3^+
1390.6	-	COO^-
1326.9	1334.6	CH_2
1124.4	1123.1	NH_3^+
1041.5	1057.8	NO_3
925.8	901.5	COO^-
887.2	-	COO^-
-	727.5	CH_2
684.7	683	COOH
605.6	591.9	COO^-
503.4	515.3	COO-

4. Conclusion

The morphological analysis reveals that the crystal is a polyhedron with 12 developed faces. The optical energy gap of GSN crystal is 4.03eV. GSN crystal is optically transparent in the visible region with lower transmission cutoff at 265 nm. The growth rate of GSN along a –axis is very less than c-axis. The metastable zone width of γ-glycine was found to be less than that of GSN.

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