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Research Article

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Nucleation kinetics, growth and studies of diglycine magnesium sulfate crystals

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ABSTRACT

A semi-organic crystal viz. diglycine magnesium sulfate crystal has been grown by solution method with slow evaporation technique. The solubility of the sample was carried out by gravitational method at various temperatures. Nucleation parameters were evaluated at different values of supersaturation ratio. The grown crystal was subjected to single crystal XRD studies to find the lattice parameters. Microhardness was measured by using a Vickers microhardness tester at different applied loads. The grown crystal does not show second harmonic generation (SHG) behavior. Functional groups of the sample have been identified. Complex impedance values were measured at different frequencies and temperatures and the results are discussed.

Key words: Semi-organic; gycine complex; XRD; hardness; impedance; FTIR; centrosymmetric

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INTRODUCTION

Glycine is one of the fundamental amino acids and it has the non-chiral zwitterionic form. It crystallizes in six different forms viz. α, β, γ, δ, ε and β'- forms. α-glycine has no asymmetric carbon atom and is optically inactive. It has been reported that glycine combines with sulpuric acid, nitric acid, calcium chloride, calcium nitrate, barium chloride, silver nitrate to form useful single crystals [1-6]. Many of the glycine complexes are observed to be non-centrosymmetric and showing nonlinear optical (NLO) effects and the NLO effects have been given increasing attention due to its wide application in the area of laser technology, optical communication and data storage technology [7,8]. Nonlinear optics is completely, a new effect in which light of one wavelength is transformed to light of another wavelength. In this work, glycine is combined with magnesium sulfate to produce diglycine magnesium sulfate crystal and it is subjected to various studies.

EXPERIMENTAL SECTON

Crystal growth

Glycine and magnesium sulfate were taken in the stoichiometric ratio 2:1 and the required quantity of the reactants were dissolved in the double distilled water to prepare the saturated solution. The solution was stirred for about to 2 hours using a hot plate magnetic stirrer to ensure homogeneous temperature and concentration over entire volume of the solution. The solution was filtered and transferred to a crystal growth vessel and crystallization was allowed to take place by slow evaporation. Transparent, colorless crystals were harvested in a period of 25 days.

RESULTS AND DISCUSSION

3.1 Measurement of solubility

Solubility is defined as the amount of solute in grams present in 100 ml of saturated solution at a particular temperature and it corresponds to saturation between a solid and its solution at the given temperature and pressure.

The sample finely powdered and used for the solubility study. A known amount of the solvent was taken in a beaker and the saturated solution was prepared using the double distilled water as the solvent by adding the sample. Initially the solution was kept at 30 °C and stirred continuously using the magnetic stirrer for about one hour. After attaining the saturation, 10 ml of the solution was taken in a petri dish and the solvent was evaporated by heating it slightly and then the solubility was determined gravimetrically [9]. The procedure was repeated for different temperatures between 30 and 60 °C. Water was found to be a better solvent for growing single crystals of diglycine magnesium sulfate because of the high solubility of the sample in water. The solubility curve for the sample is provided in the figure 1. It is noticed from the figure that the solubility of the sample increases as the temperature of solution increases and hence the sample has positive temperature coefficient solubility. Solubility data of a material gives idea of solute available for the growth and hence defines the total size limit of a crystal. Solubility of a material in a particular solvent defines the supersaturation which is the driving force for the rate of crystal growth. Hence solubility studies are essential for solution method of crystal growth. The solubility curves of the samples will be useful to prepare saturated solutions, supersaturated solutions and also to carry out the nucleation kinetic studies.

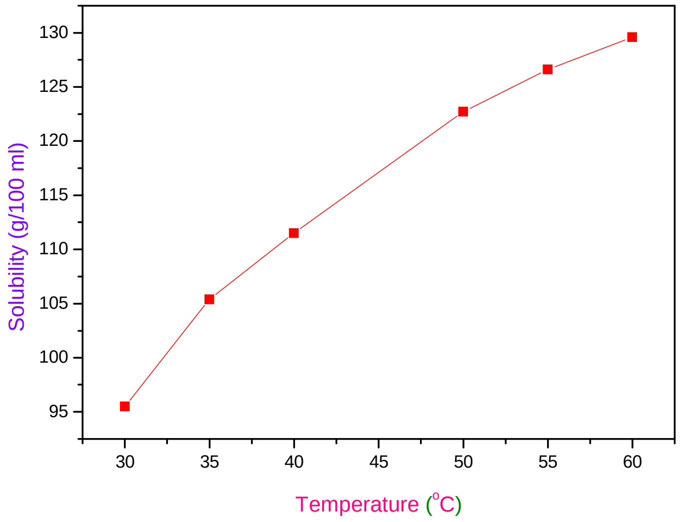

Fig.1: Solubility curve for diglycine magnesium sulfate crystal

3.2 Nucleation kinetics - theory and experiment

Nucleation is an important phenomenon in crystal growth and it is the precursor of the overall crystallization process. Nucleation is consequently a study of the initial stages of the kinetics of crystallization. Nucleation may occur spontaneously or it may be induced artificially. There are homogeneous and heterogeneous nucleation and these are initial stage of the crystallization process. On the other hand, nuclei are often generated in the vicinity of crystals or dust particles present in the supersaturated system. This phenomenon is referred to as secondary nucleation. Primary nucleation is believed to be initiated in a series of bimolecular collisions that forms an aggregate of a small number of molecules of the dissolved material. Embryos below a critical cluster size are unstable and may disintegrate, whereas embryos that exceed this critical cluster size will become stable nuclei and will grow. One should keep in mind that the size of these embryos is still beyond the limit of detection, even by dynamic light scattering. When few atoms, ions or molecules join together in a supersaturated solution, a cluster or nucleus is formed and the overall excess free energy (ΔG) between the nucleus and solute in the supersaturated solution is given by

$$\Delta G = \Delta G_s + \Delta G_v = 4\pi r^2 \sigma + (4/3)\pi r^3 \Delta G_v'$$

where ΔG_s is the surface excess free energy and ΔG_v is the volume excess free energy. Usually nucleus formed in supersaturated solution is assumed to be spherical in shape. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly and a bright sparkling particle is seen. The time of observation of the sparkling particle in the undisturbed solution from the time at which the solution reaches experimental temperature is called the induction period (τ).The expression for the induction period in terms of Gibbs free energy is given by

$$\ln \tau = -B + \Delta G / kT$$

where B is a constant, k is the Boltzmann's constant, T is the absolute temperature. This energy will be maximum for certain value of r, which is known as critical radius. Nuclei formed with radius greater than this r are stable and decrease their free energy by growing. The expression for critical radius is given by

$$r^{*}= 2\, \sigma v\, N / RT\, ln\, S$$

where R is the universal gas constant, S is the supersaturation ratio and N is the Avogadro's number. The slope (m) of the plot of $1/ (ln\, S)^2$ against $ln\, \tau$ and the Gibbs free energy change were determined using the following equation.

$$m = (16\, \pi\, \sigma^3\, v^2\, N^3) / (3R^3\, T^3)$$

$$\Delta G^{*} = mRT / [N\, (ln\, S)^2]$$

The interfacial surface tension is given by

$$\sigma = (RT/ N)\, [3m / (16\, \pi v^2)]^{1/3}$$

The number of molecules in a critical nucleus is found using the following equation

$$n = (4/3)\, (\pi/v)\, r^{*\,3}$$

The rate of nucleation can be expressed by an Arrhenius-type equation

$$J = A \exp (-\Delta G^{*} / k\, T)$$

where A is the pre-exponential factor (approximately $A= 1 \times 10^{24}$ for solution), ΔG^{*} is the Gibbs free energy. The nucleation parameters such as radius of the critical nucleus, Gibbs free energy change, interfacial tension and the number of molecules in the critical nucleus can be determined using the above equations. The experimental procedure for finding the nucleation parameters is given below.

Nucleation kinetic studies were carried out by dissolving the synthesized salt in water at different values of supersaturation ratio. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly and a bright sparkling particle is seen. The time interval between the creation of supersaturation and the formation of critical nuclei is called as the induction period (τ) and it is influenced by supersaturation, type of solvent, purity of the sample, temperature, pH value of the solution etc. To calculate the nucleation parameters, induction period is necessary and the experiment for measuring induction period for diglycine magnesium sulphate was performed at selected degrees of supersaturation (S), viz. 1.2, 1.25, 1.3, 1.35 and 1.4 at room temperature (30 ^{o}C) by isothermal method [10]. The results show that the nucleation parameters such as Gibbs free energy change, critical radius, number of molecules in the critical nucleus decrease with increase of supersaturation ratio and the nucleation rate is found to be increasing with increase of supersaturation ratio. To harvest big-sized crystal, the nucleation rate must be low and hence supersaturaiton ratio of value less than 1.2 is more suitable for growth of bulk crystals of diglycine magnesium sulfate.

Table 1: Values of critical nucleation parameters for diglycine magnesium sulfate crystals

S	$\Delta G^{*} \times 10^{-20}$ (joules)	$r^{*} \times 10^{-10}$ (m)	n	$J \times 10^{24}$ nuclei/s/volume	$\sigma \times 10^{-3}$ J/m^2
1.2	1.104	9.034	28	5.257	2.954
1.25	0.950	6.946	19	6.120	
1.3	0.734	5.240	15	7.452	
1.35	0.578	4.362	9	9.145	
1.4	0.398	3.504	6	10.234	

3.3 Single crystal XRD studies

The grown diglycine magnesium sulfate crystal was subjected to single crystal X-ray diffraction study to obtain the lattice parameters and this study was carried out using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK$_{\alpha}$ (λ= 0.71069 Å) radiation. The obtained lattice parameter values are a= 6.002(2) Å, b= 6.697(3) Å, c=13.295 (4) Å, α = 86.34 (2)^{o}, β=83.45(4)° , γ= 88.74 (3)^{o} and the results indicates that the grown crystal crystallizes in triclinic structure. The obtained values are found to be similar with the data obtained by other authors [11].

3.4. SHG studies

The second harmonic generation (SHG) behavior of the powdered material was tested using the Kurtz and Perry method [12]. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was passed through the powdered sample of diglycine magnesium sulfate. From the experiment, it is noticed that there is no green light (no SHG emission) emitted from the sample and it concluded that diglycine magnesium sulfate is not a second harmonic generator and this also confirms that this crystal crystallizes in a centrosymmetric structure.

3.5 FTIR spectral studies

FTIR study is used to identify the functional groups of the samples. The FTIR spectrum of diglycine magnesium sulfate crystal was recorded and it is shown in the figure 2. The broad envelope in the higher wave number region between 3100 and 2500 cm^{-1} was due to hydrogen interaction with other atoms such as N-H stretching of NH_2 and C-H of CH_2 stretching. The ν_{as} COO^- mode gives rise to the absorption observed at 1575 cm^{-1}. The strong band 1443 cm^{-1} is attributed to the ν_s COO^- mode. The carboxylic groups scissoring modes (δ COO^-) are expected in the region of 650-690 cm^{-1}. The peaks observed at 891 and 906 cm^{-1} are assigned to C-C-N stretching vibration. The band at 606 cm^{-1} is due to the wagging vibration of COO^- structure. Thus the functional groups of the sample have been identified.

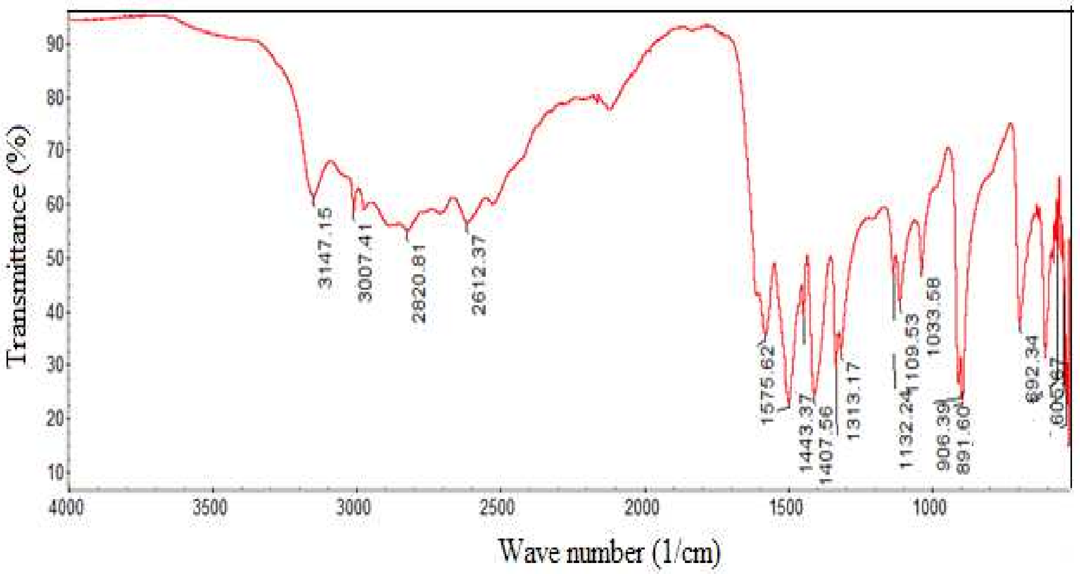

Fig. 2: FTIR spectrum of diglycine magnesium sulfate crystal

3.6 Microhardness studies

The mechanical strength of crystals was tested by carrying out microhardness studies by applying different low loads. The hardness of a solid is defined as its resistance to local plastic/permanent deformation and the simplest way to obtain it is to press a hard indenter of known geometry and to divide the applied load (P) by the area (A) of the indentation produced, i.e. hardness = P/A. The hardness of a material is usually calculated from the measured value of indentation diagonal length (d) produced by an applied load. The mean diagonal length of the indentation or impression was measured using a LEITZ microhardness tester, fitted with a Vickers diamond pyramidal indenter. The well polished crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied in a fixed interval of time. The indentation time was kept 10 s for all the loads. For each load, several indentations were made and the average value of the diagonal length (d) was used to calculate the microhardness.Vickers microhardness number was determined using the relation $H_v = 1.8544\ P/d^2$ where P is applied load and d is diagonal length of indentation impression [13]. The plot H_v versus P is shown in the figure. It is observed from the results that the hardness number was found to increase with the load. This can be explained qualitatively on the basis of depth of penetration of the indenter. For small loads, only a few surface layers are penetrated by the indenter. The measured hardness is the characteristics of this layer and H_v increases with load in this region. With increase in load, the overall effect is due to surface as well as inner layers of the sample.

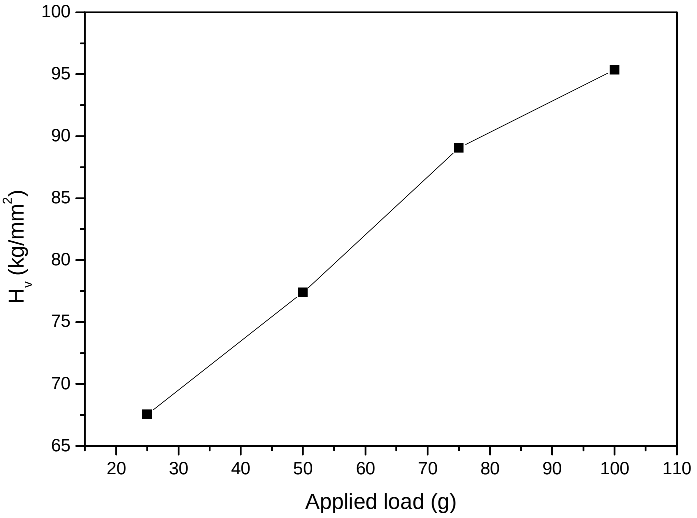

Fig.3: Variation of microhardness number with the applied load for diglycine magnesium sulfate crystal

3.7 Impedance analysis

Impedance technique analyzes the ac response of a system to a sinusoidal perturbation and subsequent calculation of the impedance as a function of frequency of the perturbation. The frequency dependent properties of a material are often represented in terms of complex impedance as $Z^* = Z^{'} - jZ''$ where Z' is the real part and Z'' is the imaginary part of impedance. The complex impedance of the sample demonstrated as the sum of the single RC circuit with parallel combination [14]. The impedance data were obtained for diglycine magnesium sulfate at different frequencies and temperatures using an impedance analyser (Model: IM6 ZAHNER/Germany-Electrochemical Workstation with Galvanostat). The variations of real part of impedance (Z) and imaginary part of impedance with frequency at temperatures of 30 °C and 70 °C for diglycine magnesium sulfate sample are shown in the figures 4 and 5. The results show that the complex impedance (Z) of the sample decreases with increase of frequency and temperature. The coincidence of the impedance at higher frequencies in the grown sample indicates the presence of space charge polarization. The decrease of impedance with increase of temperature of the sample indicates the negative temperature coefficient of resistance behavior.

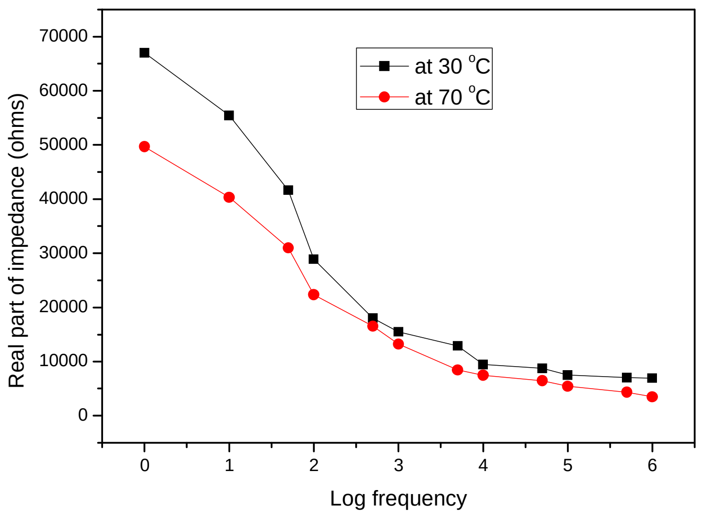

Fig.4: Variation of real part of impedance with frequency at temperatures of 30 and 70 °C

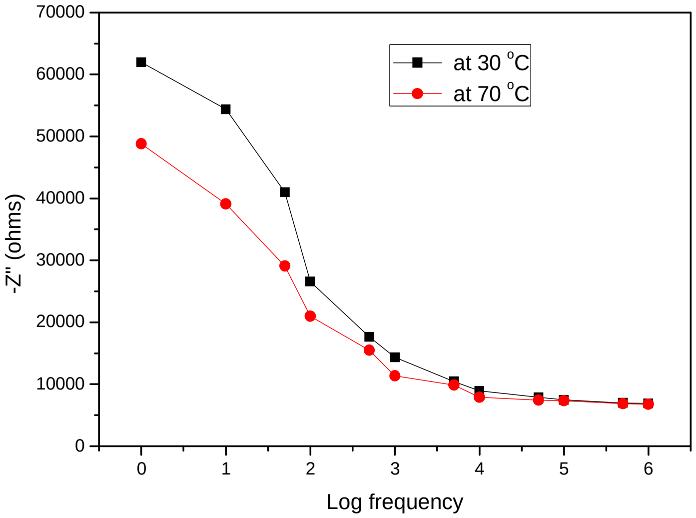

Fig.5: Variation of real part of impedance with frequency at temperatures of 30 and 70 °C

CONCLUSION

Solubility and nucleation kinetic studies for the grown sample of diglycine magnesium sulfate were carried out. Solubility of the sample is found to increase with increase of temperature. Classical theory of nucleation kinetic process was detailed and induction period was measured and it decreases with the supersaturation ratio. Critical nucleation parameters such as interfacial tension, radius of critical nucleus, Gibbs volume energy change and number of molecules in the critical nucleus were evaluated. Single crystal XRD study reveals the triclinic structure of the grown crystal. It is observed that there is no SHG emission from the sample. The microhardness study was carried out to understand the mechanical strength of the crystal. Real part and imaginary part of impedance have been measured for the sample to understand the electrical processes that are taking place in the grown crystalline sample.

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