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Research Paper

Growth and Investigation on the Nucleation Kinetics, Optical and Dielectric Properties of Zinc Succinate NLO Single Crystals

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Single crystals of Zinc Succinate (ZS) were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic system with the space group C2. Nucleation parameters such as Gibbs free energy, radius of critical nucleus, critical free energy barrier and number of molecules in the critical nucleus and nucleation rate have also been investigated. The optical band gap is found to be 2.95eV. The transmittance of ZS crystal has been used to calculate the refractive index n, both the real ε_r and imaginary ε_i components of the dielectric constant as functions of wavelength. Dielectric constant and dielectric loss measurements were carried out at different temperatures and frequencies.

Key Words: Nucleation; Metastable Zone Width; Interfacial Energy; NLO Single Crystal; Optical Transmission; Dielectric Studies

1. Introduction

Nonlinear optics (NLO) is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the emerging technologies in areas such as telecommunications, signal processing and optical interconnections. In recent years there has been a growing interest in the search for materials with large second-order nonlinearities because of their practical utility as frequency doublers, frequency converters and electro-optic modulators by means of second-harmonic generation, parametric frequency conversion (or mixing) and the electro-optic (EO) effect. Nonlinear optical crystals should meet several requirements, such as large phase-matchable nonlinear optical coefficient, a wide optical window around the visible region, mechanical and chemical stability and a high laser damage threshold for device fabrication [1, 2]. In the present work, an attempt has been made to grow single crystals of Zinc Succinate (ZS) by slow evaporation method. $Zn(C_4H_4O_4)$ crystallizes in monoclinic system with space group C2, and the cell parameter a = 7.579Å, b = 5.976Å, c = 6.265Å, β = 108.45°. The second harmonic output intensity of Zn $(C_4H_4O_4)$ was 6.5 times as large as KDP [3]. Knowledge of the solubility of the material to be grown and stability of the solution in the vicinity of the equilibrium point, is essential for the successful development, optimization, and scale up of a crystallization process. In the present study, investigations have been made to evaluate the interfacial tension (γ), the induction period (τ) and hence to calculate critical radius (r*), number of molecules in the critical nucleus (i*) and Gibb's free energy (ΔG*) for the formation of ZS. We also report optical and dielectric properties of ZS single crystals. The results obtained are discussed in details.

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2. Experimental Procedure

2.1 Synthesis

The starting materials were of analytical reagent, and the synthesis and growth process were carried out in aqueous solution. ZS compound was synthesized by taking hexahydrate zinc nitrate and succinic acid in a 1:1 stoichiometric ratio. The calculated amount of hexahydrate zinc nitrate and succinic acid were dissolved in the deionized water of resistivity 18.2 MW/cm. The prepared solution was left to dryness at room temperature. Purity of the synthesized salt was improved by successive recrystallization process. Optically clear and defect-free seed crystals of ZS obtained by slow evaporation technique were used for bulk growth.

2.2 Solubility Studies

The solubility of ZS in water was determined in the temperature range between 30ºC and 50ºC at the interval of 5ºC. The temperature of the solution was maintained at the chosen constant temperature and continuously stirred using a motorized magnetic stirrer to ensure homogeneous temperature and concentration through out the volume of the solution. The saturated solution was maintained at equilibrium for about 1 day at a chosen temperature and then the solubility was gravimetrically analyzed. The same process was repeated for different temperatures and the solubility curve was plotted as shown in Fig. 1.

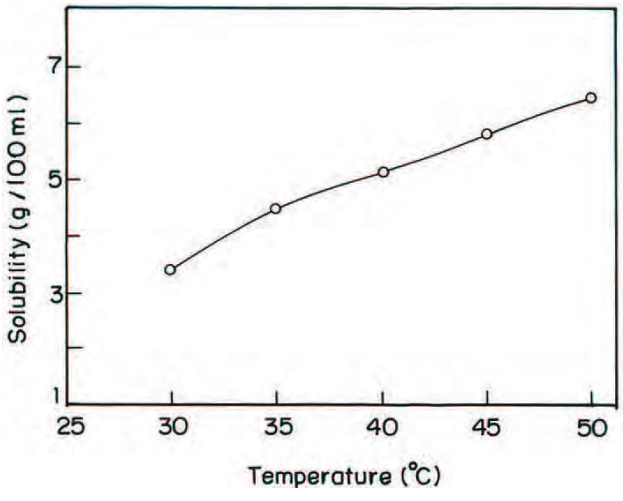

Fig. 1: The solubility of ZS

2.3 Metastable Zone Width and Induction Period

The saturated solution of ZS was obtained from solubility data. The metastable zone width was measured by the conventional method [4] in which a constant volume of 100 ml of the solution was taken in a beaker. The beaker was kept in a constant temperature bath at the saturation temperature. The bath is capable of controlling the temperature with an accuracy of ± 0.01°C. The solution was heated 5°C above the supersaturation temperature for homogenization. It was continuously stirred using a motorized stirrer to ensure homogeneous concentration and temperature throughout the entire volume of the solution. After the stabilization, the temperature of the bath was reduced at a rate of 0.5°C per minute. The temperature at which the first speck of a particle appeared was noted (Fig. 2). The first speck of crystal obtained is taken as the critical nucleus. The time taken for the formation of the critical nucleus is called induction period. The experiment was repeated for solutions saturated at temperatures 30°C, 35°C, 40°C, 45°C and 50°C. Variation of induction period as a function of super saturation ratio is shown in Fig. 3.

2.4 Interfacial Tension

Interfacial tension of the crystal-solution interface is an important parameter involved in the theory of nucleation and growth kinetics. The classical homogeneous nucleation theory has been successfully tested for the nucleation of liquid solution and for

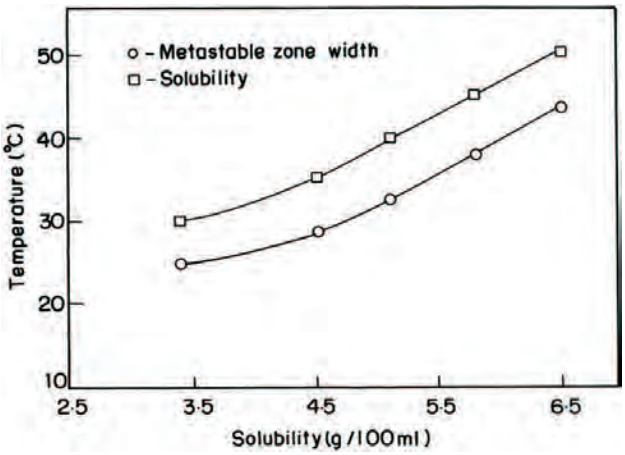

Fig. 2: The metastable zone width vs temperature of ZS

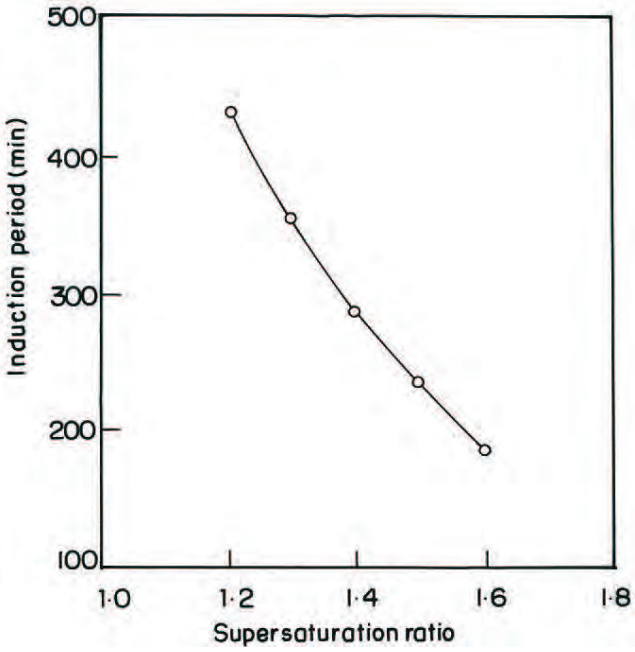

Fig. 3: Induction period *vs* supersaturation ratio

crystal formation in melts [5]. Interfacial tension in the present investigation has been calculated on the basis of the classical theory of homogeneous formation of spherical nuclei [6]

$$\ln \Gamma = -\ln B + \frac{16\pi\gamma^3 V^2 N}{3R^3T^3(\ln S)^2} \tag{1}$$

where V is the molar volume of the crystal. N is the Avogardo's number, R is the gas constant, γ-induction period of ZS solution at temperature T and B is constant. S is the supersaturaion ($S = C/C^*$), where C is the actual concentration and C^* is the equilibrium concentration.

Eq. (1) suggests a straight line for ln Γ against $1/(\ln S)^2$ and therefore is given

$$m = \frac{16\pi\gamma^3 V^2 N}{3R^3T^3} \tag{2}$$

Since ln B weakly depends on temperature therefore, the interfacial tension is evaluated from

$$\gamma^3 = \frac{3R^3T^3 m}{16\pi V^2 N} \tag{3}$$

2.5 Nucleation Parameters

In the present work, the nucleation parameters of the ZS materials have been evaluated. According to classical nucleation theory, the free energy required to form a spherical nucleus is given by

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \tag{4}$$

where ΔG_v is the energy per unit volume, γ is the interfacial tension and r is the radius of the nucleus. At critical state, the free energy formation obeys the condition d $(\Delta G)/\mathrm{d}r = 0$. Hence, the radius of the critical nucleus is expressed as

$$r^* = -\frac{2\gamma}{\Delta G_v} \tag{5}$$

where

$$\Delta G_v = -\frac{kT \ln S}{V}; \; S = C/C^*$$

The critical free energy barrier

$$\Delta G^* = \frac{16\pi\gamma^3 V^3}{3(\Delta G_v)} \tag{6}$$

The number of molecules in the critical nucleus is expressed as

$$i^* = \frac{4\pi(r^*)^3}{3V} \tag{7}$$

The nucleation rate J has been calculated using the equation

$$J = A\exp\left[\frac{-\Delta G^*}{kT}\right] \tag{8}$$

The calculated values of Gibbs free energy per unit volume, critical radius of nucleus, critical energy barrier, number of molecules in the critical nucleus and nucleation rate of the grown ZS crystals for various supersaturations are shown in the Table 1.

Table 1: Nucleation parameter of the ZS

S	ΔG_v	r^* (nm)	ΔG^*	i^*	J (nuclei/sec/ vol)
1.3	5.09	1.23	30.63	52.76	5.10×10^{27}
1.4	7.75	1.12	25.32	36.02	2.03×10^{28}
1.5	9.12	1.02	21.67	25.82	5.02×10^{28}
1.6	10.05	0.98	19.98	20.31	8.83×10^{28}

2.6 Crystal Growth

The ZS crystal was grown from low temperature solution growth using slow evaporation technique. Recrystallized salt of ZS was taken as a raw material. Saturated ZS solution was prepared at room temperature with deionized water as solvent, stirred well for about 2 hours and heated slightly to dissolve the undissolved particles. The suspended impurities were removed using a high-quality Whatman filter paper. The clear filtrate so obtained was kept aside unperturbed in a dust-free room for the growth of single crystals. Well defined, transparent crystal of average dimension 10 x 5 x 3 mm^3 was harvested collected at the end of the 20^{th} day. The grown crystal of ZS is shown in Fig. 4.

3. Single Crystal X-ray Diffraction

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD4 automatic X-ray diffractometer**.** Calculated lattice parameters are: a = 7.579Å, b = 5.976Å, c = 6.265Å, β = 108.451° and the crystals belongs to monoclinic system with space group is C2. These values are found to agree with the reported values [3].

4. Optical Studies

The UV-Vis-NIR spectrum was recorded with a highly transparent single crystal of 2 mm in the thickness in the range of 190-1700 nm using varian cary 5E model spectrophotometer. The spectrum is shown in Fig. 5. From the transmission spectrum it is observed that the crystal has good transmission in the entire visible and IR region and the lower cutoff of the ZS is at 320 nm. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \qquad (9)$$

where t is the thickness of the sample.

Optical band gap (E_g) was evaluated from the transmission spectra and optical absorption coefficient (α) near the absorption edge is given by [7]

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \qquad (10)$$

where A is a constant, E_g the optical band gap, h the Planck constant and n the frequency of the incident photons. The band gap of ZS crystal was estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 6 and

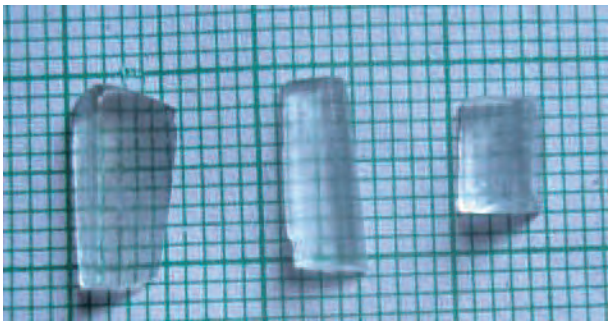

Fig. 4: Photograph of ZS single crystals

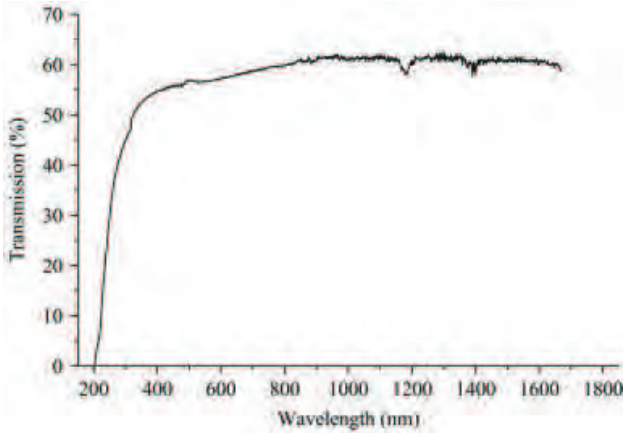

Fig. 5: Optical transmittance spectrum

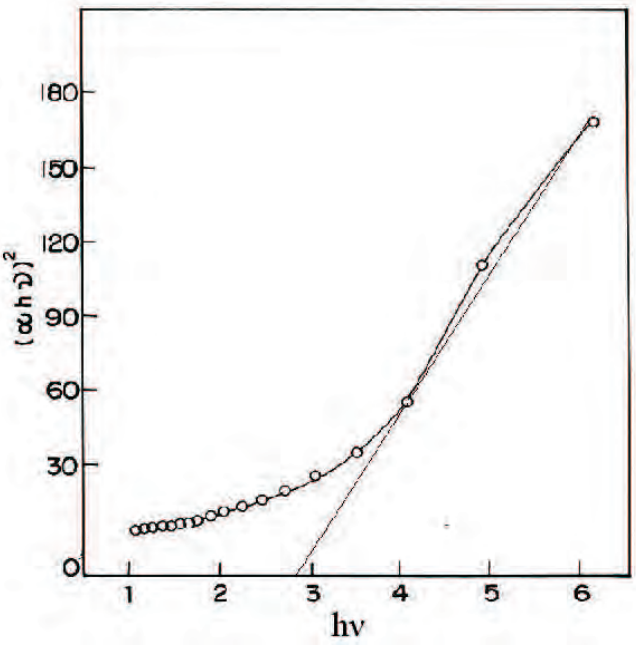

Fig. 6: $(\alpha h\nu)^2$ versus $h\nu$

extrapolating the linear portion near the onset of absorption edge to the energy axis. From the Fig. 6, the value of band gap was found to be 2.95 eV.

Extinction coefficient (K) can be obtained from the following equation:

$$K = \frac{\lambda\alpha}{4\pi} \tag{11}$$

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \tag{12}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \tag{13}$$

Refractive index (n) can be determined from reflectance data using the following equation

$$n = -(R+1) \pm 2\frac{\sqrt{R}}{(R-1)} \tag{14}$$

The refractive index (n) is 1.76 at λ = 1100 nm. From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation [8].

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{15}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{16}$$

where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The value of electric susceptibility is χ_C 0.142 at λ = 1100 nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [9]

$$\varepsilon_r = n^2 - k^2 \text{ and } \varepsilon_i = 2nk \tag{17}$$

The value of real ε_r and ε_i imaginary dielectric constants at λ = 1100 nm are 1.452 and 7.764 x 10^{-5} respectively.

5. Dielectric Studies

The dielectric constant and the dielectric loss of the ZS crystals were studied at different temperatures using HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. The variation of dielectric constant was measured as a function of frequency at different temperatures ranging from 40 to 90°C and is shown in Fig. 7, while the corresponding dielectric losses are depicted in Fig. 8. It is observed from the plot that the dielectric constant decreases exponentially

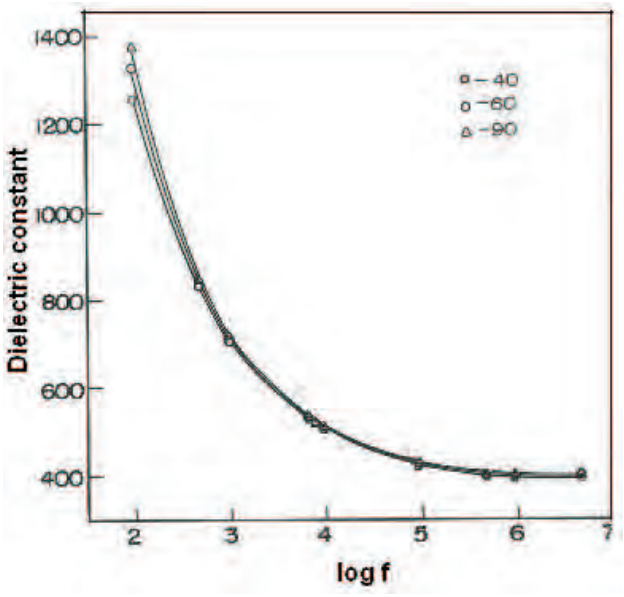

Fig. 7: Dielectric constant vs log f

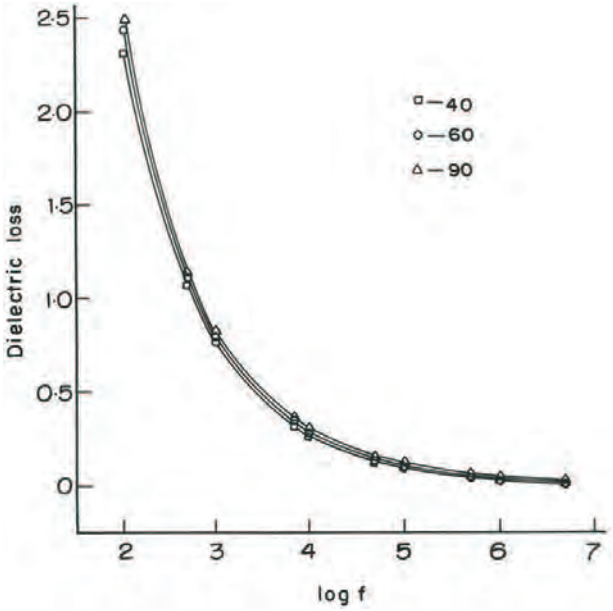

Fig. 8: Dielectric loss vs log f

with increasing frequency and then attains almost a constant value in the high frequency region. It is also observed that as the temperature increases, the value of the dielectric constant also increases. The same trend is observed in the case of dielectric loss versus frequency. The characteristic of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is highly important for making this material suitable for various nonlinear optical applications.

6. Conclusion

Good quality single crystals of ZS were grown by slow evaporation technique. Nucleation kinetics and fundamental growth parameters have also been investigated. The evaluated nucleation parameters are found to be feasible for the growth of bulk ZS crystals. Single-crystal XRD analysis confirms that the crystals belong to monoclinic system with the space group C2. Optical band gap (E_g), absorption coefficient (α), refractive index (n), electric susceptibility χ_c and dielectric constants were calculated as a function of wavelength. The dielectric constant decreases with increasing frequency at different temperatures. The dielectric study shows low dielectric loss behaviour, signifying that the grown crystal is relatively free from defect which is highly important for making this material suitable for various nonlinear optical applications.

References

1. Chemla DS and Zyss J *Nonlinear Optical Properties of Organic Molecules and Crystals* Academic Press, New York, **1&2** (1987)
2. Prasad PN and Williams DJ *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley-Interscience, New York (1991)
3. Jianguo Pan, Gongjun Zhang, Yueqing Zheng and Jianli Lin *J Cryst Growth* **308** (2007) 89
4. Nyvlt R, Rychly, Gottfried J and Wurzelova *J Crystal Growth* **6** (1970) 151
5. Nielsen AE and Sarig S *J Cryst Growth* **8** (1971) 1
6. Volmer M and Weber A *J Phys Chem* **119** (1926) 277
7. Ashour A, El-Kadry N and Mahmoud SA *Thin Solid Films* **269** (1995) 117
8. Gupta V and Mansingh A *J Appl Phys* **80** (1996) 1063
9. Gaffar MA, Abu El-Fadl A and Bin Anooz S *Physica B* **327** (2003) 43.