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Growth, Characterization and Dielectric Property Studies of Zinc Succinate Crystals Grown in Silica Gel Medium

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Abstract: *Single crystals of zinc succinate (ZS) with monoclinic structure were grown in silica gel medium. The functional groups in the crystal were analyzed by FT-IR Spectroscopy. Thermal degradation studies have been carried out by Differential Scanning Calorimetry (DSC). Dielectric constant and a c conductivity have been estimated as a function of frequency at different temperatures.*
Keywords - *a c conductivity, dielectric Property, NLO, zinc succinate*

I. Introduction

The design and synthesis of organic nonlinear optical (NLO) crystals is a promising area of current research in materials science. Organic materials are found to possess better non linear optical properties compared to inorganic materials. However organic nonlinear optical crystals have poor thermal and mechanical properties and are subjected to damage during processing [1-5]. Recently, there has been a widespread interest in the metal–organic coordination compounds, which are a combination of metal and organic ligands, having exciting NLO properties [6-8]. Zn succinate is a metal-organic coordination compound having good second harmonic generation efficiency. The growth of zinc succinate by slow evaporation technique is already reported by several authors [9-11]. In this paper we report the growth of zinc succinate crystal by diffusion technique in silica gel medium. In gel method the gel acidified with succinic acids provides a controlled medium for the diffusion of supernatant cations into it, leading to the formation of crystals. Due to the unique advantage of suppression of nucleation centers in the gel medium, gel growth is a very effective technique for growing single crystals. Also defects found in gel grown crystals are less due to the absence of convection in the medium. Optimum conditions for the growth at ambient temperature were found by investigating different growth parameters. The grown crystals were characterized by XRD, FT-IR, and DSC analysis. Electrical characterization of these crystals at different temperatures is also being done.

II. Experimental

The crystallization of zinc succinate was done using single diffusion gel technique. Reagent grade sodium metasilicate powder was dissolved in double distilled water and the resultant solution was filtered out. After making this solution at a particular specific gravity, the gel was set by acidification of sodium metasilicate solution by succinic acid so that the pH of the solution was brought to the desired value [12-14]. This mixture was taken in glass tubes of internal diameter 18 mm and length 150 mm and kept idle for gelation. After setting the gel, zinc chloride solution was poured over the gel along the sides of the test tube, without disturbing the gel. Small crystals in the form of spherical aggregates appeared near the interface and deep inside the gel within 48hrs. The growth was completed in 4 weeks. The following chemical reaction was expected to take place for the formation of the title compound

$$ZnCl_2 + C_4H_6O_4 \rightarrow Zn\,C_4H_4O_4 + 2HCl \qquad (1)$$

The experiment was performed by altering the growth parameters such as concentration of the nutrients, pH and density of the gel medium. The concentration of succinic acid and zinc chloride was varied from 0.25–1M to observe changes in the crystallization. The specific gravity of the gel is also varied between 1.02 and 1.06. The pH of the gel is set at values (4, 5, 6, 7 and 8). The optimum conditions for obtaining good quality crystals are summarized in table 1 below. The growth set up and grown crystals of copper succinate are given in fig. 1 and fig. 2 respectively.

Table 1. Optimum conditions for the growth of zinc succinate single crystals.

Growth Parameters	Optimum conditions
Gel Density	1.04
pH	6
Temperature	Room Temperature(30^{0}C)
Concentration of Succinic Acid	0.5M
Concentration of Zinc Chloride	0.5M
Gel setting time	1 days
Growth period	4 weeks

Figure 1. Growth set up

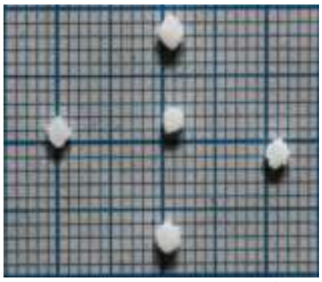

Figure 2. Grown crystals of ZS

After a growth period of four weeks the crystals were harvested and the structural analyses were carried out by X-ray diffraction method using Cu-Kα monochromator of wavelength 1.541A^0. Thermo Nicolet Avatar 370 spectrophotometer was employed to obtain IR spectrum. The DSC analysis was done employing Perkin Elmer DSC 4000. LCR Hi TESTER 3532-50 was used to conduct the dielectric studies

III. Characterizations

3.1. Powder X-Ray Diffraction Analysis

The powder XRD diffractogram of Zinc succinate crystals is shown in Fig.3. The *d*-spacing of different planes, the relative intensities of the observed peaks and FWHM data for each indexed plane are given in table 2. The crystal structure is determined as monoclinic and compared with the standard values in the JCPDS card (No 51-2305) and is found to be in close agreement. Unit cell parameters of the compound are a = 7.5597A^0, b = 5.9626 A^0, c = 6.2509A^0, α= 90^0, β = 108.44^0, γ = 90^0 and unit cell volume = 267.38(A^0)^3

Table 2. XRD Data of ZS

hkl	2Theta	d (A)	FWHM	I/I_0
[001]	14.95	5.92128	0.2316	20
[110]	19.362	4.58062	0.2232	40
[-111]	21.999	4.03721	0.1987	100
[200]	24.854	3.57948	0.2099	28
[111]	26.863	3.31618	0.2175	20
[020]	30.078	2.96867	0.4533	3
[-112]	32.473	2.75496	0.2438	20
[-221]	39.244	2.29381	0.5287	20
[310]	40.653	2.2175	0.2373	17
[022]	42.998	2.10188	0.2997	10
[-222]	44.795	2.02163	0.2732	14

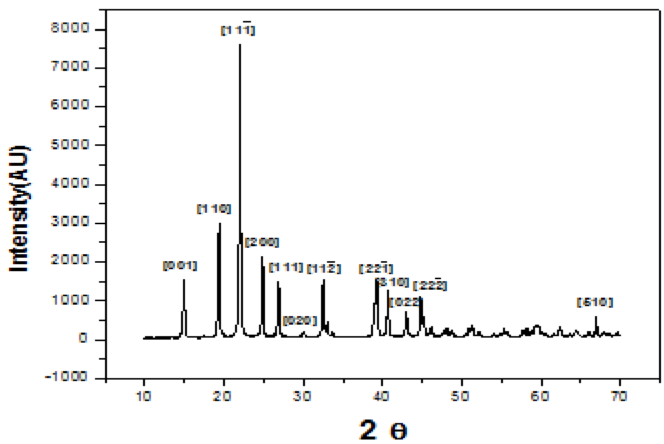

Figure 3.XRD pattern of ZS

The single crystal XRD data of zinc succinate is already reported, according to which, Zn succinate possesses a 3D network with acentric symmetry. The Zn atom is tetrahedrally coordinated by four oxygen atoms from four $(C_4H_4O_4)^{2-}$ anions, and each anion in turn bridges four neighboring Zn atoms to form a 3D network [15].

3.2. FT-IR Analyses

The Infra Red spectroscopy is a powerful technique for identifying the functional group in a compound. The FT-IR analysis of ZS crystals was done in KBr medium using powered samples, in the region from 400cm^{-1} to 4000cm^{-1}. The FT-IR spectrum at room temperature is shown in fig.4 below.

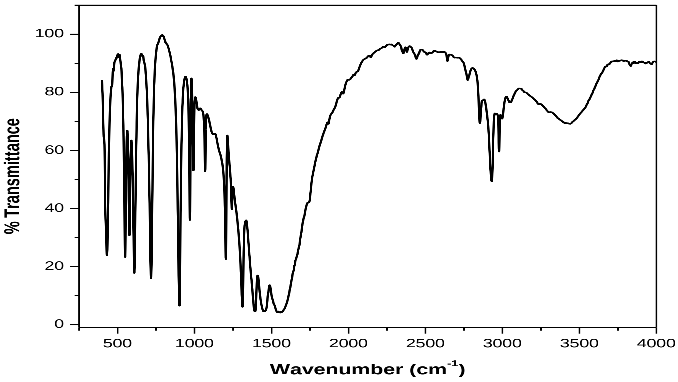

Figure 4. FT-IR spectrum of ZS

The characteristic absorption band at 1720 cm^{-1} is absent in the spectrum which assures that all the four oxygen atoms of succinic acid coordinates to zinc atoms. The strong and broad absorption band centered at 3450 cm^{-1} is indicative of lattice water present in the sample. The absorption bands at 2977 cm^{-1}, 2930 cm^{-1} and 2853 cm^{-1} can be assigned to asymmetric and symmetric C-H stretching vibrations of –CH2 group. The absorption bands at1560cm^{-1} is due to asymmetric stretching vibrations due to ionic COO^- group. The absorption band at 1456 cm^{-1} is due to C–H bending vibrations in the –CH2 groups. The absorption band with peak at 1388 cm^{-1} corresponds to symmetric O–C–O stretching vibration. The absorption bands at 1195 cm^{-1} and 1069 cm^{-1} are due to asymmetric and symmetric C-C stretching respectively. The weak band at 719cm^{-1} represents the absorption of the wagging vibration of the C–H bond in the –CH2 groups [16-18].

3.3. Thermal Characterization

Thermal studies play a significant role in the development and characterization of different materials. The differential Scanning calorimery analysis was done with a heat flow from 50.00°C to 375.00°C at 10.00°C/min. The DSC curves of Zn $(C_4H_4O_4)$ crystal is shown in Fig.5. The absence of any peak in this thermogram reveals that the compound is stable below 375^{o}C without any loss of weight. The good thermal stability of the crystals ensures the suitability of this material for possible applications in lasers, where the crystals are required to withstand high temperatures [15].

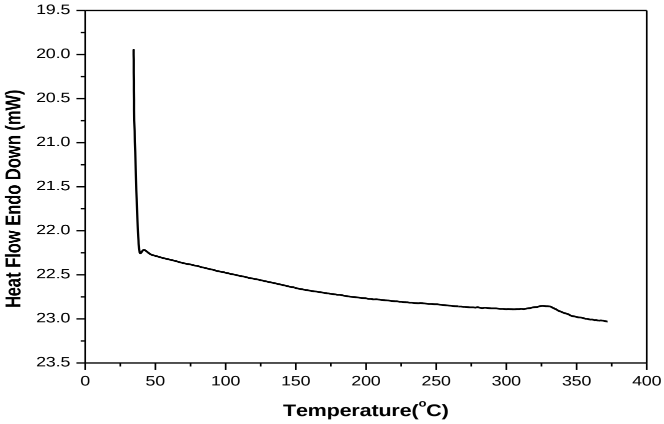

Figure.5. DSC spectrum of ZS

IV. Electrical Property Studies

The study of dielectric constant (ε_r), dielectric loss ($\tan\delta$) and a c conductivity (σ_{ac}) as a function of frequency and temperature, help us to know the various polarization mechanisms in the material. The variation of dielectric constant as well as the a c conductivity of the crystal with frequency of applied field ranging from 100 Hz to 5MHz is studied at different temperatures. The samples were finely ground and made in the form of pellets using a hydraulic press. The dielectric constant (ε_r) is calculated using the relation

$$\varepsilon_r = Cd/\varepsilon_0 A \quad (2)$$

and the a c conductivity is calculated by the relation

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta \quad (3)$$

Where C is the capacitance, d is the thickness, A is the area of cross section of pellet and $\tan\delta$ is the dielectric relaxation of the sample. It is observed that the dielectric constant decreases with increasing frequency and temperature as shown in figure 6 and 7 respectively.

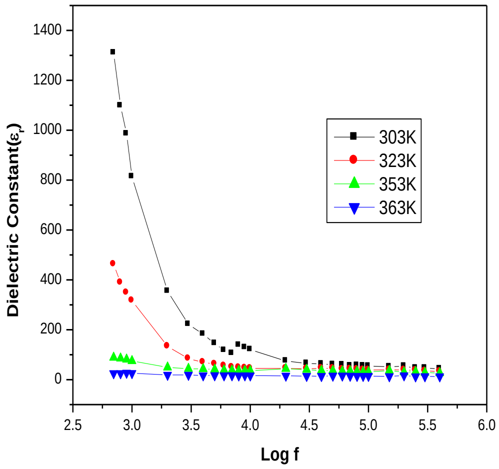

Figure 6. Variation of ε_r with frequency

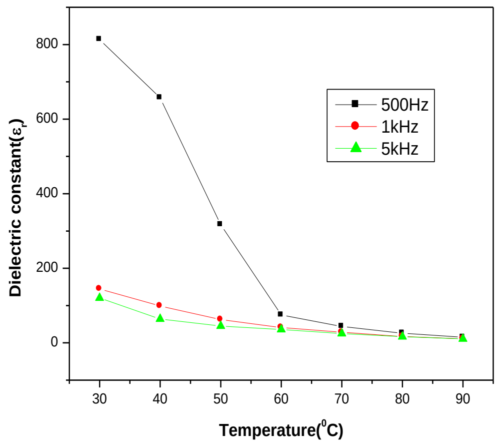

Figure 7. Variation of ε_r with temperature

Also ac conductivity value increases with increasing frequency (fig.8. and fig.9 respectively) and decrease with increasing temperature.

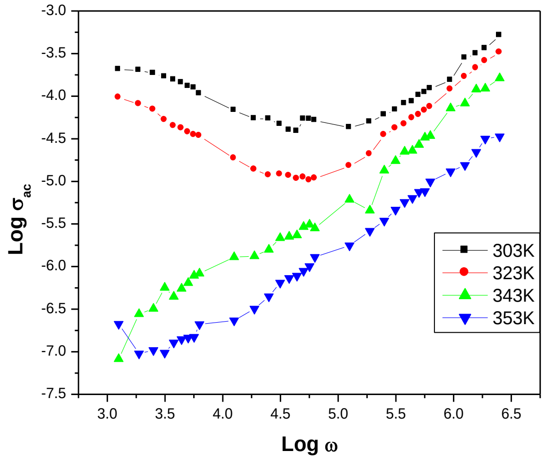

Figure 8. variation of σ_{ac} with frequency.

The dielectric constant is high at lower frequency region and decreases with increasing frequencies. The high value of dielectric constant at low frequencies is attributed to space charge polarization. At lower range of frequencies dielectric constant decreases drastically with frequency, becoming a constant at larger frequencies. The polarization occurs due to the local displacement of electrons, which is the effect of the electronic exchange of the number of ions in the crystal. As frequency increases the electron exchange cannot follow the electric field and the polarization becomes less dependent or independent of frequency. Variation of dielectric constant with temperature is generally attributed to the orientational polarization, crystal expansion, the presence of impurities and crystal defects. When temperature increases the dielectric constant decreases, as evident from the fig.7. The thermal energy disrupts the ion dipole interaction which is responsible for polarization at higher temperatures, causing the relaxation of polarization. The ac conductivity increases with frequency and decreases with temperature. Also in fig.9 the loss tangent is plotted against frequency. The peaks observed in this plot indicate the presence of relaxing dipoles in the sample [20, 21]

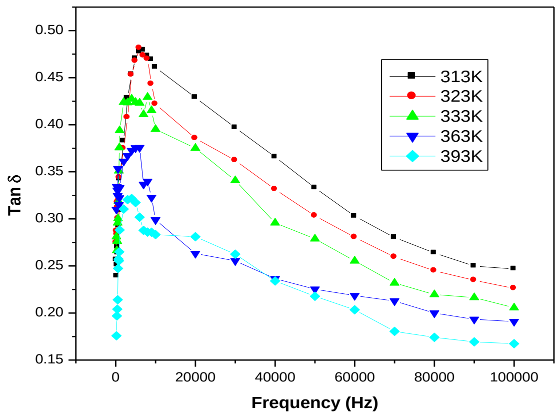

Figure 9. Variation of loss tangent with frequency

V. Conclusion

Zn succinate crystals were grown successfully by gel method and crystal structure is determined to be monoclinic. The FTIR studies confirmed the major functional groups in the crystal. . The DSC analysis depicted that the crystal is thermally stable up to 375^{o}C. The dielectric constant is found to decrease with frequency, attaining a constant value at higher frequencies. Also the dielectric constant decreases with temperature. The ac conductivity is found to be increasing with frequency and decreasing with temperature.

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