Characterization of Spectral, Dielectric, and Mechanical Studies of Zinc Sulphate Heptahydrate Single Crystal

R.Sangeetha

Received 1 January 2017 ▪ Revised 10 February 2017 ▪ Accepted 24 February 2017

Abstract: *ZincSulfateHeptahydrate, a novel inorganic optical material has been synthesized and crystals were grown from aqueous solution employing the technique of controlled evaporation. The various functional groups of the sample were identified by Fourier transform infra–red spectroscopic analysis. UV visible studies reveal that ZincSulfateHeptahydrate has UV cutoff wavelength at 200nm. Dielectric studies show that dielectric constant and dielectric loss decreases with increasing frequency and finally it becomes almost a constant at higher frequencies for all temperatures.Mechanical stability on the title crystal was carried out to propose the material for useful applications.*

Keyword*: synthesized, Zinc Sulfate Heptahydrate, FTIR spectroscopic analysis, Dielectric constant and Dielectric loss,Mechanical stability.*

INTRODUCTION

The field of nonlinear optics is one of the most attractive fields of current research because of its vital applications in various areas like optical switching, optical data storage for developing technologies in telecommunication and signal processing [1-3]. Since, the first demonstration was done in the year of 1961, which reveals that nonlinear frequency conversion is highly materials-limited field [4]. So materials should be optically transparent, quadratic susceptibility of sufficient magnitude, allow for phase matching interaction and withstand the laser intensity without damaging. To date, the most important class of materials used in nonlinear optics is inorganic single crystals. Magnitude, allow for phase matching interaction and withstand the laser intensity without damaging. To date, the most important class of materials used in nonlinear optics is inorganic single crystals.

Inorganic materials, exhibiting second order nonlinear optical properties have attracted in the recent past due to their ability to process into crystals, wide optical transparency domain, large nonlinear figure of merit for frequency conversion, fast optical response time and wide phase matchable angle [5]. These ionic bonded inorganic crystals, easy to synthesis with high melting point and high degree of chemical inertness [6]. Highly polarisable, inorganic quality crystal and their efficient active second order harmonic generation (SHG) have been observed by Franken et al and co-workers in 1961[4].

Inorganic materials have advantages over organic materials, such as architectural flexibility for molecular design and morphology, high mechanical strength and good environmental stability with non toxicityandusability in high power applications. Molecular hyperpolarizability of inorganic nonlinear optical crystal are used in optical switching (modulation), frequency conversion (SHG, wave mixing) and electro-optic applications especially in EO modulation.

In the present work, Zinc Sulfate Heptahydrate (ZSH) compound was synthesized and formed as single crystals by means of slow evaporation technique. The crystallographic data of the grown crystals were obtained and vibrational properties of ZSH were studied. Dielectri behavior, optical properties and mechanical stability of grown crystalwere investigated.

R.Sangeetha
Assistant Professor, Department of Physics, DhanalakshmiSrinivasan College of Arts and Science for women (Autonomous), Perambalur

E-mail:aalinvino@gmail.com

Experimental Technique

Crystals will grow from solution if the solution is super saturated. Crystals may be grow from a saturated solution by slow evaporation, slow cooling, and diffusion methods of all the methods of crystal growth, slow evaporation method is simplest one for growing single crystals. In this method the saturated solution is allowed to evaporate slowly at room temperature without any disturbance. Single crystals of good quality are normally produced by this method. In the present work, water is used as a solvent to grow the crystals of zinc sulfateheptahydrate.

Zinc SulfateHeptahydrate

Saturated solution of zinc sulfateheptahydrate were prepared from 20 ml of distilled water. Then the solution were stirred well using a magnetic stirrer for 3 hour. The saturated solution was filtered and kept in a beaker covered with perforated paper. After 10 days zinc sulfateheptahydrate crystal seeds were harvested.

Objective of the work

Materials in the crystalline states are common and they play an important part in everyday life. The zinc sulfateheptahydrate salts are taken in the ratio 1:1 into 20 ml of water and stirred for 3 hour. Then the solution are adopted to slow evaporation method. Within the 10 days the seeds of the crystal are grown. After 53 days the big crystals are grown.

Size of the crystal

The length and breadth of the grown crystals are 1.3cm and 5mm respectively.

CHARACTERIZATION

The absorption and transmission spectrum of ZSH has received between 190nm and 1100 nm using Perkin-ElmerLambda 35 UV–Vis spectrometer. The vibration spectral analyses have been executed under the room atmospheric condition, between 400 cm^{-1}–4000 $cm^{-1}$from FT-IR spectrum using Perkin-Elmer spectrometer. The dielectric study has been executed by LCRZ Meter 2816B between 50 Hz–200 KHz frequency range. Mechanical behaviour of the grown sample was investigated by REICHERT MD 4000E ULTRA microhardness tester

RESULT AND DISCUSSION

UV–Vis Analysis

The assessment of optical nature of the crystalline material facilitates to categorize its extensive reliability for optoelectronic and NLO device fabrications. Generally the optical transparency depends on several interior and exterior aspects which consist of the optically dynamic functional units, orientations, grain boundaries, impurities and striations. This factor that exhibits the linear optical transparency in crystal isgoverned by the electronic transition assist by the interaction of electromagneticspectrumwith crystallinematerial. The transmittanceand absorbance of 2 mm thickness ZSH was measured by spectrophotometerfor thewavelength range 200–1200nm. The resulted transmissionspectrum is displayed in Fig.1. From UV transmittancespectra, it is known that ZSH crystals have high transmittancefrom 220 to 1100 nm. This is very important for materials possessingnonlinear optical properties. The cut of wavelength of grown crystal isobserved as 200 nm. The wide range of transparency (100%) is an added advantage for this crystal to be utilized in the field of optoelectronicdevices [7]. Using the formula, $E=h\ c/\lambda$ [8] the optical energy gap was calculated as 6.2eV. As the effect of broad band gap, the ZSH crystal has a lack of absorbance in the visible spectral region [9].The resulted absorption band of synthesized ZSH crystal wasdisplayed in Fig. 2. The lower cut-off wavelength was observed asnearly 290 nm. The broad range of transmittance is observed throughoutthe visible spectral region of the optical absorption spectrum. Thepresence of weak absorption in the visible spectral range signifies thatthe ZSH single crystal is suitable for the SHG applications [10].

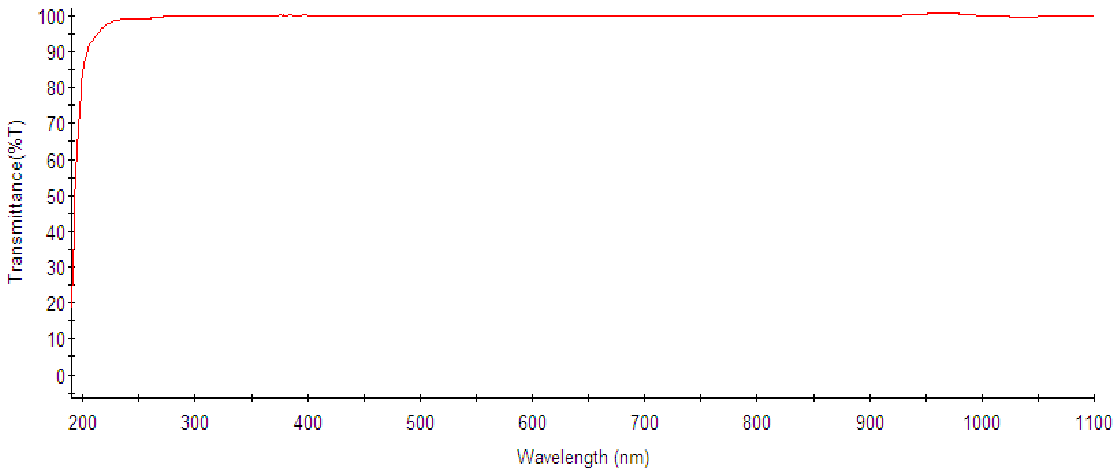

Figure 1: Transmittance Vs wavelength

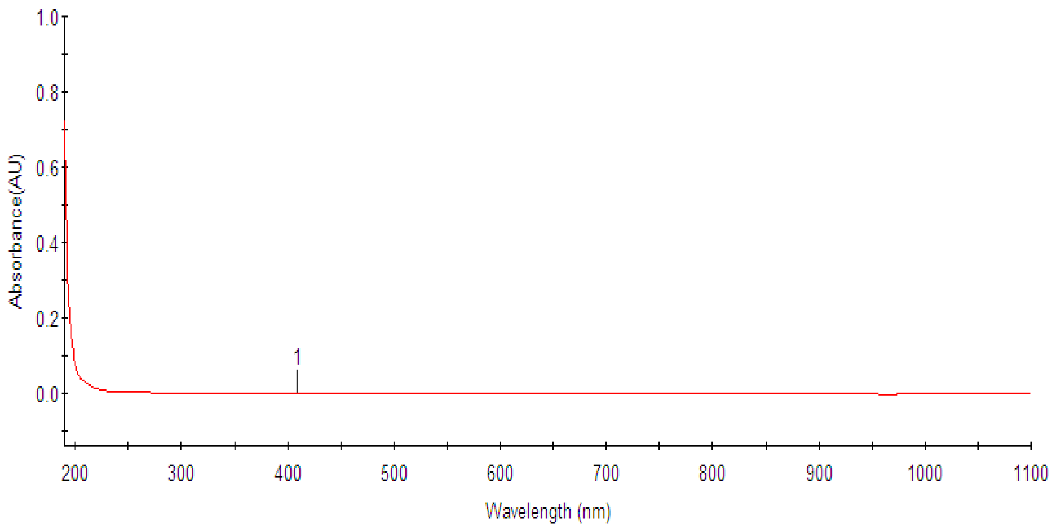

Figure 2: Absorption Vs wavelength

Spectroscopic Analysis

The absorption due to various functional groups is shown in Fig. 3. The stretching vibrations of the water molecule are expected in the region 3000-3600/cm [11]. The broad vibrational band observed at 3213.19 cm-1 is attributed to the symmetric stretching mode of water molecule. The medium broad band noticedat1652.51 cm-1 is assigned to the bending vibrational mode of water molecules. The bandobserved at 795.24 cm-1 is assigned to the liberation mode of water molecules. In general, afree SO_4^{2-} ion has four fundamental vibrations, namely a non degenerate mode (υ1) at981/cm, a doubly degenerate mode (υ2) at 613/cm and triply degenerate vibrations (υ3 andυ4) at 1104 cm-1, respectively [12]. The peak observed at 1069.50 cm-1isattributed to the triply degenerate symmetric stretching mode, (υ3) SO_4^{2-} . The bandobserved at 475.46 cm-1is assigned to the doubly degenerate mode (υ2) SO_4^{2-}mode. The mode at 596.24 cm-1is assigned as the triply degenerate vibrations (υ4) SO_4^{2-}Theabove assignment agrees with that of reported values [13-14].

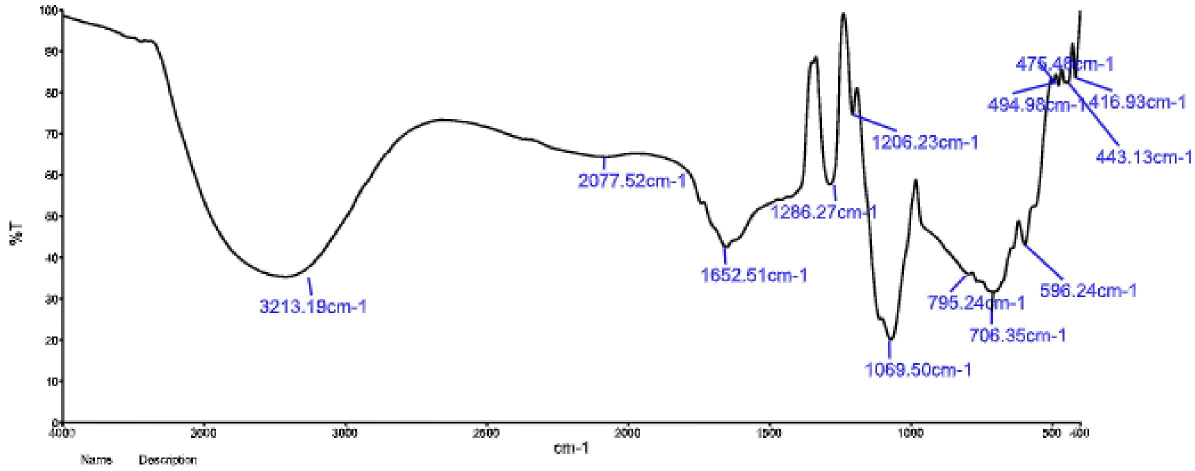

Figure 3: FTIR spectral studies on ZSH crystal

Dielectric Studies

The behavior of the crystal under the influence of electric field has good relation with the laser irradiation on the sample; hence the power dissipation factor can be studied from the dielectric studies. Dielectric studies for ZSH single crystal were carried out as a function of frequency for various temperatures. The ZSH crystal was coated with graphite on either side to form an electrode of a parallel plate capacitor. The dielectric constant was calculated using the formula

$\varepsilon r = Ct/\varepsilon_0 A$

Where C is the capacitance; t is the thickness of the crystal,ε_0 is the permittivity of the free space and A is the area of a cross section of the sample. The variations of dielectric constant and dielectric loss as a function of frequency (500 Hz to 5MHz) at different temperatures (308 -368 K) are shown in the figure 4 and 5. The dielectric constant as a function of frequency and temperatures are observed, which reveals that the dielectric constant decreases with increasing frequency. This behaviour of the sample referred as anomalous dielectric dispersion. High dielectric constant at low frequency is attributed to various polarization mechanisms of molecules. Generally, the polarization occurs as a function of time. It is obvious that at lower frequency, time taken for polarization is high. Hence, irrespective of the polarization mechanisms, measurement of dipole moment per unit volume would be high, resulting that the dielectric constant is independent of the frequency. At high frequency the change of polarization occurs even at very short time. Therefore, the polarization can occur only by the movement of electronic charge rather than the ions, results low dielectric constant. Electronic and space charge polarization predominantly in the low-frequency region suggest that the grown crystal possesses an enhanced optical quality with lesser defects and this phenomenon is an essential characteristic for nonlinear optical applications [15-17].

From the figure 5, the value of dielectric loss found to be high at low frequency region and dielectric loss found too low at higher frequency. The measure of low dielectric loss at higher frequencies is due to the dipole rotation. Also at high frequencies, the orientation polarization ceases and the energy need not be spent to rotate dipoles. It is also observed that both dielectric constant and dielectric loss depends on the temperature and increases slightly with an increase of temperature at a constant frequency. It is believed that materials with high dielectric constant lead to power dissipation. The Refractive index of the medium is related with dielectric constant according to the equation $n= (\varepsilon_r \mu_r)^{1/2}$. For non-magnetic materials, $\mu_r$is equal to one. This equation explains the electric field based refractive index of the medium could play vital role in nonlinear effect. ZSH crystals possess low dielectric constant and low dielectric loss and hence it will be suitable for electro-optic applications. Also the low value of dielectric loss at high frequency can be taken as a proof of the good optical quality of the crystal. The application part of nonlinear optics demand high quality crystals with lesser defects.

Mechanical Studies

Mechanical property of the grown sample was studied by measuring the hardness number with various applied loads. The indentation time has been kept 5 seconds for all the loads. Several indentations were made on the crystal surface with sufficient space for each load and the diagonal length (d) of the indented impressions is measured. The Vickers hardness number of the materials Hv have determined by the relation, Hv=1.8544 P/d2 kg/mm2. Where is the applied load in kg and d is the diagonal length of indentation impression in mm. The hardness number was found to be increased with load and above 100 g, significant crack and inclusion are observed, which may be due to the release of internal stress generated locally by indentation [18]. The average value of the Vickers hardness number for the grown crystal is 100 kg/mm2. The plot drawn between the corresponding loads and hardness values of ZSH is shown in figure 6. The work hardening coefficient (n) of the material is related to the load (p) by the relation P=Adn , Where A is an arbitrary constant. The work hardening coefficient 'n' of the sample has been determined from the slop of the log p vs log d (figure7) and is found to be 2.278 indicating that the crystal belongs to soft category. From careful observations on various materials OnitschandHannemanpointed out that the value of n between 1.0 and 1.6 indicates a moderately hard material and n above 1.6 represents a soft material [19-20]. The value of n indicates that the ZSH crystal has higher mechanical strength and useful in device applications.

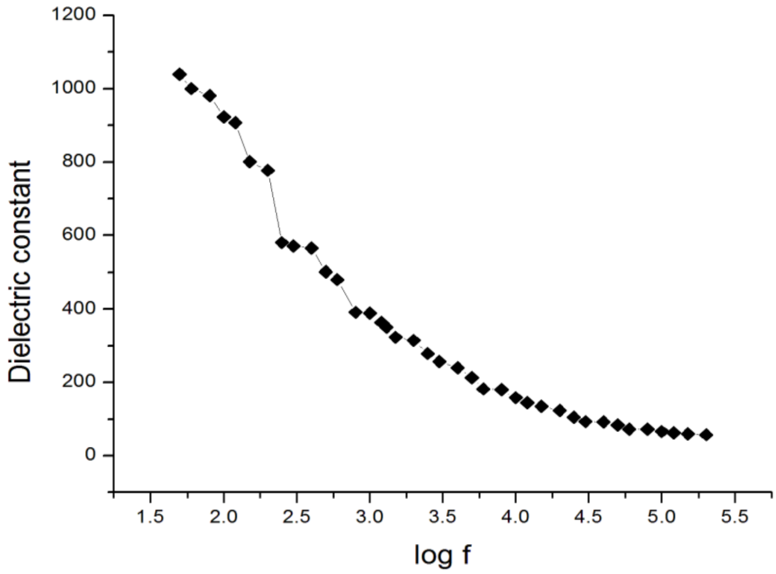

Figure 4: Variation of dielectric constant with frequency at room temperature

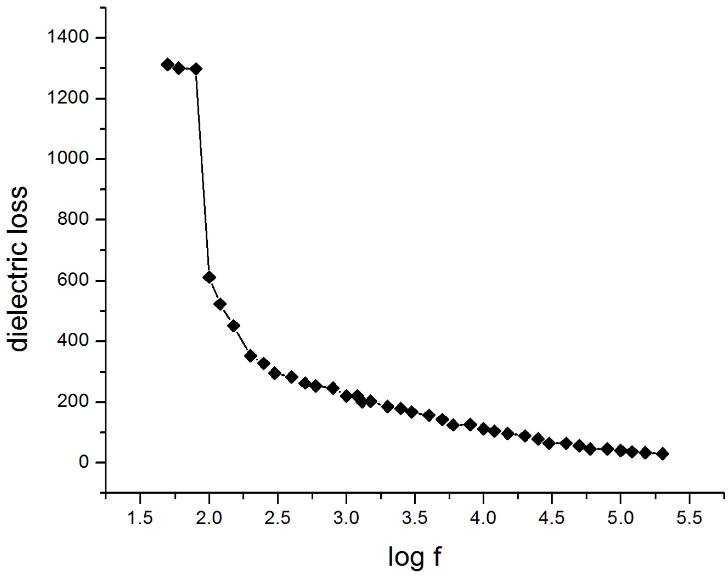

Figure 5: Variation of dielectric loss with frequency at room temperature

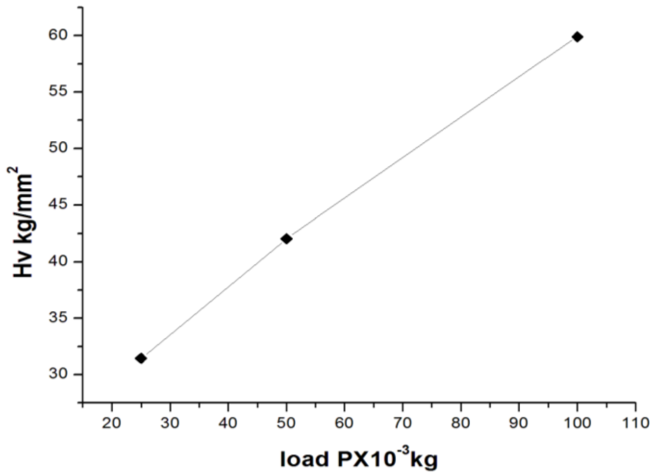

Figure 6: Variation of hardness with load for ZSH crystal

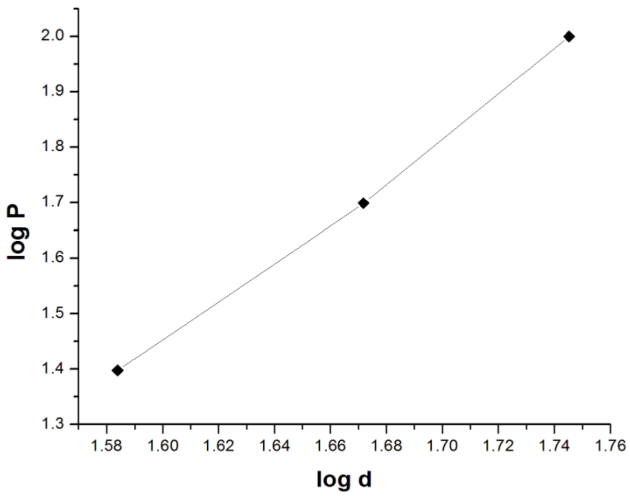

Figure 7: Plot of log d vs log P for ZSH crystal

CONCLUSIONS

The growth of ZSH single crystals has been performed by slow evaporation technique at the room atmosphere. The presence of different vibrational groups has been verified by FTIR reported experimentally. The ZSH single crystal showed the transparency in the range 200–1100 nm which has been confirmed by transmission and absorption optical spectrum. The result of the dielectric studies showed that the synthesized crystal has optical nature. From the mechanical measurements, it was observed that the hardness increases with increase of load and from the mayer index value it was concluded that the ZSH crystal is useful in device application.

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