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Research Article

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Solution growth, spectral, electrical and mechanical studies of cadmium sulfate hydrate (CDSH) crystals

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ABSTRACT

Cadmium compounds such as cadmium sulfate are used in batteries, pigments and in semiconductor industry. Commercially available cadmium sulfate was purchased and used for the crystal growth. The sample in salt form was dissolved in double distilled water and the saturated solution was prepared. Nearly 38 grams/50 ml are necessary to prepare the saturated solution and the solution was stirred well using a magnetic stirrer for 2 hours and it was filtered using a Whatmann filter paper. The filtered solution was kept in a growth vessel at room temperature and it was loaded into a constant temperature bath to maintain the temperature of the solution constant. Colourless, transparent crystals of size 18 x 17 x10 mm^3 were harvested after a growth period of 25 days. The grown crystals were characterized by using different techniques like XRD, UV-visible studies, SHG, micrhohardness and electrical studies and the results are discussed.

Key words: Inorganic crystal; solution growth; XRD; dielectric; SHG; hardness

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INTRODUCTION

Crystals find their applications in solid state devices, polarizers, radiation detectors, medicine, ultrasonic amplifiers, solid state lasers, nonlinear optics, piezo-electric, acousto-optic and photo sensitive devices etc. As far as optics is concerned, crystals can be classified into linear optical and nonlinear optical (NLO) crystals. In an NLO crystal, the polarization gives response to the electric field of light nonlinearly and the interaction of intense electromagnetic field in the material to produce modified fields that are different from the input field in phase, frequency or amplitude. This nonlinearity is only observed at very high intensity of light having values of the electric field comparable to the inter atomic electric field of 10^8 V/m. NLO effects are responsible for phenomena like Second harmonic generation (SHG), sum frequency generation (SFG), Difference frequency generation (DFG), Pockels effect, optical parametric oscillation and electro optical modulation, third harmonic generation, stimulated Raman scattering, Kerr effect and phase conjugation etc [1-5]. Cadmium sulfate octahydrate crystal is found to be a third-order NLO crystal and it crystallizes in monoclinic structure with a centrosymmetric space group [6,7]. There is an example of a centrosymmetric crystal possessing the property of SHG [8-10]. The presence of water molecules in the crystal lattice and hence the hygroscopic property of cadmium sulfate crystals have been explained by Yun-Hong Zhang et al. [11]. Gel growth method was adopted to grow the single crystals of cadmium sulphate by Rajadurai et al. [12]. Cadmium sulfate is found to be used for the electroplating of cadmium in electronic circuits and it a precursor to cadmium-based pigments such as cadmium sulfide. It is used as an electrolyte in a Weston standard cell as well as the pigments in fluorescent screens and also it can be used in NLO applications. This paper covers the growth and physico-chemical properties of cadmium sulfate hydrate (CDSH) crystals.

EXPERIMENTAL SECTION

2.1Growth of CDSH crystals

Crystal growth has prominent role to play in the present era of rapid technical and scientific advancement and crystallization is one of the important processing techniques in industries. More recently, however new applications for crystals has been discovered in what are loosely called solid-state devices. Because many properties of solid are best studied with crystals, the increasing interest in the nature of solids also has required that crystals be grown under controlled conditions for a variety of investigation. Single crystals of CDSH were grown by solution method with slow solvent evaporation technique. The saturated solution of the commercially available cadmium sulfate octahydrate (CDSH) was prepared by dissolving the salt in de-ionized water by continuous stirring of the solution using a magnetic stirrer and the saturated solution was filtered using 4 micro Whatmann filter paper. The seed crystals of CDSH were obtained by spontaneous nucleation. The supersaturation of the solution was found by observing the first crystal formed at the bottom of the glass beaker due to slow evaporation of the solvent. The supersaturated solution of CDSH was carefully transferred into another glass beaker and kept at 30 ^{o}C in the constant temperature bath. Two or three good quality seed crystals of CDSH were placed in the supersaturated solution and the solution was allowed to evaporate the solvent slowly. A typical single crystal with size 18 x 17 x 10 mm^3 was obtained within a period of 20-25 days. Grown crystals are shown in the figure 1 and they are found to be transparent and colorless.

Fig.1: Grown crystals of cadmium sulfate

2.2 Instrumentation

The grown single crystal of CDSH was subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK$_\alpha$ (λ=0.71069 Å) radiation to evaluate the lattice constants. The transmission properties of the crystals were examined using Lambda 35 model Perkin Elmer double beam UV-vis-NIR spectrometer in the range from 190 nm to 1100 nm. Optically polished single crystal of thickness 1.5 mm was used for this study. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystal using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm [15]. Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indenter and two trials have been carried out to ascertain the correctness of the values. Values of dielectric constant and dielectric loss of the GG crystal were measured using LCR meter (Agilent 4284A) in the frequency region 100 Hz-1 MHz and at different temperatures.

3. Characterization

3.1 Solubility studies

Solubility study was carried out using a constant temperature bath (CTB) by gravimetrical method. The salt of the prepared sample was added step by step to 20 ml of double distilled water in an air-tight container kept in the CTB and the stirring was continued till a small precipitate was formed at 30 ^{o}C. Then, 5 ml of the solution was pipetted out and taken in a petri dish and it was warmed up till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of the samples water was determined. Figure 2 shows the solubility curve of CDSH crystal. From the results, it is observed that the solubility of the sample in water increases with temperature, exhibiting a high solubility gradient and it has positive temperature coefficient. The figure 2 has three regions viz. supersaturated region above the curve, saturated region along the curve and undersaturated region below the curve. The solubility data will be useful to prepare saturated and supersaturated solutions at any temperature in the range 30-60 ^{o}C and these data will also be useful to carry out the nucleation kinetic studies [13].

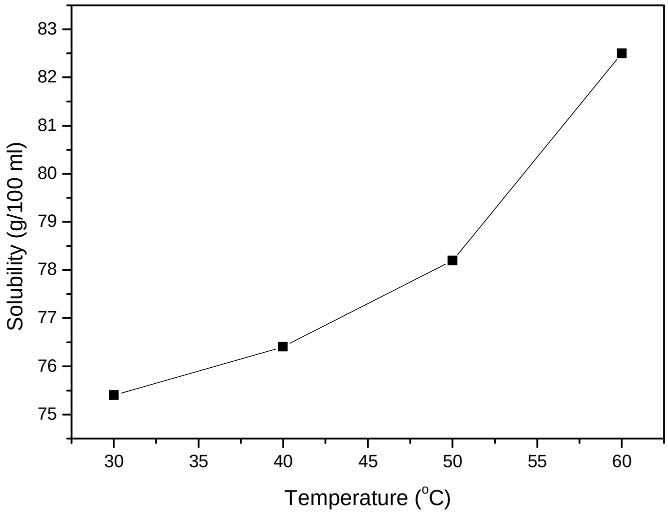

Fig.2: Variation of solubility with temperature for CDSH sample

3.2 XRD studies

The X-ray diffraction analysis on the grown CDSH crystal was used to confirm the crystallinity and identification of the unit cell parameters. The grown CDSH crystal has been subjected to single crystal X-ray diffraction study to obtain the crystallographic data which reveals that CDSH crystal crystallizes in monoclinic structure. The obtained single crystal XRD data for the grown crystal of this work are provided in the table 1.

Table 1 Crystallographic data for CDSH crystal

Temperature	293(3) K
Symmetry	monoclinic
a	15.016(2)
b	11.264(3)
c	9.748(2)
α	90°
β	98.42°
γ	90°
V	1631.01(3)

3.3 UV-visible spectral studies

UV-vis-NIR absorbance and transmittance spectra of CDSH crystal is shown in the figures 3 and 4. Low absorption in the entire visible and near infrared region with the lower cut-off wavelength at 260 nm and this strong absorption corresponds to the fundamental absorption. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. Using the formula E_g = 1240 / λ□ (nm), the band gap is calculated to be 4.77 eV.

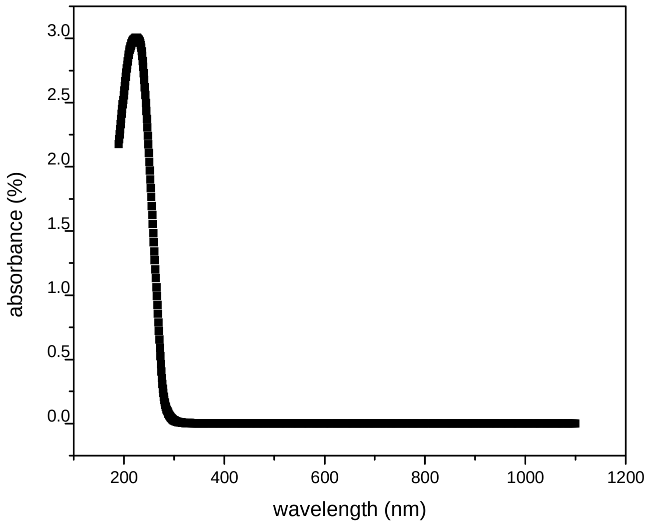

Fig.3: Absorbance spectrum for cadmium sulphate crystal

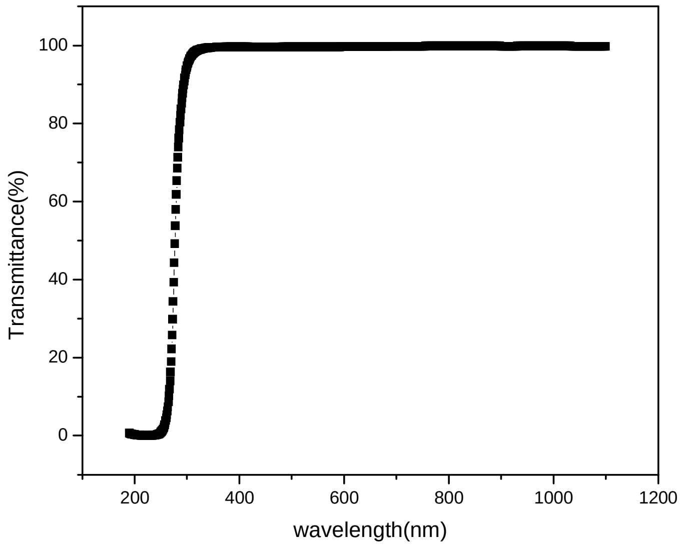

Fig.4: Transmittance spectrum of cadmium sulphate hydrate crystal

3.4 Vickers microhardness analysis

A well polished CDSH crystal of 1.5 mm thick was placed on the platform on the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. The hardness was calculated using the relation $H_v = 1.8544\ P/d^2$ kg/mm^2, where P is the applied load in g and d is the diagonal length of the indentation impression in millimetre. The variation of hardness number (H_v) with load (P) for CDSH crystal is shown in the figure 5. The hardness increases with the increase of load and this is due to reverse indentation size effect [14].

3.5 SHG studies

Second harmonic generation (SHG) efficiency is one of the second-order NLO properties and its value was found for the sample using the Kurtz and Perry method. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was passed through the powdered sample. The SHG behavior was confirmed from the output of the laser beam having the green emission (λ = 532 nm). It is observed that the SHG efficiency of the grown single crystal is 0.659 times that of the standard KDP crystal. (Here the input power is 0.68 J, output power from CDSH sample is 5.8 mJ, output power for KDP sample is 8.8 mJ).

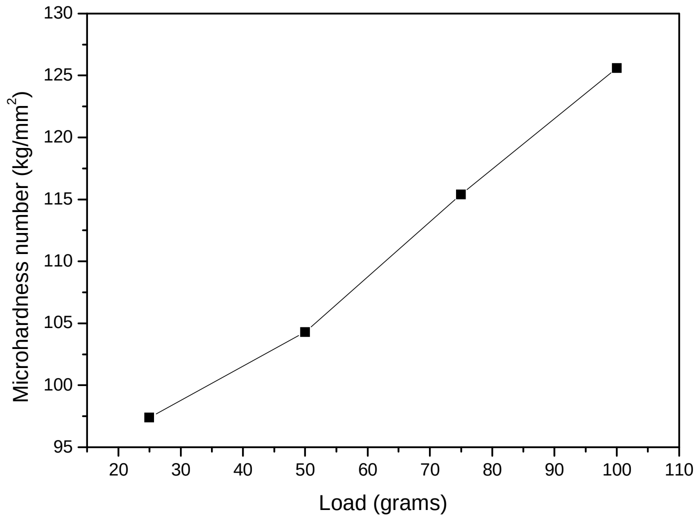

Fig.5: Plot of hardness number versus the applied load for cadmium sulfate crystal

3.6 Dielectric studies

The dielectric constant and the dielectric loss factor are measured at different frequencies for various temperatures. The frequency dependence of the dielectric constant at different temperatures for CDSH crystal is shown in figure 6. The dielectric constant of a solid is known to consist of contributions from electronic, ionic, dipolar and space charge polarizations, each dominating in a particular frequency range. It is established that the space charge polarization is very predominant at lower frequencies. This polarization is known to arise from the charged defects or impurities present and also due to the creation and distribution of dipoles either within the bulk or at the surface of the crystal. The dipolar polarization can sometimes be seen in some materials up to 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz. The obtained result reveals that the dielectric constant has high values at lower frequencies and it decreases with increase in frequency and become independent at higher frequencies. The variation of dielectric loss with frequency and temperature are presented in the figure 7. The low values of dielectric loss of the sample confirm the better dielectric quality [15]. The nature of decrease of ε_r and $\tan\delta$ with frequency suggests that the grown crystal seems to contain domains of continuously varying relaxation times. The values of dielectric constant and loss are low at higher frequencies because domains of larger relaxation times may not be able to respond to these frequencies. The results indicate that the dielectric parameters are observed to be increasing with increase of temperature. The following observations are noticed from the measurements of dielectric constant and dielectric loss.

ε_r (at 10^2 Hz frequency) > ε_r (at a10^3 Hz frequency) > ε_r (at 10^4 Hz frequency) >ε_r (at 10^5 Hz frequency)
ε_r (room temperature) < ε_r (higher temperature)
$\tan\delta$ (at 10^2 Hz frequency) >$\tan\delta$ (at 10^3 Hz frequency) > $\tan\delta$ (at 10^4 Hz frequency) > $\tan\delta$ (at 10^5 Hz frequency)
$\tan\delta$ (room temperature) < $\tan\delta$ (higher temperature)

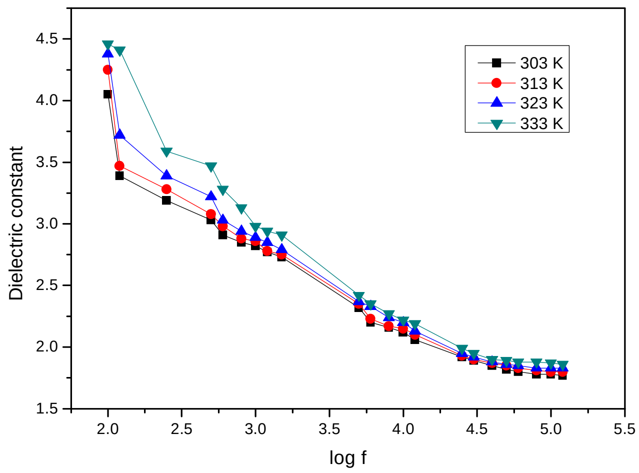

Fig.6: Variation of dielectric constant with frequency at different temperatures for CDSH crystal

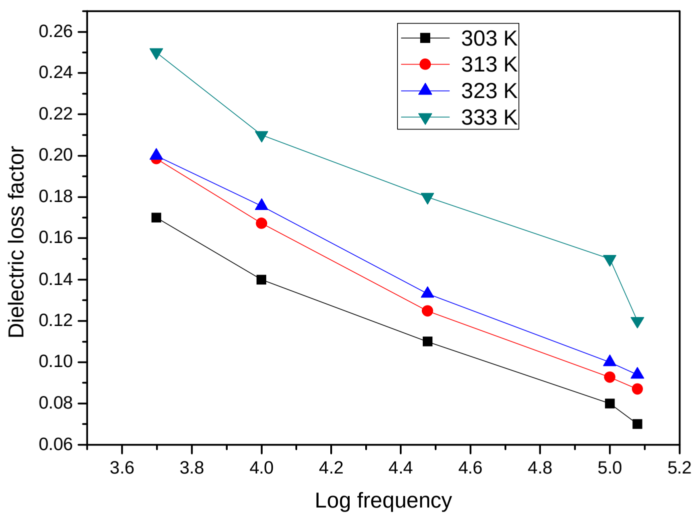

Fig.7: Variation of dielectric loss with frequency at different temperatures for CDSH crystal

CONCLUSION

Single crystals of CDSH have been grown by slow evaporation technique and the solubility of CDSH sample was estimated for water solvent at different temperatures. Solubility of the sample is found to be increasing with increase in temperature. The crystal structure of the grown crystal is found to be monoclinic. The optical band gap of the sample has been found. Relative SHG efficiency of the sample is found to be 0.65 times that of KDP. Vickers microhardness values were calculated at different applied loads in order to understand the mechanical strength. Dielectric parameters such as dielectric constant and dielectric loss factor have been measured for the grown crystal of CDSH at different frequencies and temperatures.

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