

CRYSTALLIZATION OF ZINC SULPHATE SINGLE CRYSTALS AND ITS STRUCTURAL, THERMAL AND OPTICAL CHARACTERIZATION

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ABSTRACT

Zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), an inorganic material has been crystallized by an isothermal evaporation method. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is highly soluble in water and the solubility is found to be increased almost linearly with the increase of temperature. At room temperature around 34°C , the solubility was found to be 92.41 gm/50 ml. The FT-IR spectroscopy was performed on pure zinc sulphate crystals to identify the presence of functional groups. The grown crystals have been subjected to powder X-ray diffraction to determine the unit cell dimensions and the crystal structure. The lattice parameters are found to be, $a = 9.9810 \text{ \AA}$, $b = 7.2500 \text{ \AA}$ and $c = 24.2800 \text{ \AA}$, respectively. The values were in good agreement with those of the reported values. The TGA and DTA study revealed that the grown crystals have good thermal stability. The UV-vis spectrum showed that the material has wide optical transparency in the Ultra-violet region.

Key words: Isothermal evaporation, Crystallization, Zinc sulphate, Structural characterization

INTRODUCTION

Zinc Sulphate Heptahydrate (ZSHH) possesses wide range of applications in the field of telecommunication, solar systems for solar energy storage, coagulation bath for rayon and optical information storage devices. The search for new frequency conversion materials over the past decade has led to the discovery of many organic materials with high nonlinear susceptibilities. However, their often inadequate transparency, poor optical quality, and lack of robustness, low laser damage threshold and inability to grow into large size have impeded the use of single crystal in various devices. Recent interest is centered on inorganic crystals because pure inorganic materials typically have excellent mechanical and thermal properties. Crystallization of heptahydrate sulphate material such as zinc vitriol ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) of high purity has become an important field of research for both academic and industrial applications in various areas like medical, agricultural and chemical industry (Ema *et al.* 1998, Ikeya *et al.* 2000). The pure zinc sulphate crystals were grown at low temperature from aqueous solutions (Kasatkin 2002, Ramalingom *et al.* 2001, Sgualdino *et al.* 1987, Tomas *et al.* 1969.)

The zinc vitriol is included in a group of heptahydrate sulphate with the general formula $\text{RSO}_4 \cdot 7\text{H}_2\text{O}$ ($\text{R} = \text{Zn, Mg, Ni}$) (Dana and Ford 1985). $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ belongs to a

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family of inorganic non linear optical crystal (Dhumane *et al.* 1998, Hussani *et al.* 2008). Zinc vitriol is used to supply zinc in fertilizers, in making lithopone; in electrolyte for zinc plating; as a mordant in dyeing, as a preservative for skins and leather and in medicine as an astringent and emetic. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystallizes in the orthorhombic structure. During industrial crystallization, the size and shape of the crystal plays an important factor, since the undesirable habits such as plate like or needle like causes the problems of separating, washing or drying (Cano *et al.* 2001). The physical properties such as packing density, agglomeration and re-dissolution mainly depend on the shape of the crystal. The main objective of the research was to study the growth mechanism of pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and its different physical properties. Here the synthesis, solubility, structural, optical, and thermal properties of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ have been reported.

MATERIALS AND METHODS

Analar grade zinc sulphate heptahydrate and doubled distilled water were used in the crystallization process. In the first stage a mother solution of 2000 ml was prepared using recrystallized salt of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and stirred well with a magnetic stirrer for 12 hours to attain saturation. The solubility of zinc vitriol was found to increase almost linearly with the increase of temperature. The solution was carefully filtered and distributed equally (200 ml each) in five crystallizers and allowed to evaporate at room temperature. The pure zinc sulphate seed crystals were prepared by the natural isothermal evaporation method. During natural evaporation process, the crystallizers were covered with perforated polyethylene sheet and kept in a dust free chamber. Colorless and transparent $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystals were harvested after a period of 4 - 5 weeks.

The FT-IR spectrum of the crystal was recorded by KBr pellet technique at room temperature using Shimadzu-IR 470 (Shimadzu Corporation, Tokyo, Japan) from BCSIR laboratory, Dhaka, Bangladesh. All the spectra were recorded in transmittance (%) mode in the region of 4000 to 400/cm. Powder X-ray diffraction was carried out using a Shimadzu X-ray Diffractometer with Mo ($K\alpha$) radiation ($\lambda = 1.70688\text{\AA}$) in Atomic Energy Center, Dhaka with an operating applied voltage 30 kV and current 20 mA. Scanning rate was maintained at 1° per minute. The thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and DTG of the powder sample were recorded by using Q50 W/FMC DTA analyzer at heating rate $30^\circ\text{C}/\text{min}$ in air to find the thermal stability of the as grown crystal. The optical absorption spectrum for grown zinc sulphate crystal was studied in the Ultra-violet region.

RESULTS AND DISCUSSION

Solubility of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$: The solubility data at various temperatures are essential to determine the level of super saturation. A small fluctuation in the temperature will effect the super saturation to grow the good quality bulk crystals.

Hence the solubility of the solute in the water solvent was determined before starting the growth process. The solubility of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ has been studied in the temperature range of 34 to 50°C. It is clearly seen that $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is highly soluble in water and the solubility increases almost linearly with the increase of temperature, shown in Fig. 1. At room temperature around 34°C, the solubility is found to be 92.41 gm/50 ml of water.

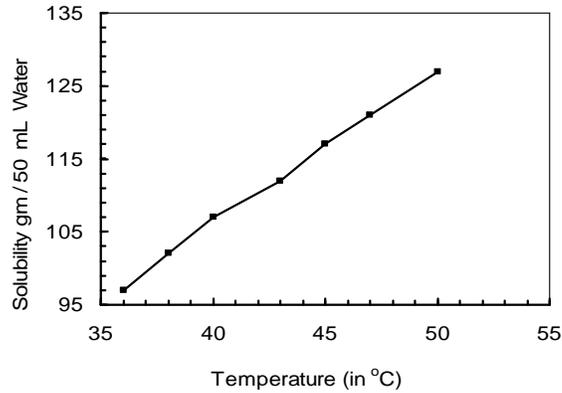


Fig. 1. Solubility vs temperature curve for pure ZnSO_4 salts.

Growth rates of the crystal: Mass growth rates of the grown crystals were determined by weighing method (Kubota *et al.* 1995). The seed crystals were placed in pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solution in a Petridish and then it was kept in a dust free glass chamber.

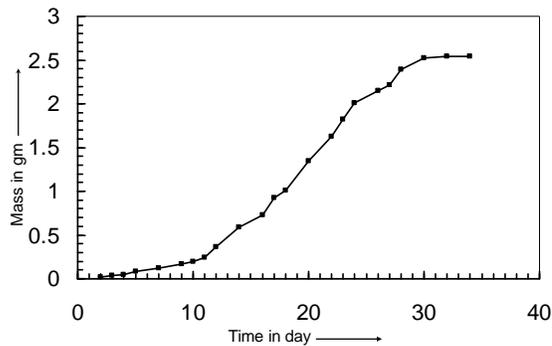


Fig. 2. Mass growth rate of ZnSO_4 crystal.

The weights of the growing crystals were recorded for every 24 hours by a digital balance. After five weeks, the crystals were collected from the solution. The growth rates with respect to the initial mass, G_S , is calculated as

$$G_S = (m - m_o) / (m_o \Delta t)$$

where, m_o is the initial mass, m is the final mass, and Δt is the growth time.

Mass growth rates of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystal are presented in Fig. 2. It was observed that the mass growth rate initially increases gently with time and then it increases rapidly up to a certain time and then it becomes constant. Highly transparent and well faceted large size single crystals with the dimension of $25 \times 15 \times 8 \text{ mm}^3$ were grown by isothermal evaporation method shown in Fig. 3.



Fig. 3. Single crystals of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Infrared spectroscopy: The FT-IR of zinc sulphate heptahydrate single crystal was recorded using KBr pellet technique at room temperature by Shimadzu-IR 470 (Shimadzu Corporation, Tokyo, Japan) in the region of 4000 to 400/cm.

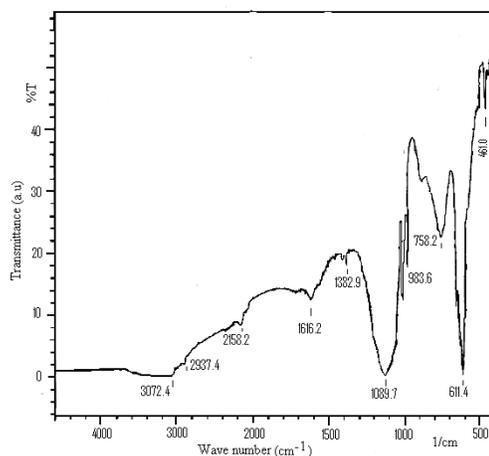


Fig. 4. FT-IR spectrum of pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystal.

The absorption due to various functional groups is shown in Fig. 4. The stretching vibrations of the water molecule are expected in the region 3000-3600/cm (Kanagadurai *et al.* 2009). The broad vibrational band observed at 3072.4 cm⁻¹ is attributed to the symmetric stretching mode of water molecule. The medium broad band noticed at 1616.2/cm is assigned to the bending vibrational mode of water molecules. The band observed at 758.2 cm⁻¹ is assigned to the liberation mode of water molecules. In general, a free SO₄²⁻ ion has four fundamental vibrations, namely a non degenerate mode (ν¹) at 981/cm, a doubly degenerate mode (ν²) at 613/cm and triply degenerate vibrations (ν³ and ν⁴) at 1104 cm⁻¹, respectively (Herzberg 1960). The peak observed at 1089.7/cm is attributed to the triply degenerate symmetric stretching mode, (ν³) SO₄²⁻. The band observed at 461.0/cm is assigned to the doubly degenerate mode (ν²) SO₄²⁻ mode. The peak appeared at 983.6/cm is reasonably assigned to the (ν¹) SO₄²⁻ non degenerate mode. The mode at 611.4/cm is assigned as the triply degenerate vibrations (ν⁴) SO₄²⁻. The above assignment agrees with that of reported values (Sivanesan *et al.* 1993).

X-ray diffraction: X-ray diffraction pattern for the powdered sample of grown crystal was presented in Fig. 5. X-ray diffraction was carried out using a Shimadzu X-ray Diffractometer with Mo (Kα) radiation (λ = 1.70688Å) with an operating applied voltage 30 Kv and current 20 mA. Scanning rate was maintained at 1° per minute.

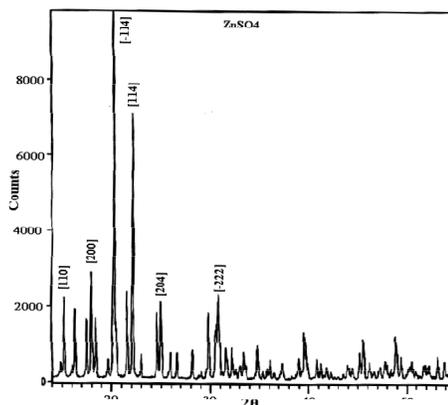


Fig. 5. X-ray diffraction spectrum of pure ZnSO₄.7H₂O crystal.

The indexed pattern of ZSHH is used to calculate lattice parameters. The lattice parameters a, b and c were calculated by using the following formula:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hence 'd' values were calculated using the Bragg's diffraction law (2d sinθ = nλ), where λ is the X-ray wavelength. The values are a = 9.9810 Å, b = 7.2500 Å and c = 24.2800 Å. These values are found to be in good agreement with that of the reported values (Anderson *et al.* 2005, Baur 1964).

Thermal analysis (TG, DTA and DTG): The grown zinc sulphate heptahydrate crystal was crushed into fine powder and thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were recorded using Q50 W/FMC DTA analyzer in the temperature range from room temperature to 700°C at a heating rate of 30°C/min (Fig. 6). The analysis was performed in air atmosphere. The compound is found to be thermally stable up to 70°C. The first weight loss occurs in the range of 70 to 120°C due to the loss of six water molecules with a sharp endothermic peak in the DTA spectrum. The sample suffers a second weight loss at 260°C due to the loss of SO^3 molecule and half of a water molecule leaving $\text{ZnO} \cdot 1/2(\text{H}_2\text{O})$. The TGA curve shows that there is a weight loss of about 32% in the temperature 70 to 120°C due to dehydration and about 7.5% weight loss due to SO^3 and half of a water molecule loss.

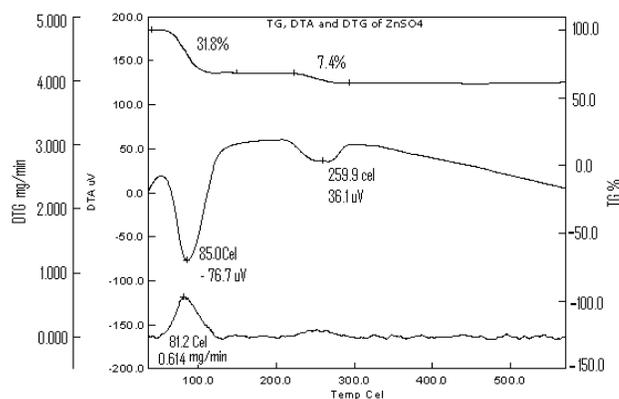


Fig. 6. TGA, DTA and DTG curve of pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystal.

The UV-visible spectral studies: The UV-visible spectrum of zinc sulphate heptahydrate was scanned in the range of 200 to 1100 nm in Fig. 7. The spectrum has low absorbance in between 200 and 400 nm.

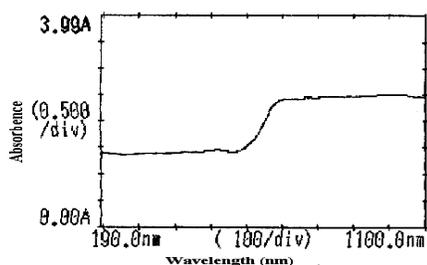


Fig. 7. UV-VIS absorbance spectrum of pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystal.

So the zinc sulphate heptahydrate crystal is expected to be transparent in the UV range and with the increase of a little bit of absorbance in the region of 400 to 1100 nm inferred that the sample is losing transparency which may be due to intrinsic loss mechanism by the interaction of electromagnetic radiation of visible-infrared region.

CONCLUSION

Pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ single crystals were grown from aqueous solutions by isothermal evaporation method. The solubility of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ has been studied in the range of 34 to 50°C. At room temperature around 34°C, the solubility was found to be 92.41 gm/50 ml. Good transparent single crystal of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was obtained over a growth period of 25 to 30 days. Crystals with the dimension of $25 \times 15 \times 8 \text{ mm}^3$ were grown from aqueous solution by an isothermal evaporation method. The presence of functional groups in zinc sulphate heptahydrate has been identified by FT-IR spectral analysis. The powder X-Ray diffraction study confirms the lattice parameter values. The TG, DTA and DTG results show that the as grown crystal is thermally stable up to 70°C. From the UV spectrum, the zinc sulphate heptahydrate crystal is found to be transparent in the UV region and it could be a useful candidate for optoelectronic applications in visible and infrared region.

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REFERENCES

- Anderson, J. L., Peterson, R. C. and Swainson, I. P. 2005. Combined neutron powder and X-ray single-crystal diffraction refinement of the atomic structure and hydrogen bonding of goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). *Miner Mag.* **69**(3): 259.
- Baur, W. H. 1964. The refinement of the crystal structure of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite). *Acta Crystallogr.* **17**: 1361-1369.
- Cano, H., N. Gabas and J. P. Canselier. 2001. Experimental study on the ibuprofen crystal growth morphology in solution. *J. Crystal Growth* **224** : 335.
- Dana, E. S. and W. E. Ford, 1985. *Crystallography and Physical mineralogy*. Wiley Eastern Limited, pp. 760.
- Dhumane, N. R., S. S. Hussani, V. G. Dongre and M. D. Shirsat. 2008. Study on the effects of Glycine on the nonlinear optical (NLO) properties of Zinc (tris) Thiourea Sulfate (ZTS) single crystal. *Optical Materials* **31**: 328-332.
- Ema, M. and A. Gebrewold. 1998. *BT Altura and BM Altura Report*, Department of Physiology, State University of New York, Health Science Centre, Brooklyn.
- Herzberg, G. 1960. *IR and Raman spectra of poly-atomic molecules*. Van Nostrand, New York, 2nd Ed.
- Hussani, S. S., N.R. Dhumane, V.V. Nawarkhele, G. Rabbani and M.D. Shirsat. 2008. Growth and High frequency study of non liner optical Zinc (tris) Thiourea Sulphate Crystal. *Frontiers of Microwaves and Optoelectronics* **141-149** ISBN 978- 81-89927-19-6.
- Ikeya, M., M. G. Hassan, H. Sasaoka, Y. Kinoshita, S. Takaki and C. Yamanaka. 2000. Strategy for finding new materials for ESR dosimeters. *Appl. Radiat. Isot.* **52**: 1209.

- Kanagadurai, R., R. Durairajan, R. Sankar, G. Sivanesan, S.P. Elangovan and R. Jayavel. 2009. Nucleation Kinetics, Growth and Characterization Studies of a Diamagnetic Crystal-Zinc Sulphate Heptahydrate(ZSHH). *E-Journal of Chemistry* **6**(3): 871- 879.
- Kasatkin, I. A. 2002. Interferometric study of MgSO₄. 7H₂O single crystal growth kinetics from solution. *Cryst. Res. Technol* **37**(2-3): 193-205
- Kubota, N., J. Fukazawa, H. Yashiro and J. W. Mullin 1995. Impurity effect of chromium (III) on the growth and dissolution rates of potassium sulfate crystals. *J. of crystal Growth* **149** : 113.
- Ramalingom, S., J. Podder and S. N. Kalkura. 2001. Crystallization and characterization of arthorhombic MgSO₄.7H₂O. *Cryst. Res. Technol* **36**(12): 1357-1364.
- Sgualdino, G., G. Vaccari, D. Aquilano and M. Rubbo. 1987. Growth kinetics of epsomite (MgSO₄. 7H₂O). *J. of Crystal Growth* **83**(4): 523-527.
- Sivanesan, G., P. Koldaivel and S. Selvasekarapandian. 1993. Laser Raman and FT-IR studies of pure and Zn-doped TGS, *Mat Chem Phys.* **34**: 73.
- Tomas, G., Petrov Evgenil, B., Trivus, P. Aleksei and K. Asatkin. 1969. *Growing crystal from solution*. Consultants Bureau, New York **21**: 99-106.

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