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Growth and characterization of cadmium sulphate single crystal by gel growth

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ABSTRACT

The growth of Cadmium sulphate octahydrate single crystals was successfully carried out by using gel growth technique. The cell parameter values were found using single crystal X-ray diffraction analysis. The purity of the material of grown crystal was detected by atomic absorption spectroscopy (AAS). The presence of sulphate functional group was determined by the FTIR and Raman spectra. The optical absorption study was done by UV-Visible spectral analysis. TGA/DTA studies explain the thermal properties of the crystal. The microhardness studies confirm that Cadmium sulphate single crystal has a high Vickers Hardness Number (VHN) in comparison to the other crystals.

Keywords: Gel growth, Cadmium Sulphate, X-ray diffraction.

INTRODUCTION

Cadmium metal and its alloys and compounds are used in a large variety of industries. Derivatives of the cadmium elements are used in active electrode material in nickel-cadmium batteries, pigments used mainly in plastics, ceramics and glasses to stabilize polyvinyl chloride [1]. The Cadmium sulphate is an important inorganic cadmium compound which is widely used in semiconductor industry with many excellent physical and chemical properties. Anhydrous Cadmium sulphate is also produced by melting cadmium with ammonium or sodium peroxodisulfate [2,3]. Cadmium sulphate octahydrate is generally available in the market with the common name of Cadmium sulphate. Cadmium sulphate structure was solved by Lipson in 1936 [4]. Molecular structure of Cadmium sulphate is shown in Figure 1. Yun-Hong Zhang et al. explained hygroscopic Property of Cadmium sulphate [5]. Raman and Infra red studies are carried out by W.Rudolph and G.Irmer in 1994 [6]. Characterization on Cadmium sulphate single crystals is not available in the literature survey. In this paper, highly transparent single crystals of Cadmium sulphate octahydrate have been grown successfully by using slow evaporation method and structural, thermal and optical properties are reported.

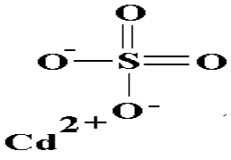

Fig. 1. Molecular structure of Cadmium sulphate

MATERIALS AND METHODS

2.1 Crystal growth

Molecular structure formula was shown in fig. 1.

The growth of Cadmium sulphate octahydrate crystals has been carried out using gel growth technique. The apparatus used for crystallization consists of borosilicate glass tubes of length 15 cm and diameter 2.4 cm placed vertical in a wooden stand. A suitable amount of Cadmium sulphate was taken for crystal growth. Figure 2 shows crystallization process of gel growth technique in the present work. After a few days good quality, colourless, transparent, single crystals of Cadmium sulphate were grown, which is shown in Figure 3.

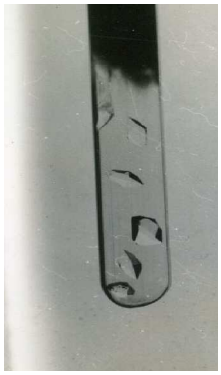

Fig. 2. Crystallization by gel method employing borosilicate glass tubes

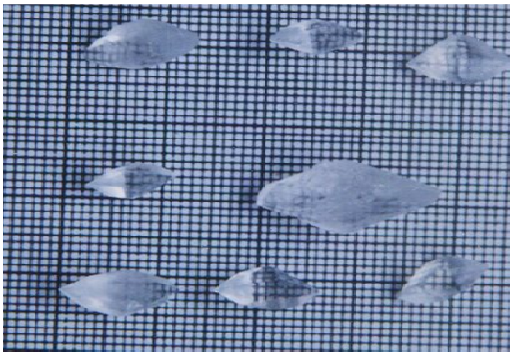

Fig. 3. Photograph of grown crystals.

2.2 Characterization

In order to study the crystal structure of Cadmium sulphate octahydrate, single crystal X-ray diffraction study was taken for a perfect crystal using Enraf Nonius CAD -4 diffractrometer with $MoK_{\alpha}(\lambda=0.7170A^{0})$ radiation. Atomic absorption spectroscopy was carried out using a Varian AA100 Atomic Absorption Spectrometer (AAS). To understand the chemical bonding and molecular structure of the compound, FTIR and FT-Raman spectra were recorded. FTIR spectrum was recorded by the KBr pellet technique using a SPECTROMRX1 FTIR spectrometer in range of of 4000–400 cm^{-1}. FT-Raman spectrum has been recorded using Thermo electron corporation USA Nexus 670 spectrometer in the range of 3500-50 cm^{-1}. Nd-YAG laser source of wave length 1064 nm and InGaAs detector were used in FT Raman measurement. Cadmium sulphate crystal optical behavior has been analyzed by UV-Vis analysis and found that transparency region of the grown crystal using Varian Cary 500 scan spectrophotometer in the range from 200 nm to 2000 nm. Thermal stability of the sample was tested using differential thermal analyzer (DTA) and thermo gravimetry analysis (TGA) using a thermal analyzer NETSZCH SDT Q600 V8.3 Build 101 at a heating rate of 20^{0}C/min in nitrogen atmosphere in temperature range 0^{0}C–900^{0}C. Vickershardness measurements were done on the grown crystals using a micro-hardness tester Model HMV-2, Shimadzu, Japan.

RESULTS AND DISCUSSION

3.1 Single Crystal XRD study

From the single crystal XRD, the lattice parameter value of Cadmium sulphate octahydrate crystal was found to be a=15.79(2) Å, b=11.75(1) Å, c=7.88(1) Å, α=90, β=102.8 and γ=90. This indicates that Cadmium sulphate octahydrate crystallizes in monoclinic system. The results are in agreement with reported values [7]. Comparison of lattice parameters is shown in the Table 1.

Table 1. Cell parameter data of Cadmium sulphate crystals

Parameters	Cadmium sulphate octahydrate [present work]	Cadmium sulphate octahydrate [7]	Cadmium sulphate mono hydrate [8]	Cadmium sulphate [6]
a (Å)	15.79(2)	14.78	7.64	4.7174
b (Å)	11.75(1)	11.87	7.46	6.5590
c (Å)	7.88(1)	9.44	7.62	4.7012
A (°)	90	90	90	90
B (°)	102.8	97.31	115.5	90
γ (°)	90	90	90	90
System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic

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3.3 Atomic absorption study

Atomic absorption spectroscopy (AAS) measurements to determine the composition of the crystals. The incorporation of impurities in Cadmium sulphate octahydrate crystals has been quantified by this study. In order to determine the exact mole percentage of compounds incorporated in the crystals, crystalline powder of Cadmium sulphate was dissolved in 100 ml of double distilled water. The solution was subjected to analysis. The results revealed that impurities are very low in in the crystal lattice of Cadmium sulphate crystal. This confirms that crystal is purely Cadmium sulphate. The observed data was tabulated in Table 2.

Table 2. Amount of elements presence in the Cadmium sulphate octahydrate crystal

Elements	Value (ppm)
Mo	**0.066**
Cr	**0.117**
Ni	**0.074**
Zn	**0.079**
Pb	**0.261**
Mn	**0.051**
Cd	**14.636**

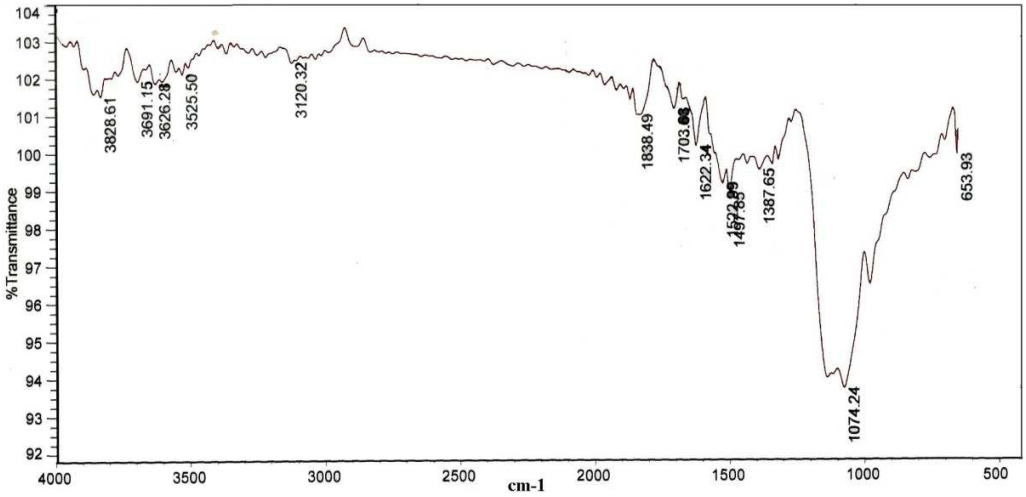

Fig.4. FT-IR spectrum of Cadmium sulphate octahydrate

3.2 FT-IR study

The Fourier transform infrared spectrum of Cadmium sulphate octahydrate was recorded in between the region 400 cm^{-1} and 4000 cm^{-1} shown in Figure 4. Observed bands along with their vibrational assignments have been tabulated in Table 3. A peak at 1622 cm^{-1} is assigned to the bending vibrational mode of water molecules. Generally a sulphate ion has four fundamental vibrations. Triply degenerate mode vibrations (ν_3) of sulphate ion are observed at 1074 and 1137 cm^{-1}. The stretching vibrations of the water molecule are observed in the region 3000-3700 cm^{-1}.

Table 3. FT-IR vibrational frequencies of Cadmium sulphate octahydrate crystals

Wavenumbers (cm^{-1})	Assignments
653	triply degenerate vibrations (ν_4) of SO_4^{2-}
1074	Stretching (ν_3) of SO_4^{2-}
1137	Stretching (ν_3) of SO_4^{2-}
1497	Stretching of S=O
1622	Bending vibration of water molecules
1703	Stretching of SO_4^{2-}
1838	Stretching of SO_4^{2-}
3000-3700	symmetric stretching mode of the water molecule

3.3 FT Raman study

In figure 5 show Raman spectra of Cadmium sulphate octahydrate crystal. The band observed at 470 cm^{-1} in the investigated Cadmium sulphate octahydrate crystal corresponds to bending mode (ν_2) of SO_4^{2-}. The assignment of the other Cadmium sulphate octahydrate bands is given in Table 4. The FTIR and Raman vibrational frequencies assignments are based on the work of W. Rudolph et al.[6].

Table 4. Raman vibrational frequencies of Cadmium sulphate octahydrate crystals

Wavenumbers (cm^{-1})	Assignment
470	Bending mode (ν_2) of SO_4^{2-}.
650	**Bending mode** (ν_4) of SO_4^{2-}.
1009	**Asymmetric** (ν_1) of SO_4^{2-}.
1118	**Anti symmetiric mode of** (ν_3) SO_4^{2-}.

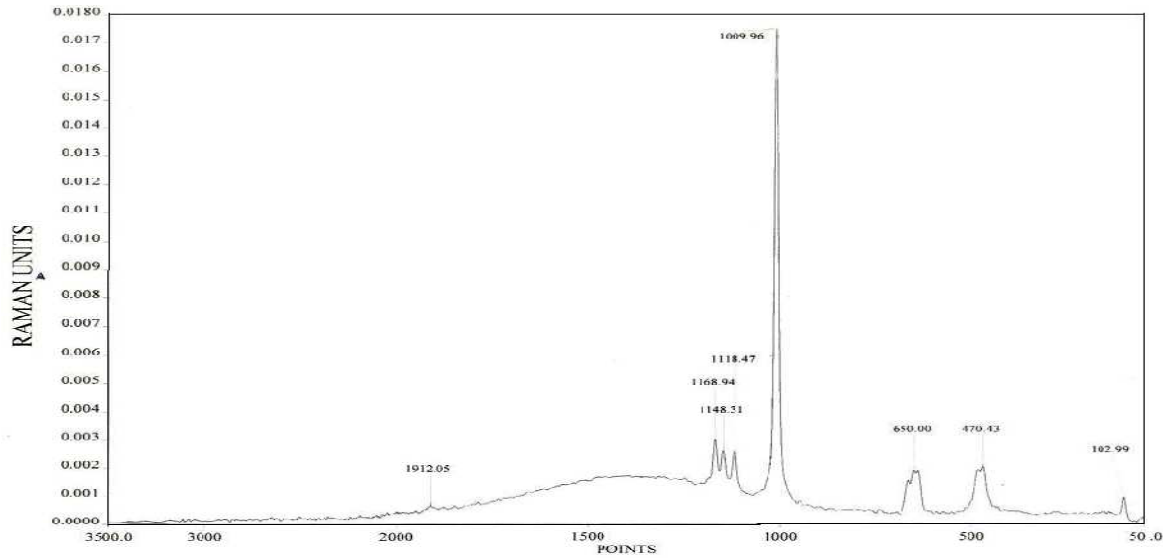

Fig. 5. Raman spectrum of Cadmium sulphate octahydrate

3.4 Optical absorption study

The optical property of the grown crystal was assessed by using Varian Cary 500 scan spectrophotometer. Single crystals are mainly used in opto electronic applications. The optical transmission range and the percentage of transparency of the single crystals impact the their applications in the field. The transmission spectrum was recorded

in the range starting from 200 nm - 2000 nm. The recorded spectrum is shown in Fig. 6. A complete transparency between 300 and 2000 nm is interesting, as it is very much required for optical applications of this crystal.

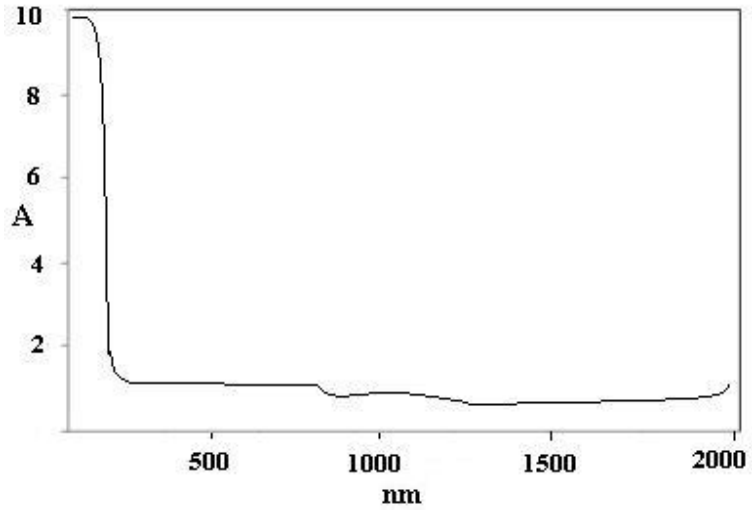

Fig. 6. Absorption spectra for Cadmium sulphate octahydrate crystal

3.5 Hardness study

Table 5. Microhardness values for the Cadmium sulphate octahydrate crystal

Load (P) gram	d1 µm	d2 µm	d µm	Microhardness Hv
10	32.11	30.45	31.28	19.00
20	31.02	31.55	31.29	37.90
30	31.56	31.18	31.37	56.50
40	31.56	31.18	31.37	75.40
50	37.55	35.59	36.57	69.30
60	34.29	34.48	34.39	94.10
70	46.80	45.47	46.15	61.60

The physical strength of the crystal was measured by Vicker's micro hardness test. The mechanical property plays a important role in device fabrication. One of the methods to determine the mechanical behavior of the grown crystal is micro hardness test. The diagonal length of the indentation for various applied loads was measured in the process. The Vickers' hardness number (Hv) is calculated using the relation $Hv = 1.8544\ P/d^2$ (kg/mm^2).Where P is the applied load in grams and d is the average diagonal length of the vicker's impression in mm after loading. Plot of H versus P for the investigated sample is shown in Figure 7. The non linear variation of H with load implies the presence of imperfection in the lattice. Hardness values for different loads are tabulate in Table 5.

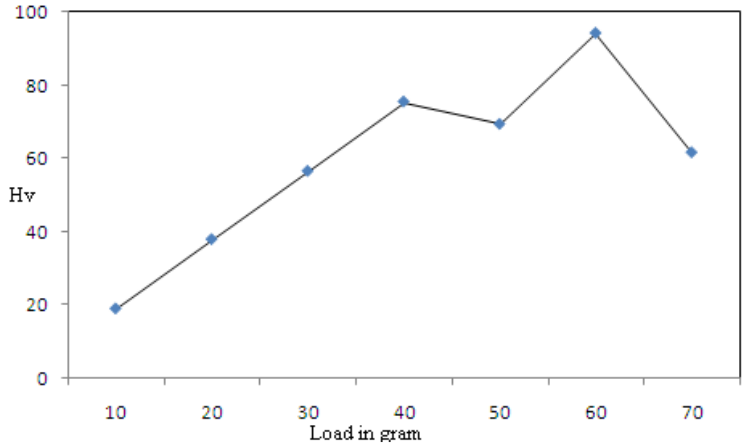

Fig. 7. Hardness value diagram

3.6 Thermal studies

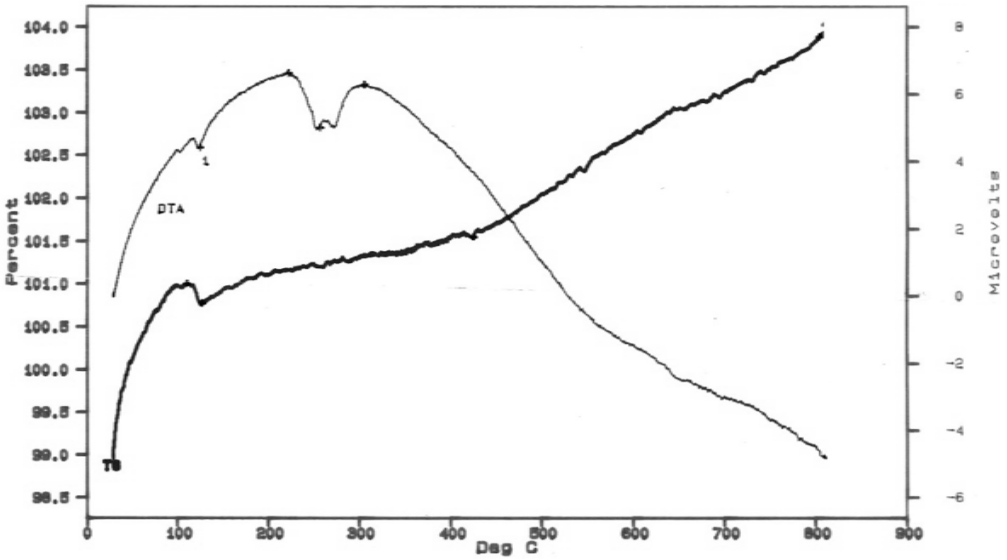

Fig. 8. TGA/DTA curve of Cadmium sulphate octahydrate crystal

Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA) of Cadmium sulphate octahydrate single crystals were carried out simultaneously at a rate of 20 ºC/min in inert nitrogen atmosphere. Figure 8 shows the TGA/DTA traces of Cadmium sulphate octahydrate crystal. There are two peaks in DTA curve at 123 and 255ºC. TGA curve shows that changes in weight at 109, 126 and 424 ºC. A gradual weight changes process takes place from 424 to 803 ºC. Cadmium sulphate cannot be quenched at room temperature. Thermal study confirms that high temperature anomaly in Cadmium sulphate.

3.7 Etching studies

Imperfections present in a material can influence seriously the device characteristics. Hence the assessment of physical as well as the chemical imperfections in crystalline materials is essential in the field of material research. Etching techniques can be applied to understand the behavior of dislocations and also to reveal the growth history of the crystals. The etch patterns produced on a crystal are related to the internal structure just as the regular geometry and external shape of the grown crystals. Etch pattern of Cadmium sulphate crystal is shown in the Figure 9. Similar shapes are observed in the crystal surfaces. The hopper structure observed in the etch pattern of the crystal.

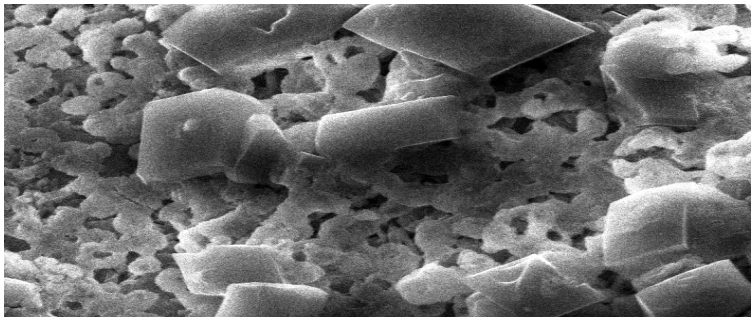

Fig. 9. Etch pattern of Cadmium sulphate octahydrate crystal

CONCLUSION

Gel growth method yielded optically transparent single crystals of Cadmium sulphate octahydrate. The grown crystals have been subjected to various characterization studies. Monoclinic structure of the crystal was confirmed by single crystal XRD. Atomic absorption spectroscopy estimated the presence of different elements in the grown

crystal. FTIR and Raman studies confirm the presence of functional groups and vibrational interactions. The optical study reveals transparent region of the crystal. The melting point of the crystal was confirmed by TGA/DTA studies. Microhardness study estimates the mechanical strength of the crystal.

REFERENCES

[1] Adams, RG. (**1992**) *Occup. Med*., 42, 101-106
[2] Hollander, M.L. & Carapella, S.c., Jr (**1978**) Cadmium and cadmium alloys. ln: Mark, H.E, Othmer, D.E, Overberger, c.G., Seaborg, G.T & Grayson, N., eds, Kirk-Dthmer Encyclopedia of
[3] Chemical Technology, 3rd Ed., VoL. 4, New York, John Wiley & Sons, pp. 387-396
[4] Lipson,Ho. "The crystal structure of $3CdSO_4.8H_2O$", Proc.RoyoSoCo(London), Ser.A, 156, (**1936**), 462-470.
[5] Yun-Hong Zhang and Chak K. Chan, *J. Phys. Chem. A* **2002**, *106*, 285-292.
[6] W. Rudolph and G. Irmer, *Journal of Solution Chemistry*, Vol. 23, No. 6, **1994**.
[7] H. E. Swanson, H. F. McMurdie, M. C. Morris, and E. H. Evans "Standard X-ray Diffraction Powder Patterns", National Bureau of Standards Monograph 25-Section 6, **1968**.
[8] H. E. Swanson, H. F. McMurdie, M. C. Morris, and E. H. Evans "Standard X-ray Diffraction Powder Patterns" National Bureau of Standards Monograph 25-Section 3, 20, **1964**.