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Growth and characterization of diammonium copper disulphate hexahydrate single crystal

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ABSTRACT

Diammonium copper disulphate hexahydrate is one of the most promising inorganic crystals with exceptional dielectric properties. A good quality crystal was harvested in a 30-day period using solution growth method. The grown crystal was subjected to various characterization techniques like single crystal X-ray diffraction analysis, thermo gravimetric, differential thermal analysis, FTIR, and UV–vis–NIR analysis. Unit cell dimensions of the grown crystal have been identified from XRD studies. Functional groups of the title compounds have been identified from FTIR studies. Thermal stability of the samples was checked by TG/DTA studies. Band gap of the crystal was calculated. The dielectric constant and dielectric loss were studied as a function of frequency of the applied field. AC conductivity was plotted as a function of temperature.

1. Introduction

Copper ammonium sulphate is one of the promising Tutton salts and their structure has been reported already [1,2]. The title compound has similar structure to that of copper ammonium sulphate. Various metal ammonium complexes like magnesium ammonium sulphate, nickel ammonium sulphate [3], lithium ammonium sulphate [4] have already been reported. The importance of these complexes is that they have good dielectric behaviour. Dielectric materials find wide applications in micro devices such as sensors, actuators used in ultrasonics. The fundamental behaviour utilized in these devices is the strong electromechanical coupling exhibited by the dielectric material [5–9]. In the current study, diammonium copper disulphate hexahydrate (DACS) has been grown by solvent evaporation method for the first time. Some of the physical parameters like UV cut off wavelength, dielectric constant and band gap have been estimated. Dielectric studies were performed to analyze their electrical properties. This crystal is belongs to one of the Tutton salts which have played a significant role in physics and chemistry; considerable attention is currently focused on the development of materials suitable for strong energy absorbed by solar collectors. For domestic heating and hot water supplies, this energy might be stored chemically in reversible reactions, thermally in the phase changes, or temperature increases of storage materials [10,11].

2. Crystal growth

The title compound was prepared by dissolving analar grade copper sulphate and ammonium sulphate in the stoichiometric ratio of 1:1 in Millipore water of resistivity 18.2 MΩ cm^{-1}. Initially calculated amount of copper sulphate was added to the solvent. Once it got dissolved, then ammonium sulphate was added. Care was taken that all the solute got dissolved in the solvent and a homogeneous mixture was obtained. The solution was continuously stirred for 5 h with the help of magnetic stirrer and filtered. The solution was left to nucleate in a beaker with porously sealed cover, so that it would evaporate at 30 °C. The grown crystals were recrystallized three times. After which, single crystal of diammonium copper disulphate grown by solvent evaporation method was harvested in 30 days. The reaction mechanism is shown below

$$CuSO_4 + (NH_4)_2(SO_4)_2 \rightarrow Cu(NH_4)_2(SO_4)_2{\cdot}6H_2O$$
$$\times(\text{diammoniumcopperdisulphatehexahydrate})$$

The as grown crystal is shown in Fig. 1(a) and structure of the grown crystal is shown in Fig. 1(b).

3. Characterization

Single crystal XRD analysis was carried out with APEX2v 2.0 diffractometer with Mo K_α rays to identify the lattice parameters. The lattice parameters of the grown DACS crystal are listed in Table 1. FTIR spectral analysis of diammonium copper disulphate hexahydrate was done by Perkin-Elmer spectrophotometer using

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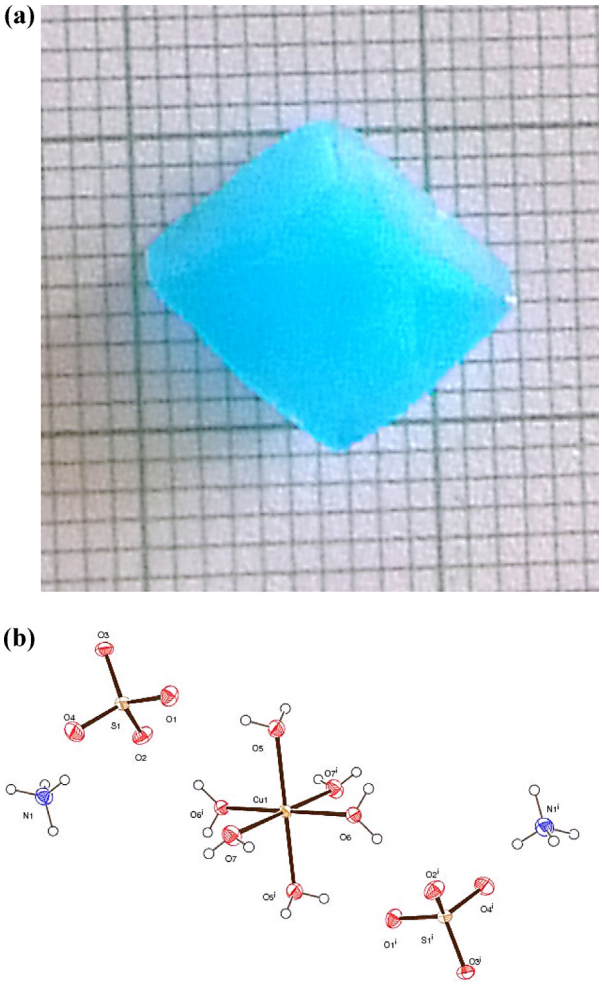

Fig. 1. (a) The as grown diammonium copper disulphate hexahydrate crystal. (b) The Ortep diagram of diammonium copper disulphate hexahydrate crystal.

the KBr pellet method to study the presence of functional groups in the sample qualitatively. FTIR analysis was done in the range 400–4000 cm^{-1}. The UV–vis–NIR spectra of diammonium copper disulphate hexahydrate were recorded with Lambda 35 spectrophotometer in the range 200–1200 nm with a crystal of thickness 1.5 mm. The thermal stability of the crystal was identified by thermogravimetric (TG) and differential thermal analysis (DTA) studies simultaneously. Thermal analysis was carried out by a Q600SDT analyzer in an atmosphere of nitrogen at the heating rate of 10 °C min^{-1} in the temperature range of 50–300 °C. Dielectric measurements were carried out by HIOKI 3532-50 LCR Hitester with a temperature range 50–150 °C. Dielectric constant (ε) and dielectric loss ($\tan\delta$) were noted for the above temperature range. AC conductivity for the same temperature range was calculated and plotted as graph.

4. Results and discussions

The single crystal XRD analysis shows that the crystal belongs to monoclinic crystal system and $P2/c$ space group. The crystallinity of the crystal is also confirmed by the structural analysis. Lattice parameters of diammonium copper disulphate hexahydrate crystals are listed in Table 1. As the title material is a new compound, the structure was submitted to Cambridge Crystallographic Centre and CCDC 934414 was obtained for the crystal structure submitted.

Table 1
Lattice parameters of diammonium copper disulphate hexahydrate.

S. no.	Lattice parameter	Value [1,2]	Value of the grown crystal
1	a	6.293(2) Å	6.294(5) Å
2	b	12.349(2) Å	12.382(5) Å
3	c	9.208(2) Å	9.210(5) Å
4	α	90.000(2)°	90.000(5)°
5	β	106.9(2)°	106.112(5)°
6	γ	90.000(2)°	90.000(5)°
7	Volume	–	689.6(7) $Å^3$

Infrared spectrum is an important characterization technique which provides structural analysis of a compound. In this technique, almost all functional group in a molecule absorb characteristically a definite range of frequency [12]. The FTIR spectra of diammonium copper disulphate hexahydrate are shown in Fig. 2. The absorption of IR radiation causes the various bands in a molecule to stretch or bend with respect to one another. The range 400–4000 cm^{-1} is of prime importance for the study of a compound by spectral analyses [13]. The broad band at 3207.8 cm^{-1} is due to the NH asymmetric stretching vibration and OH stretching. The peaks at 2253.51.61 cm^{-1} and 2075.04.34 cm^{-1} are assigned to the symmetric/asymmetric stretching of the hydroxyl group present in the crystal. The peaks at 1584.65 cm^{-1} and 1419.24 cm^{-1}, 1143.04 cm^{-1} are attributed to the bending of N–O bonding in the crystal. The peaks at 980.15 cm^{-1} and 923 cm^{-1} are attributed to O–H bending in the crystal. The narrow peak at 790.35 $cm^{-1}$and 630.34 cm^{-1} are due to N–H wagging seen in the DACS crystal.

Thermal studies were carried out by employing TA Q600 SDT thermal analyzer to study the thermal behaviour of the grown crystal. The thermogravimetric analysis and differential thermal analysis of diammonium copper disulphate hexahydrate were carried out in the temperature range of 50–300 °C in an inert nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The observed TGA and DTA curves of diammonium copper disulphate hexahydrate are shown in Fig. 3. The first exothermic peak noticed at 121.75 °C and second peak at 162.57 °C are due to the exclusion of water molecules from the crystal. The exclusion of copper sulphate from the crystal lattice can be seen at 156.77 °C and 286.5 °C. The exclusion of ammonium sulphate from the crystal lattice can be seen at exothermic peak formed at 397.30 °C. The weight loss of the sample is in two stages. The first level of weight loss starts at 188.72 °C. The second region of weight loss is seen at 357.58 °C. The crystal shows a complete weight loss at 427.28 °C and decomposes at the same temperature.

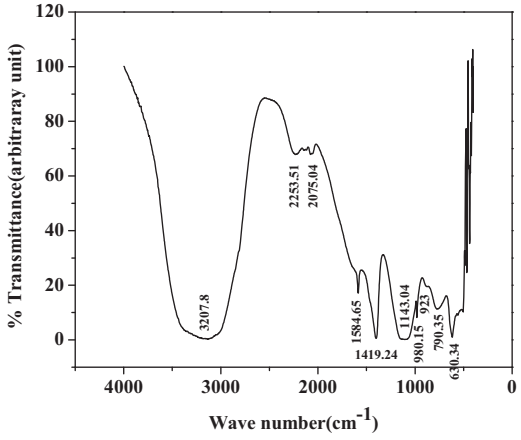

Fig. 2. FTIR spectrum of diammonium copper disulphate hexahydrate crystal.