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Contents

Universities Research Journal 2008, Vol. 1, No. 3

Ionic Conductivity and Dehydration of $ZnSO_4.7H_2O$ Crystal at High Temperature

Wut Hmon Win

Abstract

Crystals of Zinc Sulphate Heptahydrate, $ZnSO_4.7H_2O$ have been grown by the slow evaporation of aqueous solutions. Spectroscopic grade of $ZnSO_4.7H_2O$ (30g) and distilled- water (18ml) were used to synthesize for those compounds. Vibrational spectroscopic investigations of those crystal were studied by FTIR spectroscopic method between the frequencies region of $400cm^{-1}$- $4000cm^{-1}$ at room temperature. High temperature electrical conductivity and dehydration of those crystals were studied during the temperature region of 300K- 500K.

Key words: Ionic Conductivity Dehydration, FTIR spectroscopic method

Introduction

The total characterization of a material is an essential part of any investigation, not only the chemical and physical properties, such as its reactivity or its magnetic properties, but also its structure. Typically, the structure of a solid material governs its observed properties. Many industrially and technologically important materials are solids. In addition to the magnetic, optical or mechanical properties and anything else which makes them interesting, a researcher should also want to know about their structure; which atoms and/or ions are involved, where they are relative to each other and how they are bonded together. All materials fall into two groups:

(i) Crystalline : [long-range order ($>10^3$ molecules)]

(ii) Non-crystalline : [small particles with no (amorphous) long range

: order (100 Å, where $1Å = 10^{-8}$ cm)]

In the crystalline state, regular atomic order persists over distances which are very large in comparison with interatomic distances. However,

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even in the most perfect of crystals there are some small and usually random departures from regularity. These imperfections result in mirror changes to physical properties, such as resistance and conductivity, but are a feature of solid state materials in general. It is noteworthy that reactions of materials often involve the whole crystal lattice, imperfections and all, rather than just the atoms of the "pure" substance [3, 5, 6].

Nearly all materials can be prepared in the amorphous state. Interest in amorphous material has grown with the development of techniques which can be used to characterize them. Glass is a special type of amorphous material which melts at the glass transition temperature. Crystals can be formed in numerous ways, including cooling from molten salts and deposition from vapours [2, 10].

Analysis of the internal motions of a crystal relies heavily upon the symmetry properties of the crystal, which are best treated on the basic of group theory. Although upon the theory is not quite as simple as for molecules, the methods, their symmetries and hence the selection rules for Raman Scattering or IR absorption, may be carried out in the same general manner as for free molecules, a few difference is to be discussed and the absence of rotational and translational freedom for the unit cell should be noticed. Raman Spectroscopy, thus provides the internal vibration of ions / molecules in the crystals [9].

In the present work, crystals of $ZnSO_4.7H_2O$ were grown by slow evaporation method at room temperature. Vibrational analysis of sulphate and water molecules in those crystal environments was investigated by FTIR spectroscopy. Electrical conductivity and dielectric of those crystals have been investigated by temperature dependent conductivity measurement to determine the dehydration temperature of those crystals.

Experiment

Crystal growth condition, FTIR spectroscopic measurement and temperature dependent conductivity experiment are presented in this paper. Some details will be described because they are important in practice based on doing experiment in this work and also in the related fields [1, 4, 7, 8, 10, 11].

Growth of $ZnSO_4.7H_2O$ Crystal

Laboratory grade of Zinc Sulphate Heptahydrate, $ZnSO_4{\cdot}7H_2O$(30g) and distilled-water (18ml) were used to make crystals grow in the present investigation. Aqueous solution of $ZnSO_4{\cdot}7H_2O$ salt was prepared at a supersaturated concentration and taken in the nucleation cell (corning glass vessel) and allowed to equilibrate at the desired temperature. The solution was stirred and the temperature was slowly increased until all of the salts dissolved. The obtained solution was then decanting through the filter paper and funnel into a beaker to be used for growth of $ZnSO_4{\cdot}7H_2O$ crystals. Small crystals appeared in the beginning due to slow evaporation and grew larger in considerable finite time.

A perfect-like (or the best quality) $ZnSO_4{\cdot}7H_2O$ seed crystal was selected and placed in the supersaturated solution after forming the first seeds at the bottom of the beaker. Photograph of the as-grown crystal of $ZnSO_4{\cdot}7H_2O$ is shown in Fig.1. At room temperature, $ZnSO_4{\cdot}7H_2O$ crystal is colourless.

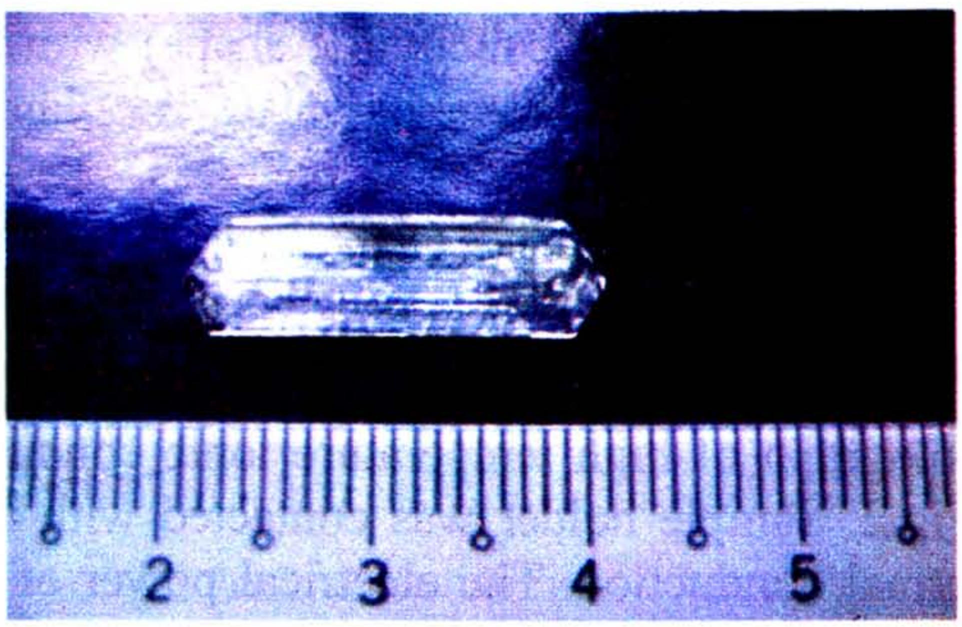

Figure.1 Photograph showing the as-grown crystal of $ZnSO_4.7H_2O$

FTIR Measurement

IR transmission spectrum of $ZnSO_4{\cdot}7H_2O$ crystals with KBr pellet method has been measured by the use of (Perkin-Elmer) FTIR Spectrophotometer at Universities' Research Centre (URC), Yangon University. For the FTIR spectrum collection, firstly, only the sample compartment was placed at the focus position or at IR beam and measured the energy spectrum with air background. Thin pellet (0.50 mm) of

$ZnSO_4 \cdot 7H_2O$ with KBr pellet was inserted into the sample compartment and collected the IR transmission spectrum.

The measurement conditions were used as follow:

Measuring time	:	60 s
Measurement mode	:	%T
Wave number range	:	$400\ cm^{-1} - 4000\ cm^{-1}$.

High Temperature Ionic Conductivity and Dielectric Measurement

Firstly, the as-grown (bulk) crystal was cut into the dimensions of (1.25 x 0.85 x 0.38) cm^3 using very thin stainless-steel thread and polished with the wet filter papers. Hence, the crystal was fixed on glass plate and silver contacts were made over the sample to ensure good electrical contacts to measure the electrical properties such as resistances that can change with temperatures.

The sample was sandwiched between two thin copper plates to ensure a good electrode contact. The crystal was placed in the sample holder of two thick copper plates (circular shape) with the dimensions of 4.5 cm (lower plate) and 1.5 cm (upper plate) in diameters and 0.5 cm (lower plate) and 0.2 cm (upper plate) in thickness. The sample holder was inserted into the steel housing/chamber that was surrounded by asbestos to prevent the heat loss and the temperature that maintained in the chamber during the measurement.

The photograph of high temperature ionic conductivity experiment is shown in Fig.2. Sample holder was contacted with the heating copper chamber to thermal conduction. The electrical power of 300 W heater-rod was inserted into the central core of cylindrical copper chamber. Mica sheets were used between sample holder and heating copper chamber to have more thermal conductivity from the heater to sample and to protect the electrical conductivity. In order to provide better electrical contact, the silver paste was applied evenly on both surfaces of the crystal.

Temperature dependent electrical conductivities of $ZnSO_4 \cdot 7H_2O$ crystal were observed in the temperature range from 27°C (300 K) to 227°C (500 K) by the use of PC-based temperature controller FOTEK MT-20. Temperature dependent resistance was measured by using FUKE FK9208X digital multimeter. At the same time, temperature dependent capacitances were also measured by using WHDZ CM9601A Capacitance meter. The temperature sensor of K-type thermocouple (up to 2000 °C) was inserted near the sample to record real temperatures throughout the measurement (see Fig.2). The dc electrical conductivity of the crystal has been calculated by using the formula

$$\sigma = \frac{l}{RA},$$

where l is the thickness of the sample, A is the area of cross-section of the sample (electrodes) and R is the resistance of the sample.

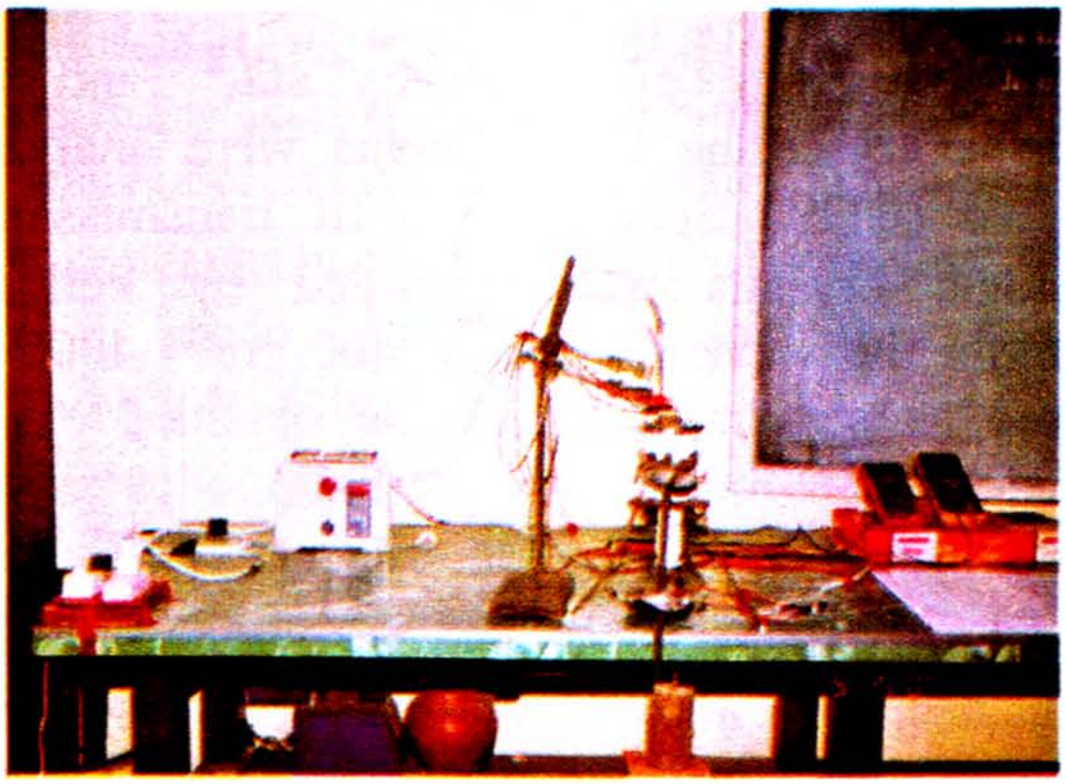

Figure 2. Experimental setup of temperature dependent ionic conductivity measurement

The value of dielectric constant ε_r has been calculated by the relation given below,

$$\varepsilon_r = \frac{1}{\varepsilon_0}\frac{Ct}{A}$$

In the above formula, C is the capacitance, t is the thickness of the crystal, A is the cross-sectional (surface) area of the crystal and ε_0 is the permittivity of free space ($8.854187817 \times 10^{-12}\ C^2 / Nm^2$).

Result and Discussion

Single crystal of $ZnSO_4{\cdot}7H_2O$ is a hydrated-ionic compound that exhibits the phase change with ionic conductivity at high temperature during the process of dehydration. Above the transition point, the numerical values of electrical conductivity enable one to classify the high temperature phases. Experimental results of some illustrations with detailed explanations such as both spectral analysis and graphical analysis are presented in this paper.

Vibrational Analysis of Sulphate and Water Molecules in $ZnSO_4{\cdot}7H_2O$ by Fourier Transform Infrared Spectroscopy

Molecular vibrations of Sulphate, SO_4^{2-} and water, H-O-H molecules in those crystalline environments were analyzed by Fourier Transform Infrared (FTIR) Spectroscopy. IR transmission spectrum of $ZnSO_4{\cdot}7H_2O$ single crystals were recorded by Perkin-Elmer FTIR Spectrometer within the wavenumbers of 400 cm^{-1}- 4000 cm^{-1} region at room temperature as shown in Fig3. The obtained experimental data (wavenumbers and corresponding vibrational modes of molecules) are assigned and presented in Table.1.

In the study of interesting crystals that consist of mainly Sulphate and Water molecules, ten absorption lines were observed in this FTIR spectrum, in which three lines are fundamental modes of the sulphate molecule in those crystals. According to vibrational analysis, the sulphate molecule in the free-state is tetrahedral-pyramidal type T_d symmetry and it has four types of fundamental vibrations [9]. Moreover, there are three types of vibrational motions of the T_d linked with H-O-H molecules; namely: rocking, twisting and wagging vibrations. As shown in the spectrum of $ZnSO_4{\cdot}7H_2O$ crystal (see Fig 3), the absorption lines at 574 cm^{-1}, 668 cm^{-1} and 748 cm^{-1} are indicated the librational frequencies of wagging, twisting and rocking vibration of S---HOH---S, (i.e., sulphate linked water molecules).

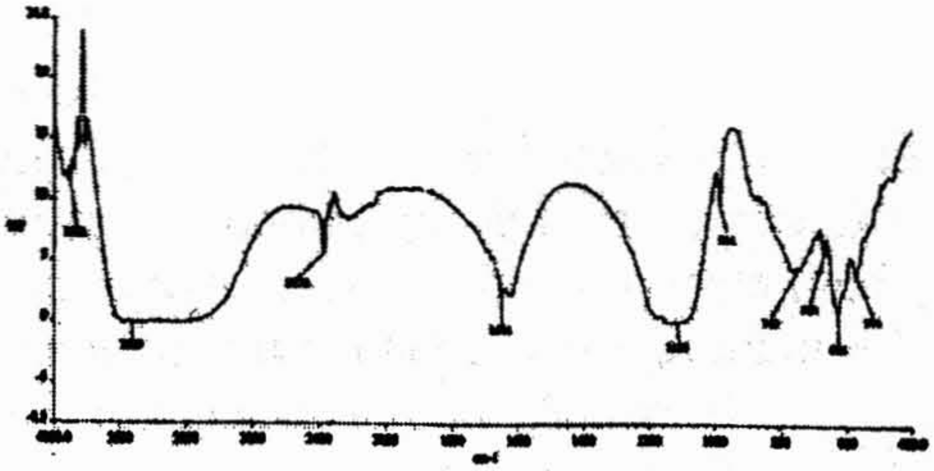

Figure 3. IR transmission spectrum of $ZnSO_4.7H_2O$ crystal at room temperature

Three normal modes (ν_1, ν_3 and ν_4) of sulphate were observed and assigned in this spectrum. The ν_2-mode (bending vibration), however, of sulphate molecule was not found in this spectrum.

Also, water molecule has three modes of fundamental vibrations, they are assigned as ν_1- mode (asymmetric-stretching), ν_2-mode (bending) and ν_3-mode (symmetric-stretching).

In the present work, only two vibrational modes of water molecule were observed in this FTIR spectrum of 400 cm^{-1} – 4000 cm^{-1} region. The ν_3-mode (symmetric-stretching) vibration of water molecule was not detected because this mode normally appears at about the region of 3100 cm^{-1} -3200 cm^{-1} and it may be overlapped with the ν_1-mode. Moreover, one combination band of water molecule and H-bonded character of water were found at 3901 cm^{-1}.

Table.1 Recorded wavenumbers (frequencies) and vibrational mode assignments of $ZnSO_4.7H_2O$ crystal

Sr No	Frequency (cm^{-1})	Mode Assignments	Types of Vibration
1	574	ν_ω(S---HOH--- S)	Librational wagging
2	626	$\nu_4(SO_4^{2-})$	Polarization
3	668	ν_τ(S---HOH--- S)	Librational twisting
4	748	ν_ρ(S---HOH--- S)	Librational rocking
5	984	$\nu_1(SO_4^{2-})$	Symmetric-Stretching
6	1113	$\nu_3(SO_4^{2-})$	Dipole
7	1651	ν_2(H-O-H)	Bending
8	2370	ν(O-C-O)	Bending
9	3529	ν_1(H-O-H)	Asymmetric-stretching
10	3901	ν_1(H-O-H)+ν(H-bonding)	Combination

High Temperature d.c Electrical Conductivity and Dielectric Results

Heat conduction is the process of thermal energy from some body to a cold body when both the bodies are brought into contact. Since, in insulators, e.g., ionic crystals, heat is carried entirely by phonons, but in metals heat may be transported by both electrons and phonons. According to theoretical approach, temperature–induced ionic conductivity in ionic crystals can involve ionic migration and changes in the orientation of defects complexes. Ionic mobility is small charge, small size and lattice geometry. A highly charged ion will polarize, and be polarized by the ions of opposite charge as it moves past them, and this will increase the height of the energy barrier that inhibits a change of site.

Ionic conductivity of an ionic material obeys an Arrhenius formula $\sigma = \sigma_0 \exp(-E_i / kT)$, where σ is the conductivity, or ion drift in materials, σ_0 is the pre-exponential factor or slope of the conductivity curve; In $E_i = E_j + \Delta H_s / 2$, E_i is the activation energy for ionic conduction, E_j is the barrier height, $\Delta H_s / 2$ is thermal changes of Schottky defects accompanying the cation vacancy plus anion vacancy and ion vacancy plus interstitial ion, k is the Boltzmann constant and T is the absolute temperature. Arrhenius plot of the variation of dc electrical conductivity of the sample within temperature region of 27 °C to 227 °C (300 K - 500 K) is shown in Fig .4.

From the plot, it is found clearly that the conductivity of the sample is abruptly increased at the temperature 129 °C (402 K) because certain of the ionic bonds in the crystal must be broken before positive or negative ions of water molecules from the crystal are released (moved) to carry current. The agency that breaks the bond is usually thermal agitation. At this temperature, the crystals of $ZnSO_4.7H_2O$ were changed to $ZnSO_4.H_2O$ (Heptahydrate to Monohydrate) due to dehydration or ionic movement of water in those crystals. This temperature can be taken as the transition temperature T_C of the crystal.

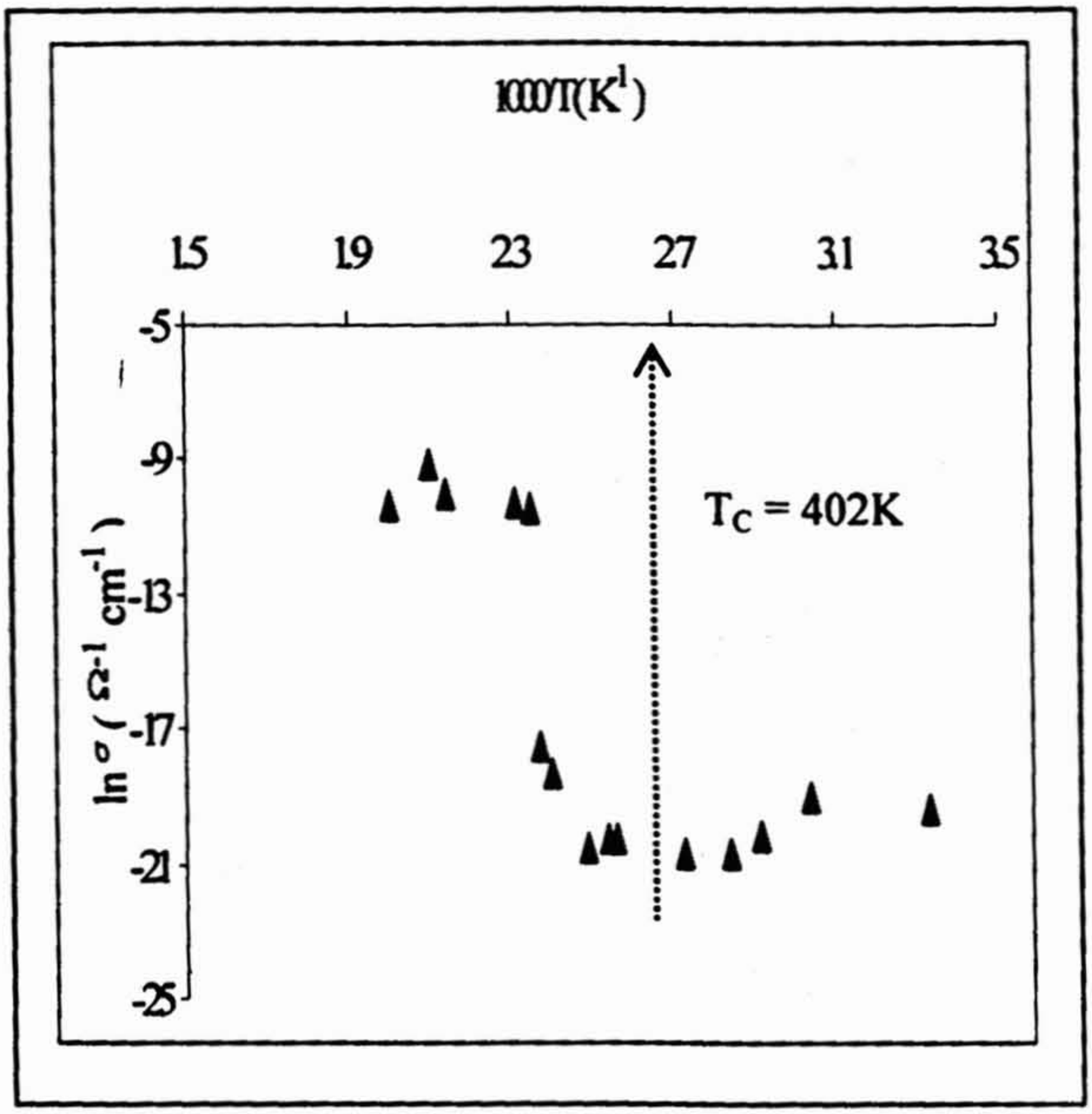

Figure 4. Temperature dependent electrical conductivity of $ZnSO_4.7H_2O$ crystal

It is shown in Fig.5. The dielectric constant of the crystal has a value of 8.75 x 10^{-8} Fm^{-1} at 300K (27 °C or room temperature) and slightly decreased with increasing temperature up to 390K. Then, after reaching the temperature of 402 K, the value of dielectric constant of the sample is up to 6.87 x 10^{-7} Fm^{-1}. This temperature can be taken as the dehydration or phase transition (T_C) temperature of the crystal of $ZnSO_4.7H_2O$ to $ZnSO_4.H_2O$ (heptahydrate-monohydrate compound). Experimental results of electrical conductivities and dielectric constants at room temperature and at T_C of the crystal are tabulated in Table 2.

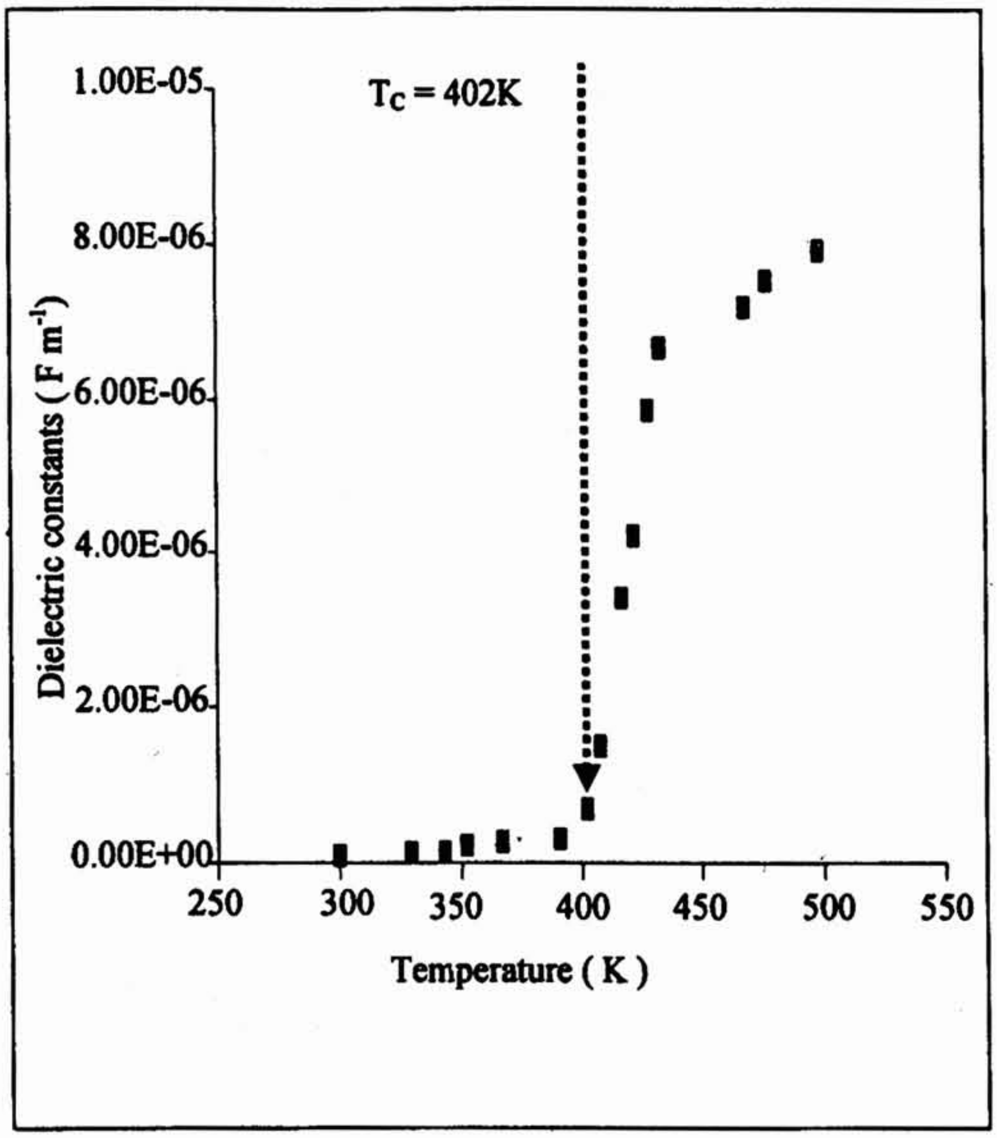

Figure.5 Temperature dependent dielectric constants of $ZnSO_4.7H_2O$ crystal

Table.2 Experimental results of electrical conductivity and dielectric constants of $ZnSO_4.7H_2O$ crystal

Sr No	Temperature (K)	Electrical conductivity (Ω^{-1} cm^{-1})	Dielectric constant (F m^{-1})
1	300	4.04×10^{-9}	8.75×10^{-8}
2	402	1.14×10^{-8}	6.87×10^{-7}

Conclusion

Crystals of $ZnSO_4.7H_2O$ have been grown by slow evaporation of aqueous solutions. Molecular vibration and temperature dependent electrical conductivity of those crystals were studied in this work. Only three fundamental modes of ν_1, ν_3 and ν_4 of Sulphate molecule were observed and assigned. However, the ν_2-mode (bending) of sulphate was not found. Also, two modes ν_1 and ν_2 of water molecule were observed but the ν_3-mode (symmetric-stretching) vibration was not found. The electrical conductivity and dielectric constant of $ZnSO_4.7H_2O$ crystal were obtained as 4.04 x 10^{-9} Ω^{-1} cm^{-1} and 8.75 x 10^{-8} Fm^{-1} at room temperature 300 K and suddenly increased up to 1.14 x 10^{-8} Ω^{-1} cm^{-1} and 6.87 x 10^{-7} Fm^{-1} at 402 K in which the dehydration process occurs in the crystal from heptahydrate to monohydrate compound.

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