Characterization of Li^{3+}/Mg $SO_4.7H_2O$ Crystal

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Abstract

Crystals of Li^{3+} (1 mol%) doped Magnesium Sulphate Heptahydrate, $MgSO_4.7H_2O$ were grown by slow evaporation of aqueous solutions at room temperature. Starting materials of Magnesium Sulphate Heptahydrate, $MgSO_4.7H_2O$, with the added of (1mol%) Lithium Sulphate, Li_2SO_4, were used to grow the crystal. The as-grown crystal was characterized by FTIR and FT-Raman spectroscopic methods to investigate the structural and vibrational properties of the crystal. Dehydration temperature (T dehydration) and activation energy of the crystal were also evaluated.

Keywords: Lithium (1mol%) doped Magnesium sulphate Heptahydrate, slow evaporation method, FTIR and FT-Raman, TG-DTA, electrical conductivity.

Introduction

Crystallization of heptahydrate sulphate materials such as epsomite of high purity has become an important field of research for both academic interest and industrial applications in various areas like medical, agricultural and chemical industry. The epsomite is included in a group of heptahydrate sulphate with the general formula $RSO_4.7H_2O$ (R=Mg, Zn, Ni). $MgSO_4.7H_2O$, as a source of Mg^{2+} ions has wide application in medical and agricultural industry (Henry & Lonsdale, 1965; Ibach & Luth, 1990). The crystal structure of $MgSO_4.7H_2O$ is orthorhombic. The presence of the foreign particles in the growth media has long been recognized in changing the growth habits of crystals (Raj, et al., 2007; Singh, et al., 1995). Structural and Vibrational properties of the as-grown crystal were characterized by FTIR and FT-Raman Spectrometry. Simultaneous Thermogravimetric Analysis and Differential Thermal Analysis (TG-DTA) were used for examination of the thermal properties of the compound. Temperature dependent electrical conductivity of the crystal was studied in the temperature range of 301 K-523 K. From technological and application point of view, in the present study, crystals of $MgSO_4.7H_2O$, by adding (1mol%) doped Li_2SO_4, as impurities were grown and characterized by FIIR, FT-Raman, TG-DTA and temperature dependent electrical conductivity measurements.

Experiment

Growth of Li^{3+} (1mol%) doped $MgSO_4.7H_2O$ Crystal

Single crystals Lithium (1mol%) doped Magnesium Sulphate Hepetahydrate were grown by slow evaporation method from aqueous solutions at room temperature. First, starting materials of (1mol%) Lithium Sulphate, $LiSO_4$ and $MgSO_4.7H_2O$ salt powders were weighed with molar ratio. The distilled-water was used as the solvent. Next, the salt powders were mixed and stirred to prepare the solid-solutions and then placed into the beaker that filled with distilled-water. Second, the solutions have been stirred well and heated above the room temperature with temperature controlled furnace to prepare for the supersaturated solutions. Then, the beaker was covered with very thin plastics and placed at the desk to growth for seed crystals. After three days, the seed

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crystals of Li^{+}/ $MgSO_4.7H_2O$ were drown at the bottom of the beaker. The seed crystals were collected with tweezers and placed on filter-paper to dry. One of the perfect like seed crystal was hung by nylon threat and placed in the supersaturated solutions. Finally, after two months, the enough size crystal was obtained with transparent and homogeneous, which are stable under normal conditions and can be handled without any special care. Photograph showing the as-grown crystal of Li^{3+} (1 mol%) doped $MgSO_4.7H_2O$ is shown in Fig. 1.

Fig. 1 Photograph showing the as-grown crystal of Li^{3+} (1 mol%) doped $MgSO_4.7H_2O$

FTIR Spectroscopic Measurement

The vibrational frequencies of a molecule can be probed by using infrared and Raman spectroscopy. IR spectroscopy is an absorption interaction, while Raman is a scattering process that accompanies changes in the wavelength of light. When incoming light has same frequency with the energy of a vibration mode, the molecule absorbs light and a record of decreased light intensity at each wavelength creates a spectra. This frequency shift gives vibrational information for the molecule. A vibration is IR active only when the dipole moment of the molecule changes due to the disphacement of atoms in the molecule relative to each other. A vibration is Raman-active only when incident radiation modifies the polarizability of the molecule. FTIR transmission spectrum of Li^{3+} (1 mol%) doped $MgSO_4.7H_2O$ crystal was observed by PC-controlled SHIMADZU FTIR -8400 spectrophotometer. Photograph of the SHIMADZU FTIR-8400 spectrophotometer is shown in Fig. 2.

method	:	KBr pellet method
Wave number range	:	$400\ cm^{-1} – 4000\ cm^{-1}$
Measurement mode	:	% T
Measuring time	:	60 S.

Fig. 2 Photograph of the SHIMADZU FTIR-8400 Stectrophotometer

FT-Raman Spectroscopic Measurement

Raman scattering is the inelastic scattering of light from molecules. When a beam of monochromatic light (laser) is passed through a transparent substance, such as crystal and the scattering is analyzed spectroscopically. The new frequencies in the spectrum of monochromatic light scattered by a substance are characteristic of the substance. This type of scattering is called Raman scattering that can be used to study the vibrational properties of crystals, powders, polymers and even coloured samples (solutions) (Ferdous & Podder, 2009; Freeda & Mahadevan, 2001). Photograph of the experimental arrangement of Perkin Elmer FT-Raman Spectrometer (Fig. 3).

wavelength	:	1064 nm (invisible laser)
scattering geometry	:	90° (laser source & detector)
measuring time	:	20 s
Raman shift range	:	100 cm^{-1} – 4000 cm^{-1}

Fig. 3 Photograph of the Perkin Elmer FT-raman Spectrometer

Temperature Dependent Electrical conductivity Measurement

Crystal were observed in the temperature range of 301 K (28°C) -523 K (250°C) by using PC-based temperature controller. FOTEK MT-20. 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 change with temperatures. Electrical conductivity measurements were made on the crystal in a stainless-steel conductivity cell in which maintained the crystal by a spring-loaded support between copper leads using two polished Cu disc as electrodes. The electrical conductivity of ionic crystals has been calculated by using the formula $\delta = \frac{L}{RA}$ where L is the thickness of the sample (cm), A is the cross-sectional area of the sample (cm^2) and R is the resistance of the sample (Ω) (Ferdous & Podder, 2009).

Results and Discussion

Generally, shapes or profile of spectral lines often contain very important information for the dynamics of the physical system under observation. Crystals of Li^{3+} (1 mol%) doped $MgSO_4.7H_2O$ are hydrated and ionic compounds that exhibit the phase changes are found in ionic conductivity at high temperatures with dehydration. Above the transition point, electrical conductivity of the crystal enables one to classify the high temperature phases. FTIR transmission spectrum of Li^{3+} (1 mol %) doped $MgSO_4.7H_2O$ crystal with KBr pellet method. The observed wavenumbers (Frequencies and corresponding vibrational characteristics and made assignments of constituent molecules (SO_4^{2-} and H_2O) in the crystal are listed in Table 1. In spectrum, eleven absorption lines were observed in the 400 cm^{-1} - 4000 cm^{-1} wavenumber region. Four normal modes of SO_4^{2-} were observed at 982 cm^{-1},432 cm^{-1}, 1088 cm^{-1}/1154 cm^{-1} and 617 cm^{-1}. The lines at 482 cm^{-1} and 845 cm^{-1} are represented by the librational twisting and rocking vibrations of water linked SO_4^{2-} (inorganic) compounds.

FT-Raman spectrum, three normal modes of SO_4^{2-} are found at 986 cm^{-1}, 434 cm^{-1} and 605 cm^{-1}/614 cm^{-1}. Furthermore, stretching vibrations are found at 2137 cm^{-1} and 2559 cm^{-1} in the spectrum. Moreover, one combination band of H_2O molecule and H-bonding was also found at 3702 cm^{-1}.

Electrical conductivity of an ionic material obeys an Arrhenius expression $\delta = \delta_0$exp(-E/KT), where δ is the conductivity, or ionic drift in materials, δ_0 is the pre-exponential factor or slope of the conductivity curve. In the present work, Arrhenius plot of the vibration of dc electrical conductivity of the Li^{3+} (1 mol%) doped $MgSO_4.7H_2O$ crystal in the temperature range of 30l K to 523 K is shown in Fig. 5.

The activations energy and electrical conductivity of the crystal are calculated as 0.31 eV and $5.40x10^{-8}$ S cm^{-1} at the temperature 389 K, and it is the dehydration temperature ($T_{dehydration}$) of the crystal from heptahydrate to monohydrate. Temperature dependent electrical conductivities of the crystal are found to increase with increasing temperatures and the maximum electrical conductivity of 6.20 $x10^{-7}$ S cm^{-1} is found at 523 K. Vibration of the electrical resistivity, conductivity of the $Li^{3+}/MgSO_4.7H_2O$ crystal with increasing temperature are shown in Fig. 6.

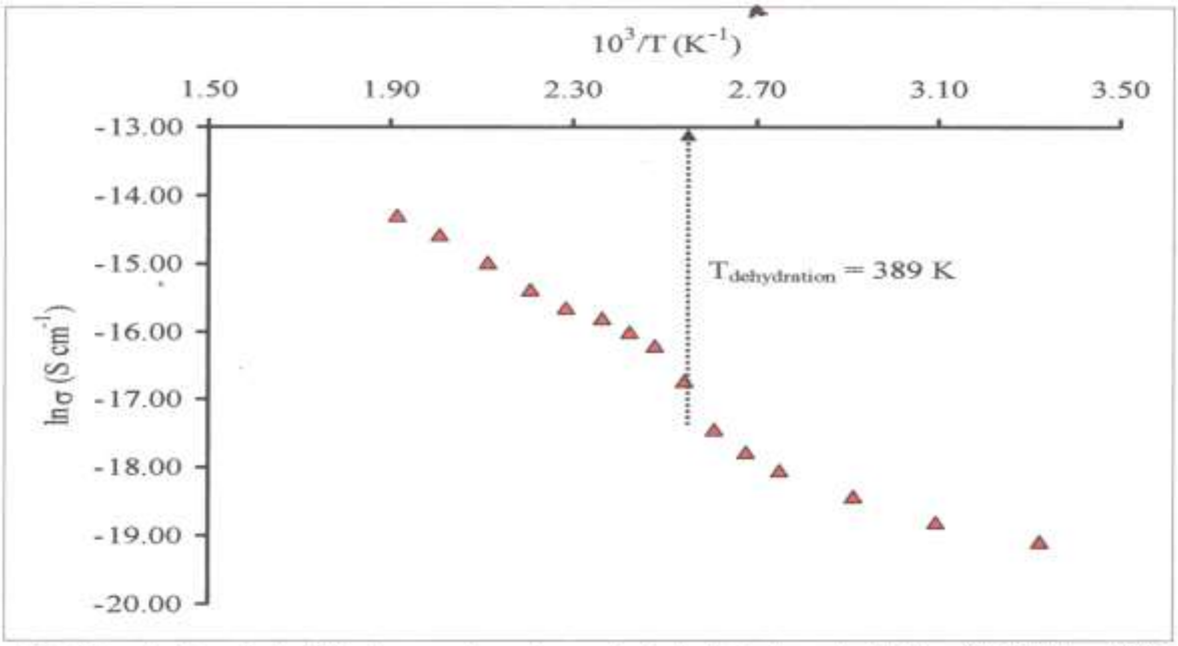

Fig 5 Arrhenius plot of the temperature dependent electrical conductivity of Li^{3+} (1 mol%) doped $MgSO_4.7H_2O$ crystal

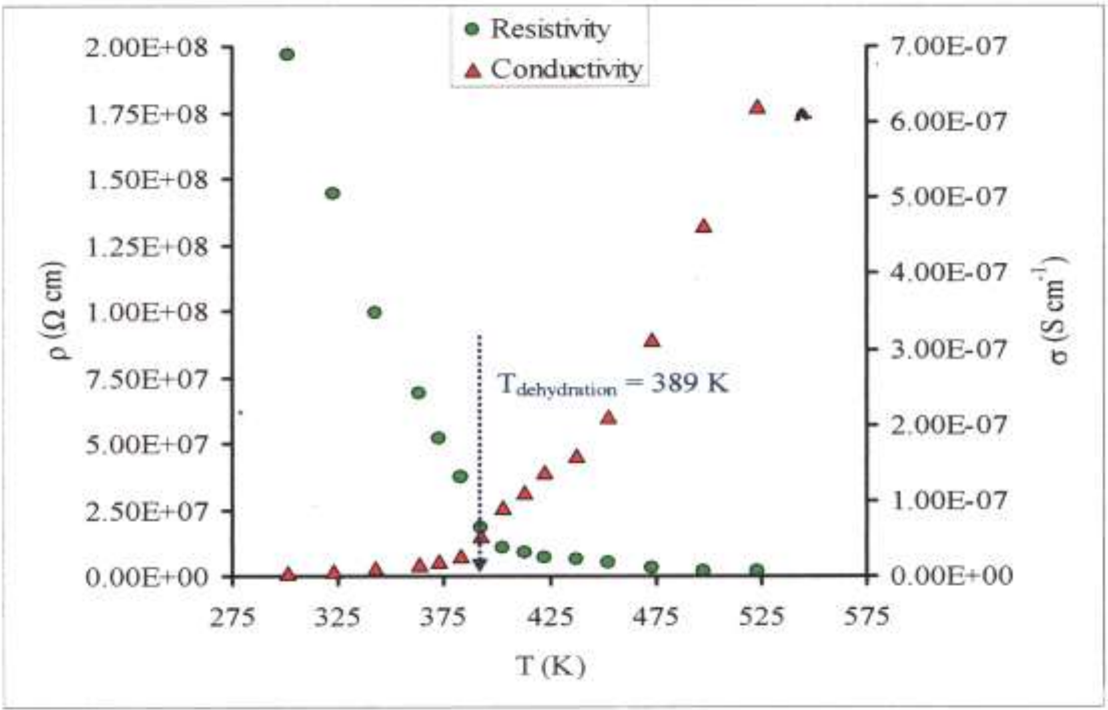

Fig 6 Plot of the electrical resistivity (ρ) and conductivity (σ) versus temperature (T) of the Li^{3-}(1 mol%) doped $MgSO_4.7H_2O$ crystal

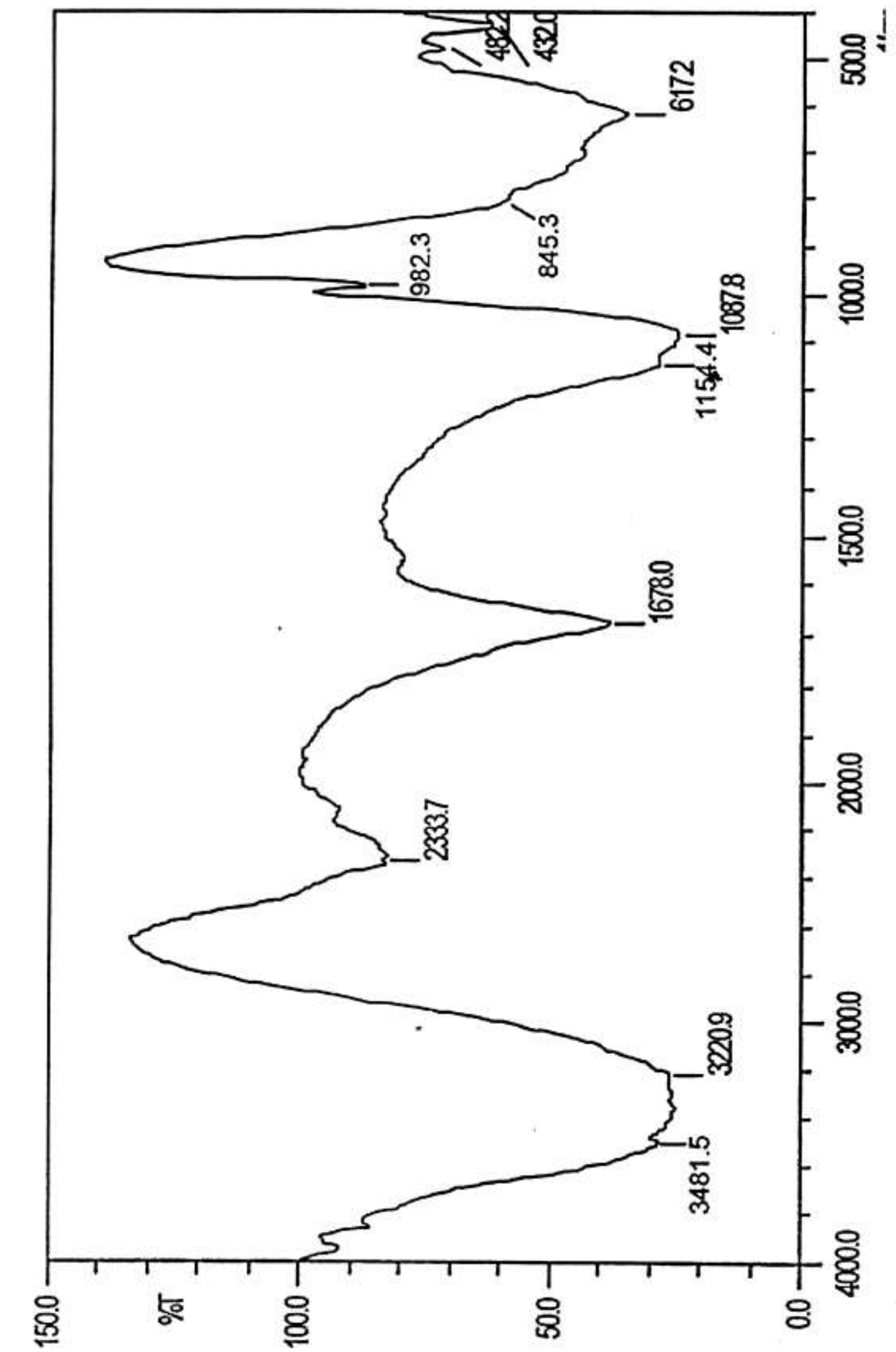

Fig 4 FTIR transmission spectrum of Li^{3+}(1 mol%) doped $MgSO_4.7H_2O$ crystal

Table 1 Wavenumbers and corresponding vibrational mode assignments of Li^{3+} (1mol%) doped $MgSO_4.7H_2O$ crystal

Line No	Wavenumber (cm^{-1})	Vibrational Characteristics	Vibrational Mode Assignment
1	432	Bending	$\nu_2(SO_4^{2-})$
2	482	Librational wagging	$\nu_\tau(SO_4$---HOH---$SO_4)$
3	617	Polarization	$\nu_4(SO_4^{2-})$
4	845	Librational rocking	$\nu_\rho(SO_4$---HOH---$SO_4)$
5	982	Symmetric-stretching	$\nu_1(SO_4^{2-})$
6	1088 / 1154	Dipole	$\nu_3(SO_4^{2-})$-splitting
7	1678	Bending	$\nu_2(H_2O)$-splitting
8	2334	Bending	$\nu_2(CO_2)$-splitting
9	3221	Symmetric-stretching	$\nu_1(H_2O)$
10	3482	Asymmetric-stretching	$\nu_3(H_2O)$

Table 2 Experimental data and results of temperature dependent electrical conductivity measurement of Li^{3+}(1 mol%) doped $MgSO_4.7H_2O$ crystal

T (K)	R (Ω)	ρ (Ω cm)	σ (S cm^{-1})	ln σ (S cm^{-1})
301	1.730 E+08	1.970 E+08	0.509 E-08	-19.09
323	1.270 E+08	1.450 E+08	0.692 E-08	-18.78
343	0.878 E+08	0.997 E+08	1.00 E-08	-18.41
363	0.606 E+08	0.688 E+08	1.45 E-08	-18.05
373	0.455 E+08	0.516 E+08	1.94 E-08	-17.76
383	0.329 E+08	0.373 E+08	2.68 E-08	-17.44
393	0.163 E+08	0.185 E+08	5.40 E-08	-16.73
403	0.097 E+08	0.110 E+08	9.08 E-08	-16.21
413	0.788 E+08	0.089 E+08	11.20 E-08	-16.01
423	0.640 E+08	0.072 E+08	13.80 E-08	-15.80
438	0.055 E+08	0.062 E+08	16.00 E-08	-15.65
453	0.042 E+08	0.048 E+08	21.00 E-08	-15.37
473	0.028 E+08	0.032 E+08	31.20 E-08	-14.98
498	0.019 E+08	0.022 E+08	46.40 E-08	-14.58
523	0.014 E+08	0.016 E+08	62.00 E-08	-14.30

Conclusion

Crystals of Li^{3+} (1 mol %) doped $MgSO_4.7H_2O$ were grown by the slow evaporation of aqueous solution. Structural, vibrational and thermal characteristics of the crystal were studied by FTIR, FT-Raman and TG-DTA methods. Temperature dependent electrical conductivities of the crystal were investigated in the temperature range of 301 K - 523 K. From the FTIR spectrum, twelve absorption lines were observed in the wave numbers ranges of 400 cm^{-1} - 4000 cm^{-1} region. Temperature dependent electrical conductivities of the crystal were found to increase with increasing temperatures. The activation energy and electrical conductivity of the crystal were 0.31 eV and 5.40 $x10^{-8}$ S cm^{-1} at the temperature of 389 K. It is suitable for electro-optic applications due to transparency of the as-grown crystal.

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References

Ferdous, S. and Podder, J., 2009. *Journal of Bangladesh Academy of Sciences* **33** (1): 47

Freeda, T. H. and Mahadevan, C., 2001. *Pramana Journal of Physics* **57** (4): 829

Henry, N. F. M. and Lonsdale, K 1965. *International Tables for X-Ray Crystallography*,(Birmingham: Kynoch)

Ibach, H., and Luth H 1990. *Solid State Physics*. (Berlin: Springer-Verlag)

Premkumar, P. S. and Shajan, X. S., 2010. *E Journal of Chemistry* **7** (1): 121

Pillai, S. O., 2006. *Solid State Physics* (New Delhi: New Age)

Raj, C. J., et al., 2007. *Crystal Research Technology* **42** (4): 344

Singh, K. et al., 1995. *Bulletins Materials Science* **18** (2): 147