STRUCTURAL AND VIBRATIONAL INVESTIGATION OF K^+(1 MOL%) DOPED $LiNH_4SO_4$ SINGLE CRYSTAL

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Abstract

Crystals of K^+ (1mol%) doped Lithium Ammonium Sulphate, $LiNH_4SO_4$, were grown by slow evaporation method of room temperature. Starting materials of Lithium Sulphate, Li_2SO_4 and Ammonium Sulphate, $(NH_4)_2SO_4$ with the addition of (1mol%). Potassium Sulphate K_2SO_4 were used to grow and synthesis the crystals. Structural investigation of the crystal will be reported by XRD method. Lattice parameters of the crystal were also examined. FTIR transmission spectrum of the crystal will be collected by pc controlled FTIR-8400 /SHIMADZU spectrometer between the wavenumber range of 400 cm^{-1} and 4000 cm^{-1} region.

Keywords: slow evaporation method, K^+/ $LiNH_4SO_4$, XRD, FTIR

Introduction

Several Li-based binary sulphates of the type $LiASO_4$ (where A = Na, K, Rb, NH_4, Cs) have been found to exhibit temperature induced phase transition characters. Under ambient conditions, $LiNH_4SO_4$ crystallizes in the hexagonal system under the space group *P31c* (C_{3v}^4)with six formula units per unit cell but two formula unit per unit cell of $LiNH_4SO_4$. Hence, the compound has 22 atoms in the unit cell. The sulphur atoms of the sixsulphate ions are located on three sets of three-fold-axes with one of the S-O bonds of the sulphate ions lying on the axis. The three pairs of the sulphate ions have different bond lengths and bond angles, since their immediate neighbours are different. One pair of SO_4 has only lithium neighbours, while the remaining two pairs are closely coordinated by ammonium. Consequently, one pair is elongated and another is compressed along the three-fold axis, while the third one is nearly regular.

Techniques using electromagnetic radiation are among the most fruitful of these. The very short wavelengths of X-rays are instrumental even

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essential in examining the atomic Lattice that define crystalline solids. Wavelengths from the ultraviolet through the visible and infrared to the millimeter range have enormous power to examine all aspects of solids.

Infrared spectroscopy is a versatile analytical technique. The most popular way of obtaining infrared spectra is to pass the infrared beam directly through the sample, known as the transmission technique. Transmission method is the oldest and most basic infrared method. The method is based upon the absorption of infrared radiation at specific wavelengths as if passes' through a sample. The advantage of this technique is the transmission spectra have signal-to-noise ratio. It is relatively easy to obtain spectra from solids, liquids and gases. Potassium Bromide (KBr) pellets are used to obtain the infrared spectra of solids, and are particularly well suited to powder samples. The most commonly used alkali halide is Potassium bromide (KBr), which is completely transparent in the middle IR region. KBr is an inert, infrared transparent material, and acts as a support and a diluent for the sample.[1,2,3]Due to the vast application of practical work, the present study deal with structural and vibrational analysis of $K^+/LiNH_4SO_4$ crystal was investigated by X-Ray Diffraction XRD method and FTIR spectroscopy.

Experimental Result

Growth of K^+(1 mol%) doped $LiNH_4SO_4$ Crystal

Crystals of K^+(1 mol%) doped Lithium Ammonium Sulphate, $LiNH_4SO_4$ were grown by slow evaporation method from aqueous solutions at room temperature (29°C). Starting materials of Lithium Sulphate, Li_2SO_4 and Ammonium Sulphate, $(NH_4)_2SO_4$ with equimolar ratio were used to grow and synthesis the crystals. (1 mol%) Potassium Sulphate, K_2SO_4 was used as the dopant material. Transparent and homogeneous crystals were selected for measurements. Preparation process of K^+ (1 mol%) Doped $LiNH_4SO_4$ single crystalis shown in figure 1.

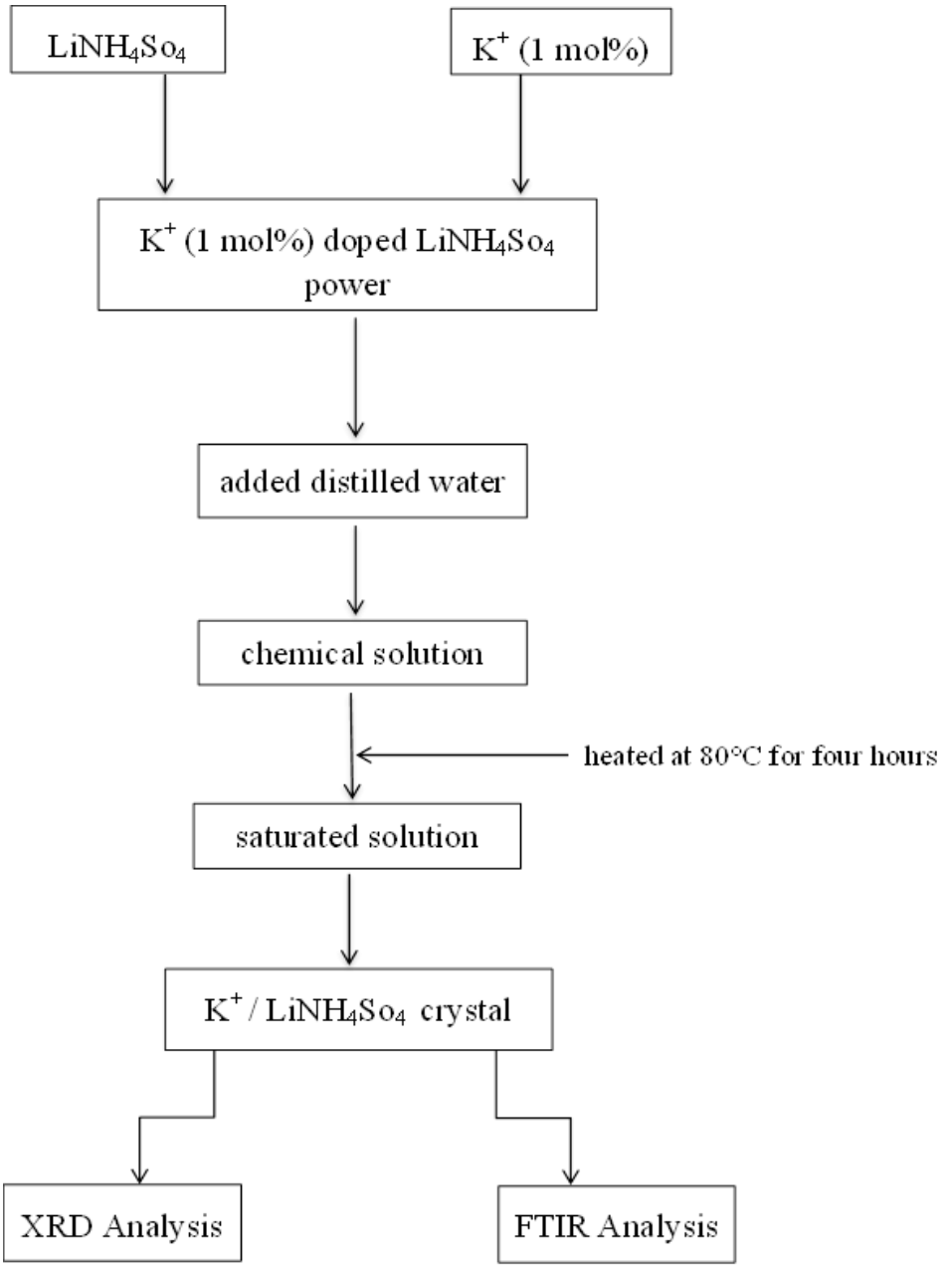

Figure 1: Preparation process of K^+ (1 mol%) Doped $LiNH_4SO_4$ single crystal

At room temperature, $K^+/LiNH_4SO_4$ crystal is colourless. Photograph showing the as-grown $K^+/LiNH_4S0_4$ crystal (duration of growth is two months) is shown in Figure 2.

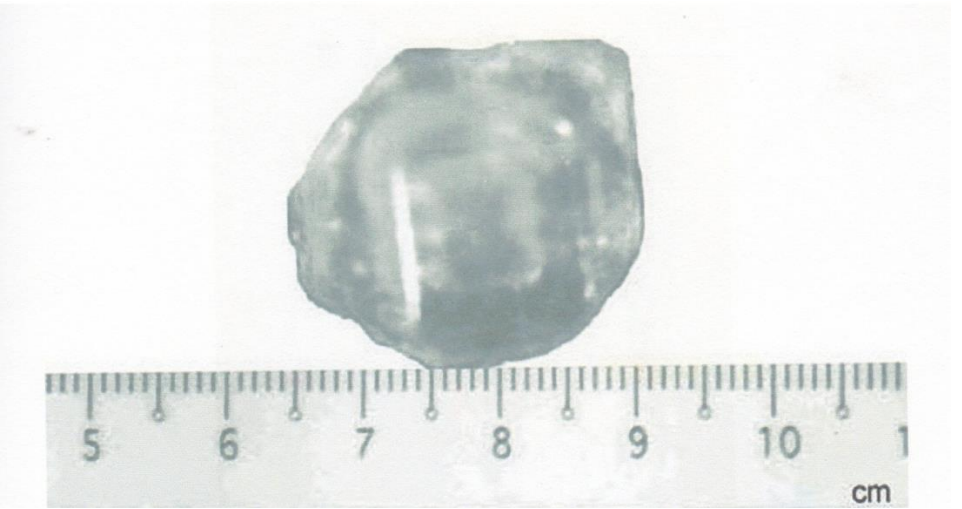

Figure 2: Photograph showing the as-grown crystal of K^+(1mol%) doped $LiNH_4SO_4$

X-Ray Diffraction Measurement

X-ray diffractometry was mainly used for identification and qualification of crystals by their diffraction patterns. The X-ray diffraction measurements were carried out by using RIGAKU MULTIFLEX X-ray powder diffractometer at URC, University of Yangon. Photograph showing the RIGAKU MULTIFLEX X-ray powder diffractometer is shown in Fig 3. The X-ray diffractometry consists of three basic parts: a source of radiation, consisting of (1) X-ray tube and high voltage generator, (2) the detector and counting equipment, and (3) the diffractometer.

The powder sample of $K^+/LiNH_4SO_4$ crystal was placed at the center of the goniometer. The samples were scanned through an angle 2θ from 10° to 70°. The surface of the sample was radiated by X-ray beam from Cu fine focus tube. The applied voltage and current were maintained at 40 kV and 40 mA. The diffracted X-ray beams entered the detector and then recorded.

The recording scan speed was 4º/min. Each diffracted ray is recorded as a peak. The peak heights are roughly proportional to the X-rays intensity. The diffraction patterns of specimens were identified by using Material Data Inc. data book. The initial "d" spacing was determined using a second derivative peak search algorithm, followed by careful editing of the raw data to improve the position accuracy and to resolve ambiguous lines. The "d" values were determined using the Cu K_α radiation with wavelength of 1.54056Å. The lattice parameters can be examined by using the following equation.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

where d is interplanar spacing (Å), *a, b* and *c* are lattice parameters (Å) of the unitcell, *(h k l)*are Miller indices, θ is diffraction angle (◦) and λ is wavelength of incident X-ray (Å).The experimental conditions were as follows:

Tube Voltage	:	40 kV. 40 mA
Target	:	Cu
Filter	:	Ni
Wavelength	:	1.54056 Å (CuK_u-radiation)
Scan Speed	:	4º/min
20 range	:	10° - 70°

Figure 3: Photograph of the RIGAKU MULTIFLEX X-ray Difractometer

FTIR Spectroscopic Measurement

In the present work, FTIR transmission spectrum of K^+(1 mol%) doped $LiNH_4SO_4$ crystal with Potassium Bromide, KBr pellet method was observed by SHIMADZU FTIR-8400 Spectrophotometer to investigate the vibrational characteristics of the SO_4^{2-} molecules in the crystalline environments of Li-NH_4 and K. Experimental conditions were as follows:

Measurement mode	:	%T
Wavenumber range	:	400 cm^{-1} - 4000 cm^{-I}
Number of scan	:	60 s
Apodization function	:	Happ-Genzel
Resolution	:	4 cm^{-1}
Method	:	KBr disc

Photograph of the SHIMADZU FTIR-8400 Spectrophotometer is shown in Figure4.

Figure 4: Photograph of the SHIMADZU FT IR-8400 Spectrophotometer

Results and Discussion

Powder XRD Analysis

Powder XRD pattern of K^+(1mol%) doped $LiNH_4SO_4$ crystal is shown in Figure5. As shown in XRD pattern, the collected diffraction lines are identified by using JCPDS data files. The observed diffraction peaks and corresponding diffraction angles (2θ), atomic spacings (d), Miller indices (hkl) and peak height of the sample are tabulated in Table 1. Most of the diffraction lines are well assigned by JCPDS. However, some of the diffraction lines for 2θ such as 21.30°, 30.28° and 30.58° are not assigned with JCPDS because the ratio of the starting materials and the standard file of $Li(NH_4)_{0.97}K_{0.03}SO_4$ are not precisely equal to those of candidate sample of $K^+/LiNH_4SO_4$. Furthermore, it shows the dopant effects of K_2SO_4 on $LiNH_4SO_4$ crystal.

According to XRD pattern, $K^+/LiNH_4SO_4$ crystal belongs to hexagonal structure at room temperature. Lattice parameters of the crystal are calculated by using the equation of $\frac{1}{d^2}=\frac{4}{3}(\frac{h^2+hk+k^2}{a^2})+\frac{l^2}{c^2}$. Lattice parameters of the crystalre a=b=11.19Å and c=9.40Årespectively.

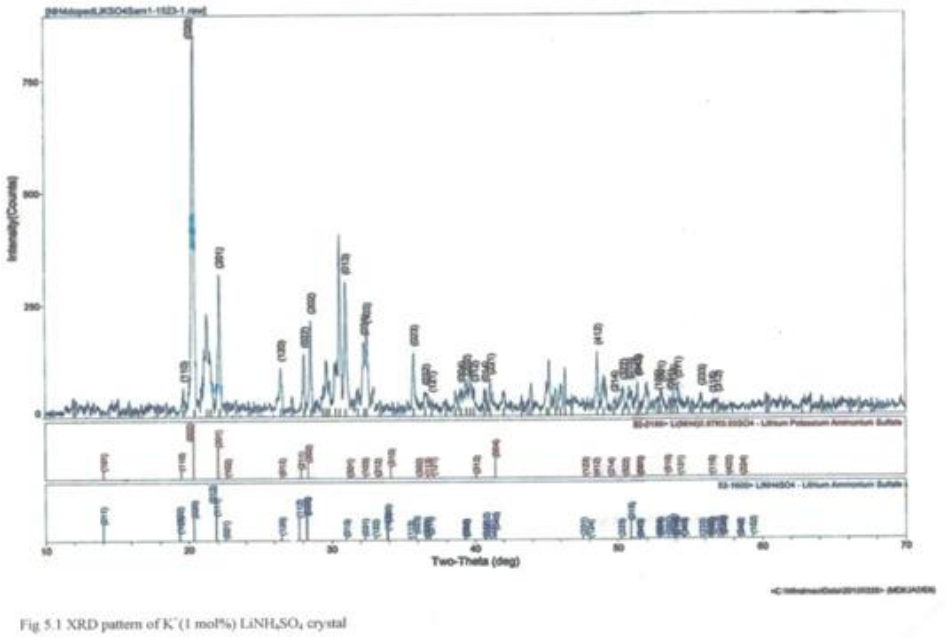

Fig 5.1 XRD pattern of K^+(1 mol%) $LiNH_4SO_4$ crystal

Figure 5: XRD pattern of K+(1mol%) $LINH_4SO_4$ crystal

Table 1 XRD data of K^+(1 mol%) $LiNH_4SO_4$ crystal

Line No	2θ (°)	(*hkl*)	*d* (Å)	Peak height (%)
1	19.66	(110)	4.51	6.60
2	20.43	(020)	4.34	100.00
3	22.18	(201)	4.00	36.00
4	26.46	(120)	3.37	11.90
5	28.10	(022)	3.17	15.60
6	28.58	(202)	3.12	24.90
7	30.98	(013)	2.88	34.30
8	32.28	(031)	2.77	17.60
9	32.46	(103)	2.76	20.90
10	35.74	(023)	2.51	14.80

FTIR Spectroscopic Analysis

According to vibrational analysis of SO_4^{2-} or NH_4^+ using factor group theory, which obeys the (tetrahedral) T_d-symmetry and it has four types of fundamental modes of vibrations. These four modes are (1) v_1-mode (symmetric-stretching), v_2-mode (bending), v_3-mode (dipole) and v_4-mode (polarization) respectively. Also H_2O molecule obeys (2-fold vertical rotation) C_{2v}-symmetry and it has three types of fundamental modes of vibrations, namely; (1) v_1-mode (symmetric-stretching),v_2-mode (bending) and v_3-mode (asymmetric-stretching). Moreover, vibrational frequencies of (1) metal compound molecules (e.g., ZnO, $A1_2O_3$,...)lies under 400 cm^{-1}, (2) inorganic compound molecules (e.g., $P0_4^{3-}$, $S04^{2-}$,…) lies between 400 cm^{-1} and 1500 cm^{-1} and (3) organic compound molecules (e.g., NH_4^+, H_20,...) lies over 1500 cm^{-1} region. Sometime, most of the vibrational frequencies of molecules are appeared in the boundary region of about 400 cm^{-1}, 1500 cm^{-1}, etc.

FTIR transmission spectrum of K^+(1 mol%) doped $LiNH_4SO_4$ crystal is shown in Figure6. As shown in figure, the recorded wavenumbers (absorption lines or resonance lines of molecules with the frequencies of incident infrared beam) and their corresponding vibrational characteristics of molecules in crystalline environments of Li - NH_4 - K are compared to those of $LiNH_4SO_4$ crystal. These are tabulated in Table 2.

In the observed FTIR spectrum, fourteen absorption lines are found in the wavenumber range of 400 cm^{-1} - 4000 cm^{-1}. These lines are represented by the vibrational characteristics of sulphate (SO_4^{2-}), ammonium (NH_4^+), water (H_2O), carbon dioxide (CO_2) and ($S0_4^{2-}$-NH_4^+-SO_4^{2-}) molecular network respectively.

The lines at 982 cm^{-1}, 432 cm^{-1}, 1079 cm^{-1} / 1151 cm^{-1}, and 625 cm^{-1} are indicated by four fundamental vibrational modes (v_1-mode, v_2-mode, v_3-mode andv_4-mode) of $S0_4^{2-}$.

The lines at 1431 cm^{-1} and 1470 $cm^{-1}$are indicated by v_4-mode of NH_4^+. Others three fundamental modes (v_1-mode, v_2-mode and v_3-mode) are not found because these lines are normally appeared in the high frequency region.

The line at 723 cm^{-1} is represented by the librational rocking vibration of (SO_4^{2-} -NH_4^+-SO_4^{2-}) molecular network.

The band observed in the high wavenumbers region of 2000cm^{-1} - 4000cm^{-1} are vibrational characteristics of organic molecules: i.e., CO_2 and H_2O, etc. The lines at 2056 cm^{-1}, 2127cm^{-1} and 2245 cm^{-1} are represented by the bending vibrations of CO_2. The lines of 3214 cm^{-1}, 1676 cm^{-1} and 3413 cm^{-1} are attributed by three fundamental modes (v_1-mode, v_2-mode and v_3-mode) of H_2O. These lines are often appeared in the FTIR transmission spectrum of KBr pellet method.

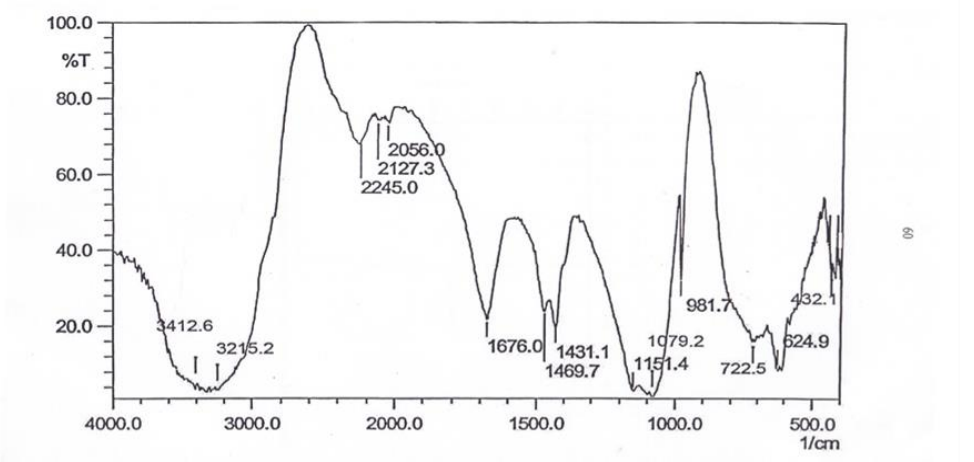

Figure 6: FTIR transmission spectrum of K^+(1mol%) doped $LiNH_4SO_4$

Table 2: Wavenumbers and corresponding vibrational mode assignments of K^+(1 mol%) doped $LiNH_4SO_4$ crystal

Line No	Wavenumber (cm^{-1})	Mode Assignment	Molecular Vibration
1	432	$\nu_2(SO_4^{2-})$	Bending
2	625	$\nu_4(SO_4^{2-})$	Polarization
3	723	$\nu_\rho(SO_4^{2-}\text{---}NH_4^{+}\text{---}SO_4^{2-})$	Librational rocking
4	982	$\nu_1(SO_4^{2-})$	Symmetric-stretching
5	1079, 1151	$\nu_3(SO_4^{2-})$	Dipole
6	1431, 1470	$\nu_4(NH_4^{+})$	Polarization
7	1676	$\nu_2(H_2O)$	Bending
8	2056, 2127, 2245	$\nu(CO_2)$	Bending
9	3214	$\nu_1(H_2O)$	Symmetric-stretching
10	3413	$\nu_3(H_2O)$	Asymmetric-stretching

Conclusion

Crystals of K^+(1 mol%) doped Lithium Ammonium Sulphate $LiNH_4SO_4$ were grown by slow evaporation method from aqueous solutions at room temperature. The as grown crystal was characterized by powder X-ray diffraction (XRD) to investigate the structural properties of the sample. According to XRD pattern, the crystal belongs to hexagonal structure and lattice parameters of the crystal are a=b=11.19Å and c=9.40Å. From the recorded FTIR spectrum, fourteen absorption lines are observed and precisely assigned by using molecular vibration theory. The absorption lines at 982cm^{-1}, 432cm^{-1}, 1079 cm^{-1} / 1151 cm^{-1} and 625 cm^{-1} are indicated by four fundamental modes of SO_4^{2-}. The lines at 1431 cm^{-1} and 1470 cm^{-1} are indicated by γ_4-mode of NH_4^+. All others absorption lines are represented by the CO_2 and H_2O due to KBr pellet method. Thus crystal of K^+ (1 mol%) doped $LiNH_4SO_4$ can be considered as the solid electrolyte material.

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