STRUCTURAL, THERMAL AND ELECTRICAL CHARACTERISTICS OF NICKEL POTASSIUM SULPHATE HEXAHYDRATE (NPSH) CRYSTAL

Win Win Mon[1], Aye Aye Lwin[2], Kywe Kywe Aung[3] & Win Kyaw[4]

Abstract

Single crystals of Nickel Potassium Sulphate Hexahydrate, $NiK_2(SO_4)_2.6H_2O$ (NPSH) were grown by slow evaporation of saturated solution containing equimolar ratio of Nickel Sulphate Hexahydrate, $NiSO_4.6H_2O$, and Potassium Sulphate, K_2SO_4, salt powders. Structural analysis of the green colour crystal was investigated by XRD method. The crystal was characterized by simultaneous Thermogravimetric and Differential Thermal Analysis (TG-DTA) method to study the high temperature phases of dehydration and meeting of the crystal. Electrical conductivity with temperature of the crystal was investigated in the temperature range of 299 K – 653 K. Dehydration temperature ($T_{dehydration}$) of the crystal was determined from the (ln σ vs 1000/T) relationship. The activation energies of the crystal in the $T \leq T_{dehydration}$ and $T \geq T_{dehydration}$ regions were evaluated in this work.

Keywords: Nickel Potassium Sulphate Hexahydrate, XRD, TG-DTA, Electrical conductivity

Introduction

Crystals of Nickel Potassium Sulphate hexahydrate, $NiK_2(SO_4)_2.6H_2O$ (abbreviated as NPSH) have attracted attention recently because of their "order - disorder" dynamics of SO_4^{2-} dipoles. NPSH crystal belongs to the isomorphous series of sulphates of which Nickel Cesium Sulphate Hexahydrate, $NiCs_2(SO_4)_2.6H_2O$ (abbreviated as NCSH) is a member [Dhandapani, (2006); Zhaung, (2006)]. The crystalline hexahydrate, for example, form is found in two known phases: α-phase: blue to blue-green tetragonal crystals β-phase: green transparent crystals (stable at 40°C) [Kasatkin, (2002)]. The α to β phase transition occurs at 53.3°C

1. Dr, Demonstrator, Department of Physics, Hpa-an University
2. Dr, Lecturer, Department of Physics, Bago University
3. Dr, Associate Professor, Department of Physics, Hpa-an University
4. Dr, Associate Professor, Department of Physics, Sagaing University

[Theivanayagom, (2001)]. Nickel Sulphate Hexahydrate, $NiSO_4.6H_2O$ is a water soluble salt which forms hexahydrate (six water) molecules. It is a green colour. Potassium sulphate, K_2SO_4 is used in the production of fertilizers and potassium alums. It is a water soluble salt and it is white colour powder. In this work, $NiK_2(SO_4)_2.6H_2O$ crystals were grown and characterized by X-ray Diffraction (XRD) Simultaneous Thermogravimetric Analysis and Differential Thermal Analysis (TG-DTA) and temperature dependent electrical conductivity measurements.

Materials and Method

Growth of $NiK_2(SO_4)_2.6H_2O$ (NPSH) Crystal

$NiK_2(SO_4)_2.6H_2O$ (NPSH) Crystals were grown by slow evaporation method from the starting materials of Nickel Sulphate Hexahydrate, $NiSO_4.6H_2O$ and Potassium Sulphate, K_2SO_4. Distilled-water was used as the solvent to grow the crystal. The chemical equation was as follow:

$$NiSO_4.6H_2O + K_2SO_4 \longrightarrow NiK_2(SO_4)_2.6H_2O$$

As indicated above chemical reaction, in the present work, the crystals were grown by using equimolar ratio of $NiSO_4.6H_2O$ and K_2SO_4. Firstly, starting materials were weighted and mixed each others. The mixed salt powders were placed into the beaker. Distilled-water was added and stirred with glass stick to occur the chemical reaction and then heat treated to get super saturated solution. The solution was filtered into the beaker and covered with very thin plastic. The solution was placed at room temperature (28°C) for seven days.

The seed crystals may be withdrawn in the saturated solution and collected with tweezers placed on filtered paper to dry. A perfect like (good quality or transparent and homogeneous) seed crystal was selected and placed into the saturated solution to get a large (enough size) crystal. After two months, the enough sized crystal was obtained. At room temperature, $NiK_2(SO_4)_2.6H_2O$ mixed crystal is green in colour. Photograph of the as-grown NPSH crystal (19.90 mm in length) is shown in Figure 1.

Figure 1. Photograph of the as-grown $NiK_2(SO_4)_2.6H_2O$ (NPSH) crystal

XRD Measurement

Structural analysis and lattice parameters evaluation of the crystal were investigated by XRD method. XRD pattern was observed by RIGAKU MULTIFLEX X-ray Diffractometer (Universities' Research Centre (URC), University of Yangon) using Ni-filter with CuK_α radiation, $\lambda = 1.54056$ Å.

TG-DTA Measurement

The Differential Thermal Analysis (DTA) measurement with higher accuracy was carried out along with Thermo-Gravimetric Analysis (TGA) using the (SHIMADZU) DTG-60H Thermal Analyzer. This measurement was performed at Universities' Research Centre (URC), University of Yangon. In this work, 4.510 mg powdered sample was used to analyze the high temperature phases. Aluminum (Al) pan was used as the standard sample.

Electrical Conductivity Measurement

For the electrical conductivity measurement, the crystal was cut to get the dimensions of $(1.29 \times 1.29 \times 0.34)$ cm^3. Then the crystal was fixed on glass plate and silver contacts were made over the sample to ensure good electrical contacts. Temperature dependent electrical resistances were observed in the temperature range of 299 K – 653 K. Photograph of the experimental set-up of temperature dependent resistances measurement is shown in Figure 2. The resistances of the sample were measured by using FLUKE 45 DUAL DISPLAY MULTIMETER. CAHO SR-T903 and K-type thermocouple were used as the temperature controller and temperature sensor. 300 W heater coil was inserted into the cylindrical copper holder (2.50 cm in diameter and 12.00 cm in length) that used as the heating element.

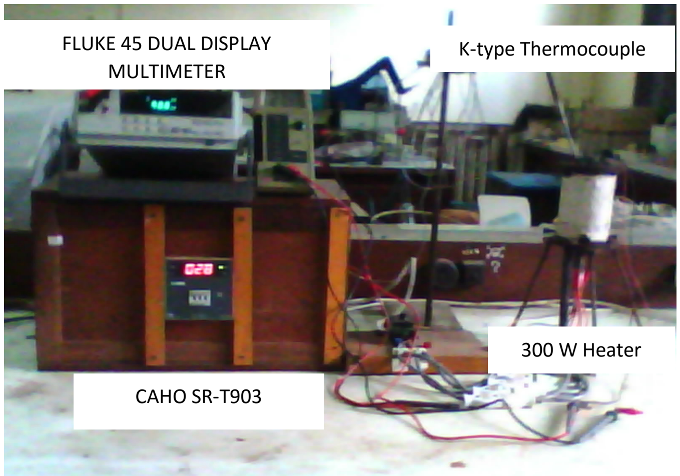

Figure 2. Photograph of the experimental setup for the temperature dependent resistance measurement

Results and Discussion

XRD Study

XRD pattern of the NPSH crystal is shown in Figure 3. The observed diffraction lines were identified by JCPDS to examine the crystal structure and to investigate the lattice parameters. The observed XRD lines were assigned by standard JCPDS data library file of Cat. No. 35-0760> $K_2Ni(SO_4)_2.6H_2O$ - Potassium Nickel Sulphate Hydrate. The appearance of the intensities of the diffraction peaks demonstrates the good crystal quality of NPSH crystal. The line at the diffraction angle 21.54° or (111) plane was the strongest in intensity among the observed XRD lines. XRD pattern shows that the crystal belongs to orthorhombic structure. The lattice parameters are evaluated by using crystal utility of the equation of

$$\frac{1}{d^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}=\frac{4\sin^2\theta}{\lambda^2}$$ where *a*, *b* and *c* are the lattice parameters (Å), *d* is the atomic spacing (Å), λ is the wavelength of incident X-ray (Å) and (hkl) is the miller indices. The lattice parameters were obtained as *a* = 15.80 Å, *b* = 12.19 Å and *c* = 5.91 Å respectively.

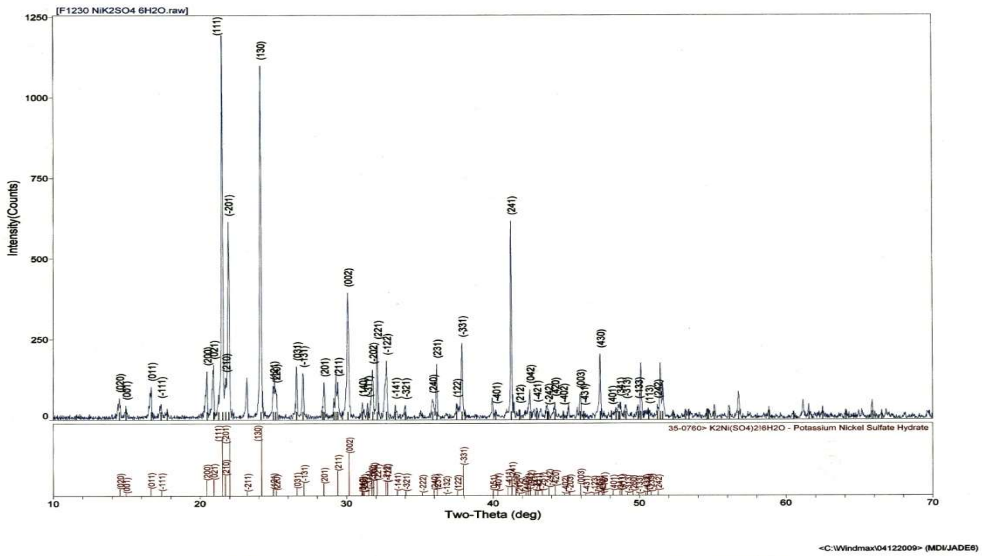

Figure 3. XRD pattern of $NiK_2(SO_4)_2.6H_2O$ (NPSH) crystal

TG-DTA Study

TG-DTA thermograms of NPSH crystal are shown in Figure 4. As shown in observed TGA thermogram, one step mass variation (weight loss) of the $NiK_2(SO_4)_2.6H_2O$ (NPSH) sample occurs between the temperature range of 39°C and 600°C with the weight loss is about 27.85%. This step takes place the dehydration of six water molecules from the $NiK_2(SO_4)_2.6H_2O$ (NPSH) to anhydrous compound of $NiK_2(SO_4)_2$ (NPS). The deep endothermic reaction peak in DTA thermogram around 180°C that indicates the dehydration of six water molecules from hydrated to anhydrous compound. One exothermic reaction peak in DTA thermogram around 333°C indicates the irreversible characteristic of the $NiK_2(SO_4)_2.6H_2O$ (NPSH) sample after heating or it is not recovered when cool-down to room temperature.

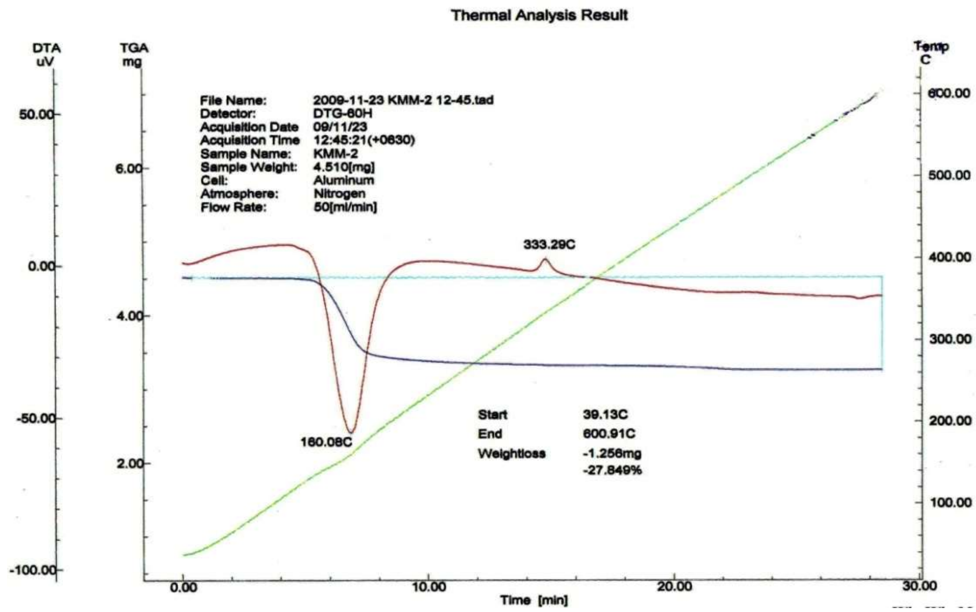

Figure 4. TG-DTA thermograms of $NiK_2(SO_4)_2.6H_2O$ (NPSH) crystal

Temperature Dependent Electrical Conductivity Study

The electrical conductivity of a crystal obeys an Arrhenius formula, $\sigma = \sigma_0 \exp(-E_a / kT)$ where σ is the conductivity (S m^{-1}), σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature (K). In the present work, Arrhenius plot of the variation of dc electrical conductivity of the NPSH crystal in the temperature range of 299 K – 653 K is shown in Figure 5. Slope of the curve is found to be changed at 433 K in which the $NiK_2(SO_4)_2.6H_2O$ (NPSH) undergoes to $NiK_2(SO_4)_2$ (NPS) and it can be taken as the dehydration temperature ($T_{dehydration}$) of the crystal.

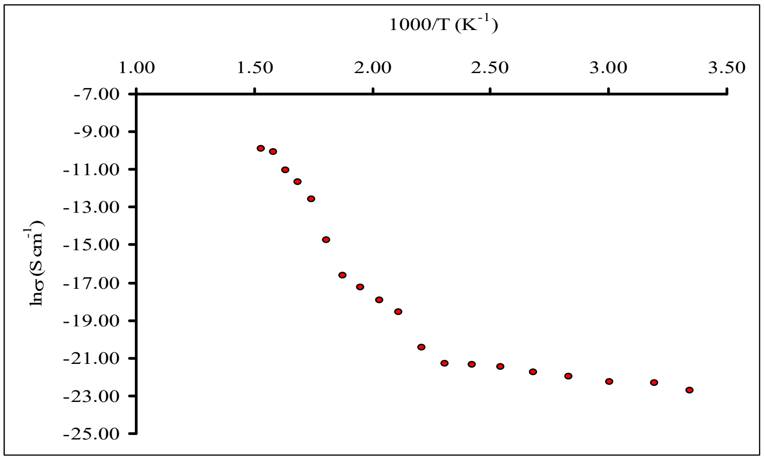

Figure 5. Plot of the variation of dc conductivity of the NPSH crystal in the temperature range of 299 K – 653 K

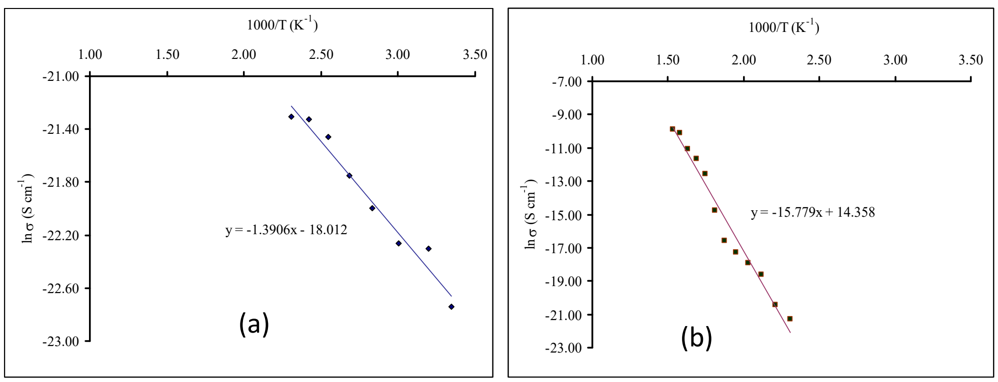

Figure 6. Plots of the variation of dc conductivity of the NPSH crystal in the temperature range of (a) 299 K – 433 K and (b) 433 K – 623 K

The electrical conductivity (σ) of the crystal for $T \le T_{dehydration}$ can be written in the form:

$$\sigma = \sigma_0 \exp(-E_a / kT)$$

$$\ln(\sigma) = -E_a / kT + \ln(\sigma_0)$$

$$= (-E_a / k)(1/T) + \ln(\sigma_0)$$

Comparing the above equation with the experimental linear equation, y = mx + c, where the value of slope will give the value of ($-\frac{E_a}{k}$). From Figure 6(a), the activation energy E_a can be evaluated as follows:

$$\frac{E_a}{k} = 1.3906 \times 1000$$

$$E_a = 1.3906 \times 1000 \times k$$

$$E_a = 1.3906 \times 1000 \times 1.38 \times 10^{-23}$$

$$E_a = 1.919 \times 10^{-20}\ \text{J}$$

$$E_a = 0.12\ \text{eV}$$

The obtained activation energy and electrical conductivity of the crystal over the dehydration temperature ($T \geq T_{dehydration}$) are greater than that of before ($T \leq T_{dehydration}$) and as presented in Table 1. From the experimental results, the electrical conductivity of the crystal increased with increase in temperature.

As shown in Figure 6(a), electrical conductivity of the crystal is slowly increased with increasing temperature range about 299 K – 593 K in which the crystal is exhibited as a normal ionic conductor or normal inorganic salt. After reaching the temperature at 593 K, electrical conductivity of the crystal is abruptly increased until up to pre-melting temperature 613 K. The observed value of electrical conductivity at the temperature 613 K is obtained as 1.5608 $\times 10^{-5}$ S cm^{-1}.

However, the activation energy of the sample under the dehydration temperature ($T \leq T_{dehydration}$) is obtained as 0.12 eV and the electrical conductivity curve over $T \geq T_{dehydration}$ of the sample is shown in Figure 6(b). Experimental results of conductivity (σ) and ($\ln \sigma$) are tabulated in Table 2.

Table 1. Activation energies of the NPSH crystal in different temperature regions

Temperature range (K)	*Activation energy (eV)*
299 - 433	*0.1200*
433 - 653	*1.3616*

Table 2. Experimental data of electrical conductivity measurement of the NPSH crystal

T (K)	**1000/T (K^{-1})**	**R (Ω)**	**σ ($S\ cm^{-1}$)**	**ln σ**
299	3.3445	1.55E+09	1.3262E-10	-22.7435
313	3.1949	9.97E+08	2.0618E-10	-22.3023
333	3.0030	9.57E+08	2.1479E-10	-22.2613
353	2.8329	7.35E+08	2.7967E-10	-21.9974
373	2.6810	5.76E+08	3.5687E-10	-21.7536
393	2.5445	4.29E+08	4.7916E-10	-21.4590
413	2.4213	3.76E+08	5.4670E-10	-21.3271
433	2.3095	3.69E+08	5.5707E-10	-21.3083
453	2.2075	1.57E+08	1.3093E-09	-20.4538
473	2.1142	2.43E+07	8.4453E-09	-18.5897
493	2.0284	1.24E+07	1.6537E-08	-17.9177
513	1.9493	6.49E+06	3.1673E-08	-17.2678
533	1.8762	3.33E+06	6.1729E-08	-16.6005
553	1.8083	5.35E+05	3.8422E-07	-14.7720
573	1.7452	6.02E+04	3.4146E-06	-12.5875
593	1.6863	2.36E+04	8.7175E-06	-11.6502
613	1.6313	1.32E+04	1.5608E-05	-11.0677
633	1.5798	4.94E+03	4.1611E-05	-10.0871
653	1.5314	4.13E+03	4.9772E-05	-9.9081

Conclusion

Crystals of Nickel Potassium Sulphate Hexahydrate $NiK_2(SO_4)_2.6H_2O$ (NPSH) have been grown by the slow evaporation of aqueous solution. Structural, thermal and temperature dependent electrical characteristics were reported in this paper. Experimental results are concluded as follows:

XRD pattern indicates that the $NiK_2(SO_4)_2.6H_2O$ (NPSH) crystal belongs to orthorhombic structure at room temperature. Lattice parameters of the crystals are obtained as a = 15.80 Å, b = 12.19 Å and c = 5.91 Å respectively.

TG-DTA thermograms of NPSH crystal give the one step mass variation from NPSH to NPS occurs in the temperature range of 39°C – 600°C due to the dehydration. The deep endothermic reaction peak in DTA thermogram around 180°C that also indicates the dehydration of six water molecules. One exothermic reaction peak in DTA thermogram around 333°C indicates the irreversible characteristic of the $NiK_2(SO_4)_2.6H_2O$ (NPSH) crystal.

Electrical conductivities with temperatures of the crystal were increased with increasing temperatures. The measurement of σ show anomalous behaviour at the transition point about 433 K. It is the dehydration temperature ($T_{dehydration}$) of the crystal. The σ-T relationship reveals activation energy of 0.12 eV below ($T \leq T_{dehydration}$) and 1.3616 eV above ($T \geq T_{dehydration}$) the dehydration temperature. The observed electrical conductivity at the temperature range about 613 K is ~ 1.5608 x 10^{-5} S cm^{-1} that indicates the superionic conductivity of the sample. Thus $NiK_2(SO_4)_2.6H_2O$ (NPSH) crystal can be used as the solid electrolyte materials at high temperature.

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