CHARACTERIZATION OF NICKEL SODIUM SULPHATE HEXAHYDRATE (NSSH) CRYSTAL

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Abstract

Crystals of Nickel Sodium Sulphate Hexahydrate, $NiNa_2(SO_4)_2.6H_2O$ (abbreviated as NSSH) were grown by slow evaporation method at room temperature. Structural, vibrational and thermal properties of the crystal were investigated by XRD, FTIR and TG-DTA methods. XRD pattern shows that the NSSH crystal belongs to orthorhombic structure with the lattice parameters a = 15.82 Å, b = 9.34 Å and c = 5.21 Å. FTIR spectrum showed that the vibrational characteristics of SO_4^{2-} and H_2O molecules in the crystalline environments of Ni and Na. TG-DTA thermograms indicated the high temperature phases of dehydration, decomposition and melting of the crystal.

***Keywords*:** Nickel Sodium Sulphateb Hexahydrate, XRD, FTIR, TG-DTA

Introduction

Nickel sulphate, $NiSO_4$ occurs in nature in a hydrated form, such as $NiSO_4.1H_2O$ (monohydrate), $NiSO_4.5H_2O$ (pentahydrate), $NiSO_4.6H_2O$ (hexahydrate) and $NiSO_4.7H_2O$ (heptahydrate), as several minerals, including morenosite and retgersite. 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). The α to β phase transition occurs at 53.3°C. Nickel Sulphate Hexahydrate, $NiSO_4.6H_2O$ is a water soluble salt which forms hexahydrate (six water) molecules. It is a green colour. [Arivuoli, (2001); Dhandapani, (2006)]

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Sodium sulphate, Na_2SO_4, is a white crystalline solid or powder. It is obtained by the treatment of sodium chloride with sulphuric acid. The crystallized product is a hydrate, $Na_2SO_4.10H_2O$, commonly known as Glauber's salt. [Dhandapani, (2006); Hulliger, (2001)]

In this paper, crystals of Nickel Sodium Sulphate Hexahydrate, $NiNa_2(SO_4)_2.6H_2O$ (NSSH) were grown by using slow evaporation method and the structural, vibrational and thermal characteristics were studied by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and simultaneous Thermogravimetric and Differential Thermal Analysis (TG-DTA) methods.

Crystal Growth and Measurements

Growth of $NiNa_2(SO_4)_2.6H_2O$ (NSSH) Crystal

Most of the single crystals grow from liquid solutions. The liquid is the carrier of the atoms or ions necessary for the growth of the crystal, and may be water or a molten substance at high temperature. If the substance chosen is soluble in water, specimens are usually best prepared by crystallization from the appropriate solvent. Inorganic salts are usually soluble enough in water.

Crystals of Nickel Sodium Sulphate Hexahydrate, $NiNa_2(SO_4)_2.6H_2O$ (NSSH) were grown by slow evaporation method from aqueous equimolar ratio of Nickel Sulphate Hexahydrate, $NiSO_4.6H_2O$ and Sodium Sulphate, Na_2SO_4. Laboratory grade of salt powders and distilled-water were used to grow and synthesis for the crystals. At room temperature $NiNa_2(SO_4)_2.6H_2O$ (NSSH) crystal is green in colour. Photographs of the NSSH crystal growth condition and as-grown NSSH crystal (15.64 mm in length) are shown in Figures 1(a) and (b).

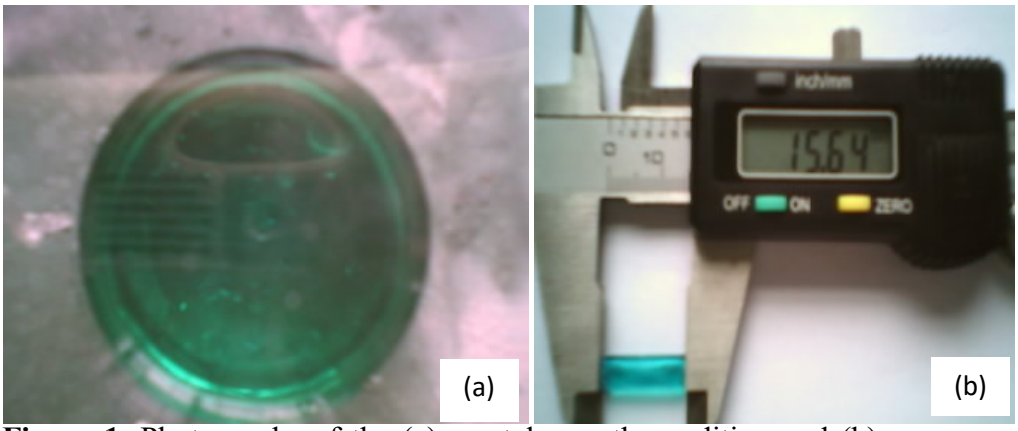

Figure 1. Photographs of the (a) crystal growth condition and (b) as-grown $NiNa_2(SO_4)_2.6H_2O$ (NSSH) crystal

XRD Measurement

Structure analysis and lattice parameters examination of $NiNa_2(SO_4)_2.6H_2O$ (NSSH) crystal were investigated by RIGAKU MULTIFLEX X-ray Diffractometer (Universities' Research Centre (URC), University of Yangon) using Ni-filter with CuK_α radiation, λ = 1.54056 Å. The main reflections in the range of $10° < 2\theta < 70°$were observed, and the collected data were used to refine the unit cell parameters from the observed 2 θ values with JCPDS (Joint Committee on Powder Diffraction Standards).

FTIR Spectroscopic Measurement

FTIR transmission spectrum of $NiNa_2(SO_4)_2.6H_2O$ (NSSH) crystal was observed by PC controlled SHIMADZU FTIR-8400 spectrophotometer in the wave number range of 400 cm^{-1} – 4000 cm^{-1} using Potassium Bromide, KBr, pellet method.

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, 8.220 mg powdered sample of the crystal was used to analyze the

high temperature phases. Aluminum (Al) pan was used as the standard sample.

Results and Discussion

Structure Analysis

Powder X-ray diffraction pattern of $NiNa_2(SO_4)_2.6H_2O$ (NSSH) crystal is shown in Figure2. The observed XRD lines were compared with the JCPDS data library file of Cat. No. 29-1253>Nickelblodite - $Na_2Ni(SO_4)_2.6H_2O$, to identify the crystalline phase formation and to analyze the crystal structure of the sample.

As shown in XRD pattern, most of the observed diffraction lines were assigned by the use of JCPDS. The diffraction line at 19.58° or (011) plane was found to be the strongest among all lines and it indicated the ($\bar{2}01$) peak was dominated in the crystal. The diffraction lines of very low in intensities situated in the diffraction angle range of about 46° – 70° were not assigned with JCPDS data library.

XRD pattern shows that the NSSH crystal belongs to orthorhombic structure. The lattice parameters were examined 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, λ is the wavelength of incident X-ray and (hkl) is the Miller indices. The lattice parameters of the crystal were obtained as *a* = 15.82 Å, *b* = 9.34 Å and *c* = 5.21 Å respectively.

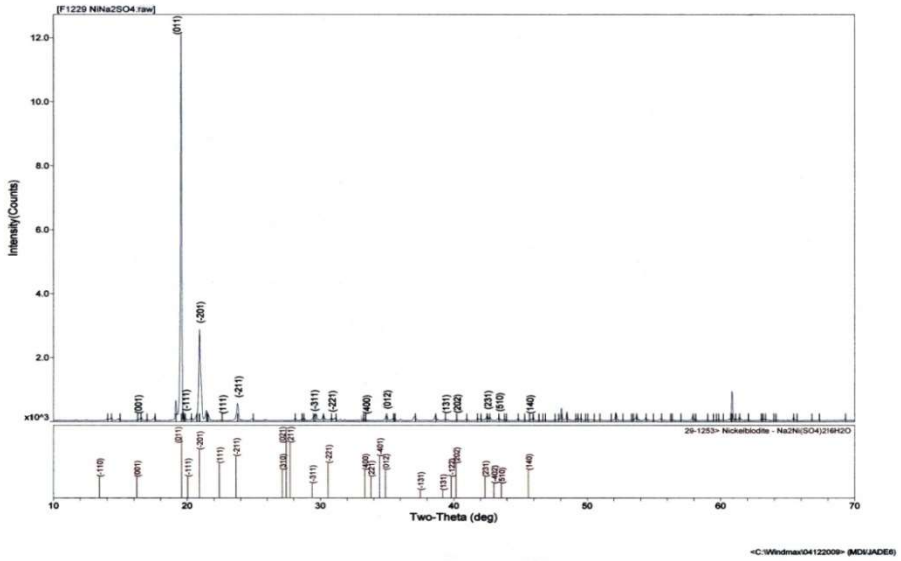

Figure 2. XRD pattern of $NiNa_2(SO_4)_2.6H_2O$ (NSSH)crystal

Vibrational Analysis

FTIR transmission spectrum of $NiNa_2(SO_4)_2.6H_2O$ (NSSH) crystal is shown in Figure3. The observed wavenumbers and corresponding vibrational characteristics and modes assignments of the molecules in the crystal are tabulated in Table 1. As shown in FTIR spectrum, thirteen absorption lines were observed and identified by using standard data files of free SO_4^{2-}, H_2O, and their molecular networks [Ross, (1972)]. Four fundamental modes of SO_4^{2-} were found in the spectrum and assigned as 982 cm^{-1} (υ_1-mode; symmetric-stretching), 438 cm^{-1} (υ_2-mode; bending), 1096 / 1148 cm^{-1} (υ_3-mode; dipole) and 623 cm^{-1} (υ_4-mode; polarization) respectively. The intensity of υ_3-mode (dipole) was found to dominate on others vibrational modes because in a FTIR transmission spectrum, the intensity of dipole characterization is the strongest one.

The absorption lines at (1431 cm^{-1}/1470cm^{-1} /1688cm^{-1}) and 3202 cm^{-1} were indicated by the υ_2-mode (bending) and υ_1-mode (symmetric-stretching) of H_2O molecule. The υ_3-mode (asymmetric-stretching) of H_2O was not found. The absorption line at 2206 cm^{-1} is represented by the bending vibration of carbon-dioxide molecule. The lines at 546 cm^{-1}, 745 cm^{-1} and 831

cm^{-1} were represented by the librational wagging, twisting and rocking vibrations of Ni—H_2O—Na and SO_4—H_2O—SO_4 molecular networks.

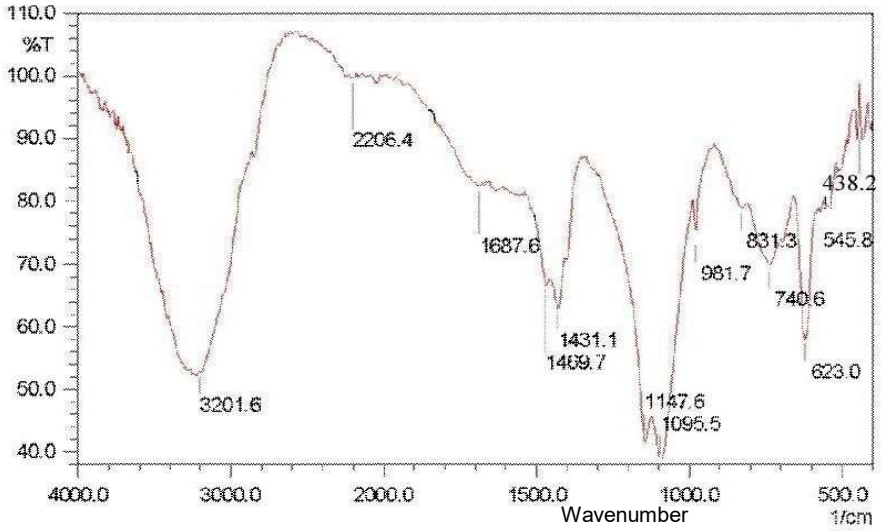

Figure 3. FTIR spectrum of $NiK_2(SO_4)_2.6H_2O$ (NSSH)crystal

Table 1. Wavenumbers and corresponding vibrational mode assignments of molecules in $NiNa_2(SO_4)_2.6H_2O$ (NSSH) crystal

Line No	Wavenumber (cm^{-1})	Vibrational mode & characteristics	Molecule
1	438	υ_2-mode (bending)	SO_4^{2-}
2	546	υ_ω(librational wagging)	Ni—H_2O—Na
3	623	υ_4-mode (polarization)	SO_4^{2-}
4	741	υ_τ(librational twisting)	SO_4—H_2O—SO_4
5	831	υ_ρ(librational rocking)	SO_4—H_2O—SO_4
6	982	ρ_1-mode (symmetric-stretching)	SO_4^{2-}
7	1096 / 1148	υ_3-mode (dipole)	SO_4^{2-}
8	1431 / 1470 / 1688	υ_2-mode (bending)	H_2O
9	2206	υ_2-mode (bending)	CO_2
10	3202	υ_1-mode (symmetric-stretching)	H_2O

Thermal Analysis

TG-DTA thermograms of $NiNa_2(SO_4)_2.6H_2O$ (NSSH) crystal at nitrogen atmosphere in the temperature range of 30°C - 600°C as shown in Figure 4.TGA curve shows the mass variation (weight loss) of the sample recorded during the measurement (heating). In the present work, the first step base line was changed between the temperature 39°C and 328°C in TGA thermogramand it showed the dehydration of six water molecules ($6H_2O$) or hydrated compound of $NiNa_2(SO_4)_2.6H_2O$ (NSSH) to anhydrous compound of $NiNa_2(SO_4)_2$ (NSS) with the weight loss of the sample was about 36%. In this temperature range, the strong endothermic reaction peak in DTA curve was found at about 130°C and it also indicated by the removal of six water molecules.

Second step base line changes was occurred between 328°C and 600°C in TGA thermogram that showed the decomposition of the anhydrous compound andpre-melting started on the surface of the sample with the mass variation of about 6%. While, one endothermic reaction peak was found at 391°C in DTA thermogram that showed the decomposition and pre-melting started on the surface of the sample.

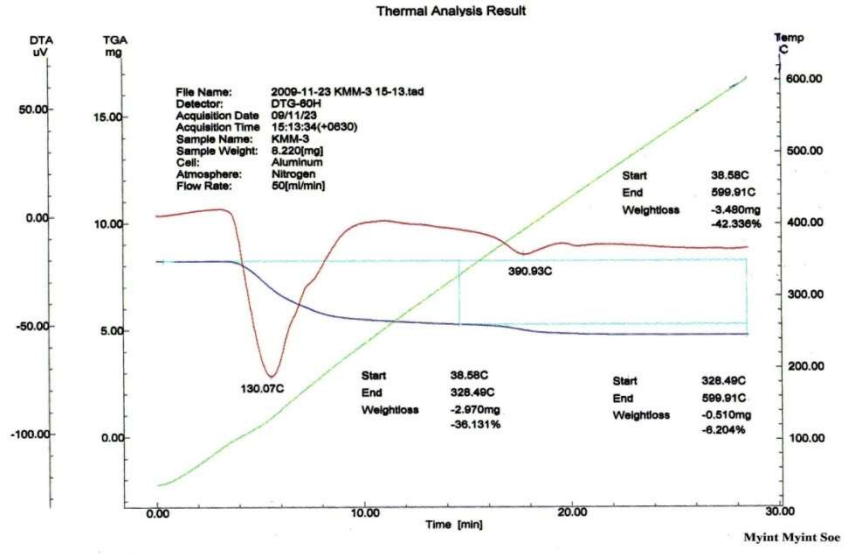

Figure 4.TG-DTA thermograms of $NiK_2(SO_4)_2.6H_2O$ (NSSH)crystal

Conclusion

Crystals of Nickel Sodium Sulphate Hexahydrate, $NiNa_2(SO_4)_2.6H_2O$ (NSSH) were grown by slow evaporation method. Structural, vibrational and thermal characteristics were reported in this paper. XRD pattern shows that the NSSH crystal analogous to orthorhombic structure and the lattice parameters are obtained as a = 15.82 Å, b = 9.34 Å and c = 5.21 Å respectively. According to FTIR spectrum, thirteen absorption lines were observed in this spectrum. Four fundamental modes of SO_4^{2-} were found and precisely assigned. The intensity of υ_3-mode (dipole) of SO_4^{2-} was found to be dominated on others vibrational modes. Only two fundamental modes of H_2O were observed and assigned as υ_1-mode (symmetric-stretching) and υ_2-mode (bending). The υ_3-mode (asymmetric-stretching) of H_2O was not found. Three librational motions of Ni—H_2O—Na and SO_4—H_2O—SO_4 molecular networks were also observed and assigned. From the TG-DTA thermograms, DTA thermogram confirmed with the result of TG. DTA analysis suggested two phases of the molecular changes of dehydration and pre-melting processes were occurred in the NSSH crystal at about 130°C and 391°C.

Acknowledgement

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