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Crystal Growth and Characterization of Potassium Manganese Nickel Sulphate Hexahydrate— A New UV Filter

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ABSTRACT

Potassium Manganese Nickel Sulphate Hexahydrate (KMNSH) crystals have been successfully grown by using traditional slow evaporation method. The empirical formula of KMNNSH is $K_2Mn_{0.1}Ni_{0.9}(SO_4)_2{\cdot}6H_2O$ with formula weight 430.7698. KMNNSH crystal revealed monoclinic space group P2(1)/c, a = 6.12(4) Å, b = 12.19(9) Å, c = 8.96(7) Å, α = γ = 90˚, β = 105.3(2), V = 645(1)Å3, Z = 2, Dc = 2.2281 g/cm^3 with deep green color. IR confirms that there is strong interaction between free water molecules. The thermal analysis indicates that the water molecules are present in the KMNNSH crystals. The transmission spectrometry of KMNNSH in the range from UV to near IR wavelengths is reported. Atomic Absorption Spectroscopy also have been studied and discussed.

Keywords: Ultraviolet Filter; Potassium Manganese Nickel Sulphate; Transmission Spectrum; Thermal Stability

1. Introduction

In general majority of the crystals show continual optical transmission from UV to near IR wavelengths range. Only selected, very few crystals show discontinuity in the above range. The best example is Nickel Sulfate Hexahydrate (NSA) crystal and it posses high transmission efficiency (>80%) in the narrow range 250 - 340 nm, and moderate transmission at 450 - 600nm, and strong absorption over all other wavelengths and is considered as an UV light filter. There are a variety of devices which use ultraviolet (UV) light filters that allow selected wavelengths of light to pass through. Such filters are used in missile approach warning systems which locate and track sources of ultra-violet energy, enabling the system to distinguish the plume of an incoming missile from other UV sources that pose no threat. The benefit of this system is the ability to estimate missile range. The success and efficiency of the system for helicopters or transport-type aircrafts depends on the UV sensors. Commercially available nickel sulfate hexahydrate crystals are widely used for these sensors. The biggest problem for these sensors arises due to low thermal stability of nickel sulphate crystals which is 72˚C. The Potassium Nickel Sulfate Hexahydrate (KNSH) crystals [1,2] have higher thermal stability as 97˚C and are also used in Missile approach warning systems and sensors in spaceships. Several other crystals such Cesium Nickel Sulfate Hexahydrate (CNSH) [3], Iron Nickel Sulfate twelve hydrate (FNSH) [4], Rubidium Nickel Sulfate Hexahydrate (RNSH) [5], and Ammonium Cobalt Nickel Sulfate Hexahydrate (ACNSH) [6] are reported being used as UV filter materials.

In the search of newer crystalline materials with better filter transmission property and higher thermal stability, the growth of Potassium Manganese nickel sulfate, with chemical formula $K_2Mn_{0.1}Ni_{0.9}(SO_4)_2{\cdot}6H_2O$ have been successfully grown by slow evaporation method. The grown crystals were analyzed by XRD and AAS. The degree of dopants inclusion was ascertained by AAS. The presence of water and SO_4^{2-} ions are confirmed by FTIR. The thermal stability of the grown crystals is 110˚C confirmed by TGA/DTA.

2. Experiment

All the starting materials used in the growth process of KMNNSH were purchased as AR grade (purity >98.0%). Equimolar ratio of $NiSO_4.6H_2O$ & K_2SO_4 and 0.1 mol of $MnSO_4\,7H_2O$ were taken and dissolved in double distilled water and stirred thoroughly. The solution mixture is heated to 60˚C for four hours to promote the reaction, the reaction equation can be expressed by the following:

$$K_2SO_4+Ni(SO_4)_2\cdot 6H_2O+Mn(SO_4)\cdot 7H_2O \rightarrow$$
$$K_2Mn_xNi_{1-x}(SO_4)_2\cdot 6H_2O+H_2O$$

The solution was filtered through a film of pore size of 0.22 μm, transferred into the glass container and allowed to cool slowly and further to evaporate at room temperature (32˚C) using a constant temperature bath. Single crystals of size 10 × 10 × 10 mm^3 were grown in a period of 10 days with deep-green in color and are shown in **Figure 1**.

3. Results and Discussion

X-ray diffraction studies of grown crystal was carried on Enraf Nonius CAD4-MV31 single crystal X-ray diffracttometer to find the lattice parameters values. The FTIR spectrum of KMNNSH crystals was recorded in the range 400 - 4000 cm^{-1} employing a Perkin-Elmer spectrometer by KBr pellet method in order to study the presence of functional groups of the grown $K_2Mn_{0.1}Ni_{0.9}(SO_4)_2{\cdot}6H_2O$ single crystal and also to identify lattice water molecule. Linear optical properties of the crystals were studied using a UV-Visible Spectrophotometer. Thermal analysis was performed on the grown crystals to study the thermal stability of the sample. Atomic Absorption studies were made on the KMNNSH crystals to know the presence of dopant concentration.

3.1. XRD

The lattice parameters of KMNNSH crystals were determined by single crystal X-ray diffraction analysis. The structure belongs to monoclinic space group, $P2_1/c$ with unit cell parameters a = 6.12 Å, b = 12.19Å, c = 8.96 Å and β = 105.3(2). This lattice parameter is comparable with the lattice parameters of Potassium Nickel Sulfate Hexahydrate and is presented in **Table 1** for comparison.

3.2. Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy (AAS) is one of the most widely used quantitative analytical methods. It is used for quantitative determination of metals and metalloids down to absolute amount as low as 10^{-14} g. AAS determines the presence and concentration of metals in liquid samples. To determine the mole percentage of dopants (Mn) incorporated in the grown crystals, finely powdered sample about 100 mg were dissolved in 10 ml of dilute acid and subjected to AAS. The results showed that 0.1 M manganese is present in the grown sample and confirmed the stochiometric.

3.3. Transmittance Studies

Optical transmission spectra was recorded on a PE-lambda 900 spectrometer with performing wavelength ranging from 200 to 1000 nm as shown in **Figure 2**. KMNNSH has three transmission peaks approximately centered at 316.5 nm, 486.5nm, 837.5 nm; and other wavelengths are strong absorption. This discontinuous spectral characteristic mainly arises from the absorption of hydrated transition metal ions $Ni(H_2O)_6$. The transmission intensity of KMNNSH crystal in the UV band is comparable with those of similar type material Potassium Cobalt Nickel Sulphate Hexahydrate (KCNSH) [7]

3.4. Ftir Spectroscopy

FTIR spectroscopic studies were effectively used to identify the functional groups present in the synthesized compound. To analyze qualitatively the presence of the functional groups in KMNNSH crystals, FTIR spectra

Table 1. Lattice parameters of KMNNSH and KNSH.

Crystal Name	$K_2Mn_{0.1}Ni_{0.9}(SO_4){\cdot}H_2O$	$K_2Ni(SO_4)_2{\cdot}6H_2O$
Space group, Z	P21/c, (Z = 2)	P21/c, (Z = 2)
a (Å)	6.12(4)	6.129(12)
b(Å)	12.19(9)	12.174(2)
c(Å)	8.96(7)	8.9915(1)
β(°)	105.3(2)	105.06(3)
V(Å)	645 (1)	647.8(2)
Dc(gm/cm^3)	2.2281	2.241

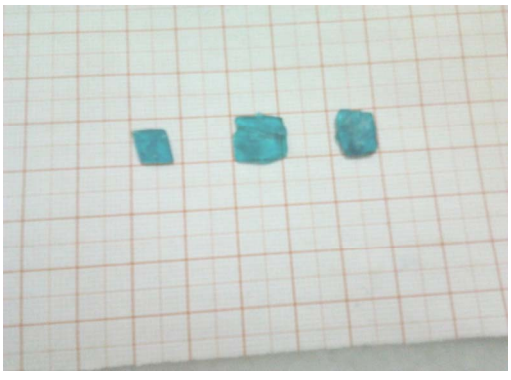

Figure 1. A Photograph of KMNNSH crystal.

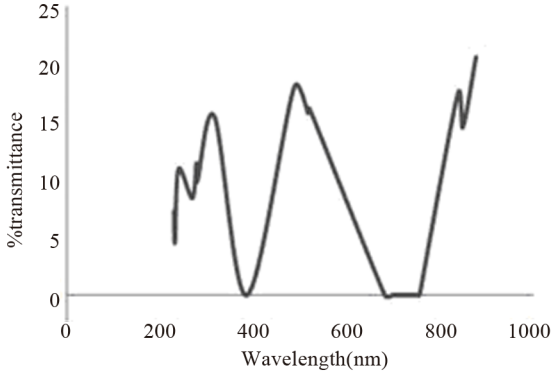

Figure 2. Transmission Spectra of KMNNSH crystal.

were recorded using Bruker IFS 66V spectrophotometer by KBr pellet technique in the region of 400 - 4000 cm^{-1}. The recorded spectra are shown in **Figure 3**. **Table 2** shows the vibration assignments for KMNNSH crystals.

The stretching vibrations of the water molecule are expected in 3000 - 3600 cm^{-1} [8,11]. The broad vibration band observed at 3233 cm^{-1}, is attributed to symmetric stretching mode of water molecule. The medium broad-band noticed around 1560 cm^{-1} is assigned to the vibration mode of water molecules. The band observed at 763.8 cm^{-1} is assigned to liberation mode of water molecules. In general free SO_4^{2-} ion has T_d symmetry and has 4 fundamental vibrations namely a non degenerate mode (ν_1) at 984.6 cm^{-1}, and a doubly degenerated mode (ν_2) and a triply degenerated vibrations (ν_3 and ν_4) at 1140 cm^{-1} and 631.6 cm^{-1} respectively [9]. The peak observed at 1140 cm^{-1} is attributed to triply degenerate symmetric stretching mode (ν_3) of SO_4^{2-} the band observed at 461 cm^{-1} is assigned to the doubly degenerate (ν_2) SO_4^{2-} mode. The peak appeared at 984.6 cm^{-1} is reasonably assigned to the (ν_1) SO_4^{2-} non degenerate mode. The mode at 631.6 cm^{-1} is assigned to the triply degenerate vibrations (ν_4) of SO_4^{2-}. The above assignment agrees well with that reported by Sivanesan *et al.* [10] for triglygine sulphate (TGS).

3.5. Thermo Gravimetric Analysis

The grown crystal was crushed into fine powder and Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were recorded using Q50 W/FMC DTA analyzer in the temperature range from room temperature to 800˚C at a heating rate of 25˚C/min in nitrogen inert atmosphere to study the weight loss and thermal stability of KMNNSH crystal. The thermo grams recorded for the grown crystals and are presented in **Figure 4**. The compound is found to be thermally stable up to 110˚C and decompose afterwards. The thermogram shows that these crystals decompose on heating. The thermo gram (**Figure 4**) indicates that small weight loss is at temperature near 110˚C, it may be due to physically adsorbed water. The TGA curve shows that the dehydration temperature is 110˚C which is higher than that of those in KNSH (97.2˚C) and KCNSH (98˚C). There is a major weight loss of 24.5036% around 250˚C due the loss of water molecules in the lattice site. The following decomposition pattern is formulated.

$$K_2Mn_{0.1}Ni_{0.9}(SO_4)_2\cdot 6H_2O \rightarrow K_2Mn_{0.1}Ni_{0.9}(SO_4)_2\uparrow +6H_2O$$

430.7698 322.7698

108 (25.07% weight loss)

The theoretical value of weight loss of six water molecule is 25.07% and very close to those of experimental weight loss. The DTA curve depicted in **Figure 4** (dotted line) shows a endothermic dip between 150˚ and 200˚C corresponding to the decomposition of KMNNSH.

Table 2. FTIR Peak Assignments.

Vibrational frequencies	Assignments
3233 (m,br)	ν_{as} OH stretching
2885(s)	intermolecular hydrogen bonding between the water molecules
1684 (w)	$\delta(H_2O)$
1560 (m)	υ H_2O
1140 (w)	υ_3 SO_4
1096 (m,br)	υ_3 SO_4
984.6 (s)	υ_1 SO_4
763.8 (m)	ρ_r (H_2O)
631.6 (s)	υ_4 SO_4
574.7(w)	υ_4 SO_4
461 (w)	υ_2 SO_4

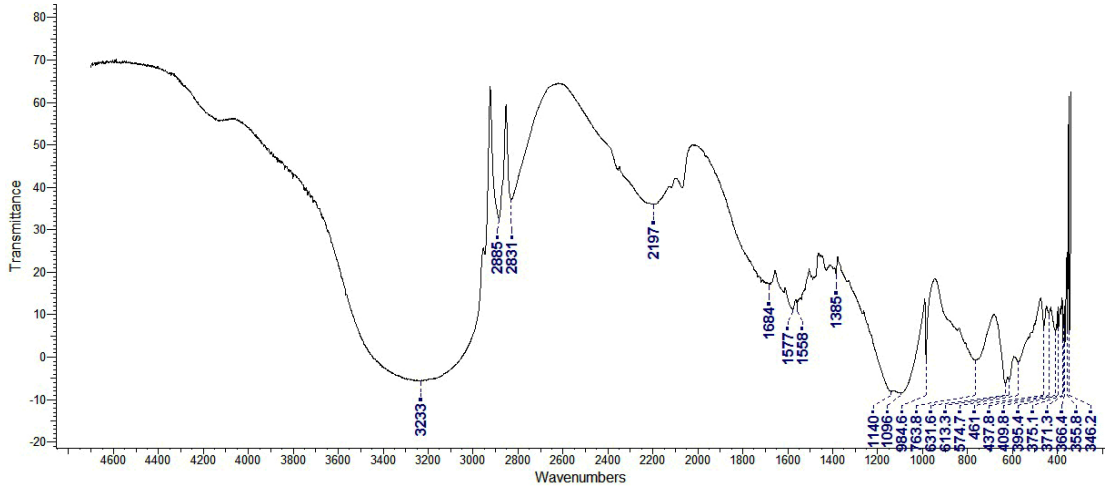

Figure 3. FTIR Spectrum.

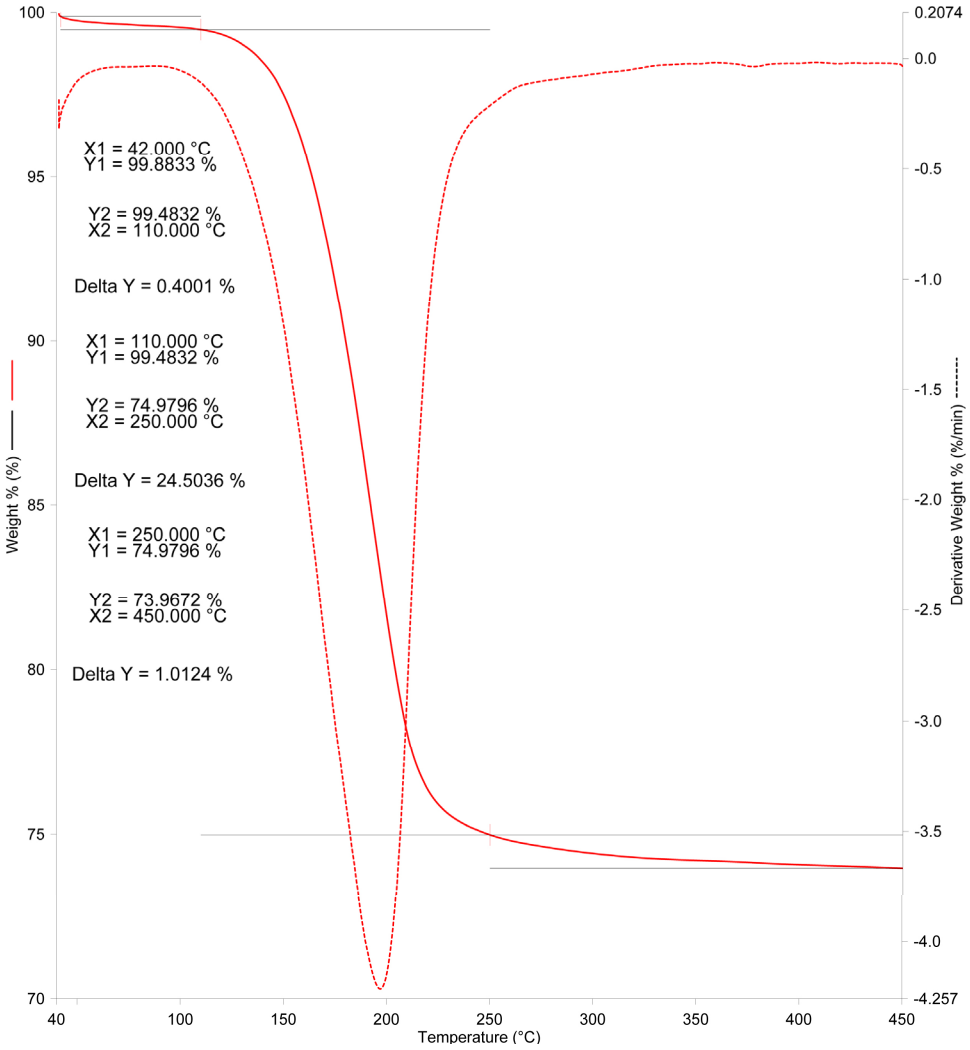

Figure 4. TG/DTA trace of KMNNSH crystal.

4. Conclusion

A mixed crystal of KMNNSH has been grown by slow evaporation method. Crystals of dimensions 50 × 15 × 10 mm^3 were obtained in the present study. The grown crystals were confirmed by XRD analysis. It is subjected to UV-VIS, FTIR, AAS and TGA/DSC analysis. The UV-VIS study confirmed the doped crystal filter blocks the unwanted transmission in the range 400-600 nm and 800 - 1000 nm ranges, and hence act as efficient filter. FTIR confirmed the presence of water molecule and sulphate group. AAS confirmed the presence of Mn atoms in the expected stochiometry. Enhancement of thermal stability was observed by thermal analysis. Hence the grown crystal is a new efficient ultraviolet filter material.

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