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Synthesis and Characterization of Potassium Manganese Nickel Sulphate Hexahydrate: A Potential UV Filter

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Single crystals of potassium manganese nickel sulphate hexahydrate were crystallized by the slow evaporation technique from aqueous solutions. Crystals obtained have been analyzed by powder XRD, single crystal XRD, SEM-EDX, FTIR, UV transmission, atomic absorption spectral analysis and TG-DTA. The lattice parameters were calculated from the XRD data. Atomic absorption spectral analysis showed that the Mn atoms were present in the mixed crystals and it is confirmed by EDX. Scanning electron microscopic studies used to understand the morphology of the calculi. The thermal analysis, TGA and DTA showed that the mixed crystals have higher thermal stability than the potassium nickel sulphate hexahydrate crystals. UV-visible spectral studies confirmed that the grown crystal is transmissive in the ultraviolet region.

Keywords: Ultraviolet filter, Potassium manganese nickel sulphate hexahydrate, Transmission spectrum, Thermal stability.

INTRODUCTION

An UV filter is needed to enable the system to distinguish this source of UV light from other natural sources of UV energy, such as the sun, moon and stars [1]. Nickel sulfate hexa hydrate (NSH, $NiSO_4{\cdot}6H_2O$) crystal is an important ultraviolet band optical filter with high transmission efficiency and narrow spectrum bandwidth between 300 and 500 nm wavelength [2-4]. The detection of UV radiation is widely used in commercial and military fields. The UV light filters allow only selected wavelengths of light to pass through. The success and efficiency of the missile approach warning system for helicopters or transport-type aircraft 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 sulfate crystals. The crystals start deteriorating as the temperature starts rising above 60 °C. This rise can be due to atmosphere as well as heat generated by working systems in the aircraft. Aircraft parked in tropical and desert areas can experience very high temperatures. In such cases, the heat stability of these systems is highly questionable. There is an urgent need for an ultraviolet filter material with higher temperature stability, good crystal growth suitability and desired filter transmittance and bandwidths.

Nickel sulfate hexahydrate (NSH) crystals, commercially available as ultraviolet light filters and UV sensors are particularly useful in solar-blind optical systems and sensing devices, which seek to identify the presence of UV light sources in the UV missile warning systems [5]. In order to improve the transmittance and the dehydration temperature, the two important parameters of a crystal when used as UV filter, other nickel sulfate based crystals such as ANSH, KNSH, CNSH *etc.* have been prepared, other nickel sulfate based crystals such as ANSH, KNSH, CNSH, *etc.* have been prepared [6-8]. The potassium nickel sulphate hexa hydrate (KNSH) crystals which have higher thermal stability as 97 ºC are used in missile approach warning systems and as sensors in spaceships [9].

The filter should have high transmittance at the desired wavelength. For missile warning systems, the crystal should be transmissive in the ultraviolet spectral region and have strong absorption at longer wavelengths. Furthermore, the crystal should be able to survive prolonged exposures to temperatures above 85 °C and preferably not be adversely affected by temperatures range 100 to 115 °C [9].

To increase the thermal stability, the mixed crystals were grown by varying the concentration of Mn and Ni sulphate using traditional slow evaporation method. The purpose of this study is to find the influence of changing Mn and Ni with different ratios by their corresponding thermal properties, optical transmittance and infrared spectroscopy. The degree of dopant inclusion was ascertained by atomic absorption spectroscopic studies (AAS) and confirmed by EDX. The presence of water and SO_4^{2-} ions are confirmed by FTIR.

EXPERIMENTAL

Mixed crystals $K_2Mn_{0.5}Ni_{0.5}(SO_4)_2{\cdot}6H_2O$ (KMNNSHH-A) and $K_2Mn_{0.9}Ni_{0.1}(SO_4)_2{\cdot}6H_2O$ (KMNNSHH-B), were grown with varying proportions such as $NiSO_4$ and $MnSO_4$ (0.5:0.5, 0.1:0.9). These single crystals were prepared by dissolving AR grade 1 mol K_2SO_4 (0.5, 0.1) mol $MnSO_4$ and (0.5, 0.9) mol $NiSO_4$ in double distilled water and heated up to 70 °C for 4 h by slow evaporation solution growth technique. The photographs of the grown crystals are presented in the Fig. 1a and 1b. The chemical reaction can be expressed as

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

The resulting 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 a constant temperature of 32 °C using a constant temperature bath. The good quality mixed single crystals were obtained within two weeks as shown in Fig. 1. The single crystal X-ray diffraction data was collected using Rigaku AFC7S diffractometer with graphite monochromated Mo-Ka radiation. The TG and DTA analyses were done using Mettler TA 3000 system. Atomic Absorption studies of the grown crystals were carried out on AA Perkin Elmer spectrophotometer. SEM and EDX studies were carried out by The FTIR absorption spectra for this crystal were taken using BRUKER IFS66V FT-IR spectrometer. The visible absorption data was obtained using HITACHI U-2000.

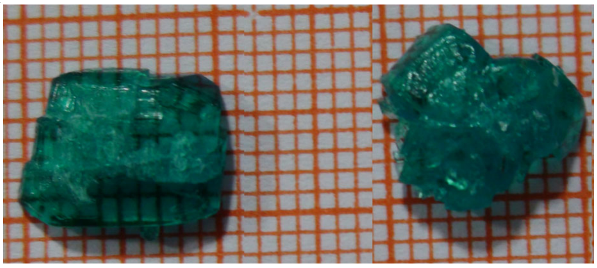

Fig. 1a. Photograph of KMNNSHH-A crystals

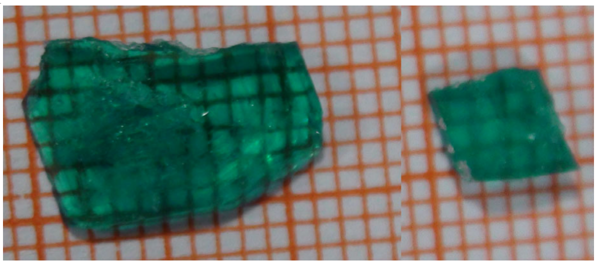

Fig. 1b. Photograph of KMNNSHH-A crystals

RESULTS AND DISCUSSION

Powder crystal X-ray diffraction analysis: The grown crystals were crushed to a uniform fine powder and subjected to powder X-ray diffractometer to identify the reflecting planes of the powdered samples of KMNNSHH-A and KMNNSHH-B. In this, the strong observable peaks indicate the highly crystalline nature of the sample. Powder XRD reveals the crystalline nature of the grown crystals. XRD patterns of the grown crystals are shown in Fig. 2.

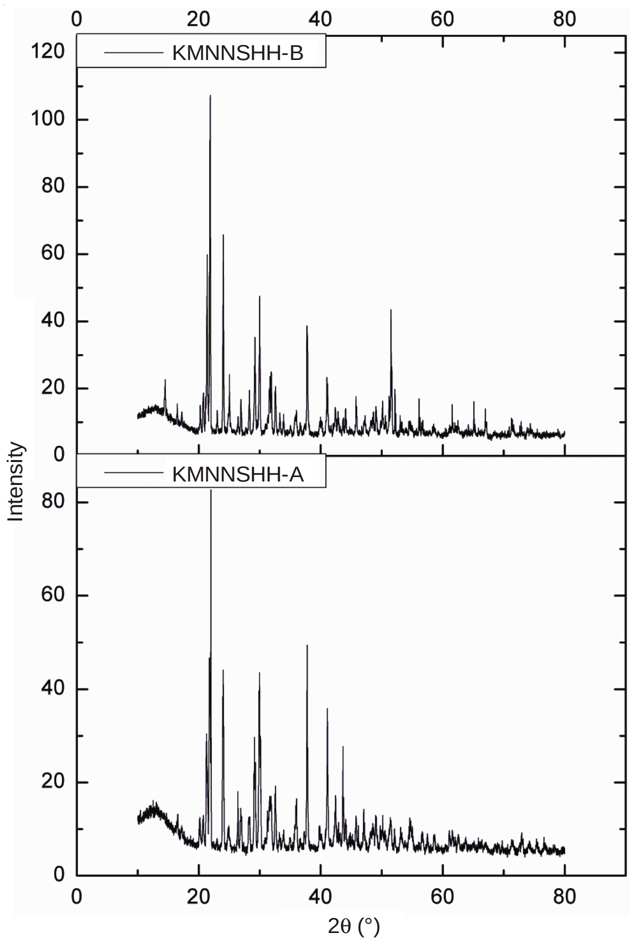

Fig. 2. XRD patterns of the grown crystals

Unit cell determination by single crystal XRD studies: The single crystal X-ray diffraction studies have been carried out by Enraf Nonius CAD4 diffractometer. Lattice parameters of both the crystals are presented in Table-1. The mixed crystals crystallize in monoclinic system (space group $P2_1/c$).

Elemental analysis by atomic absorption spectroscopy (AAS): Atomic spectroscopy is one of the most widely used methods for quantitative elemental analysis. Atomic absorption studies of the grown crystals were carried out on AA Perkin Elmer spectrophotometer to know the dopant concentration. The recommended flame used in this for Mn is nitrous oxide/acetylene flame. The wavelength of light used is 280.1 nm. To estimate the concentration of Mn ion, the solution has been prepared by dissolving 0.01 g of the grown crystal in a 10 mL of 1:1 Nitric acid and used. Appropriate hollow cathode lamp was employed. The molar concentration of manganese in the growth solution and the grown crystals are listed in the Table-2.

UV transmittance studies: Optical transmission spectra were recorded on a PE-lambda 900 spectrometer with performing wavelength ranging from 100 to 1000 nm. The UV-visible spectra of KMNNSHH-A and KMNNSHH-B crystals are shown in Fig. 3. In KMNNSHH-A crystals show discontinuous optical transmission. The discontinuous spectral characteristics can be due to the absorption of hydrated transition metal ions $Ni(H_2O)_6$. The band gap was calculated as 5.93 eV (KMNNSHH-A) and 6.069 eV (KMNNSHH-B).

TABLE-1
UNIT CELL PARAMETERS OF THE GROWN CRYSTALS WITH DIFFERENT CONCENTRATIONS

Cell parameters	$K_2Mn_{0.9}Ni_{0.1}(SO_4)_2·6H_2O$	$K_2Mn_{0.5}Ni_{0.5}(SO_4)_2·6H_2O$	$K_2Ni(SO_4)_2·6H_2O$
a (Å)	6.1342	6.2217	6.129(12)
b (Å)	12.2056	12.5343	12.174(2)
c (Å)	9.0133	9.2557	8.9915(18)
β (°)	105.207	106.912	105.06(3)
V (Å^3)	651.21	648.03	647.8(2)
Space group, Z	$P2_1/c$, (Z = 2)	$P2_1/c$, (Z = 2)	$P2_1/c$, (Z = 2)

TABLE-2
MOLAR CONCENTRATION OF MANGANESE IN THE DOPED CRYSTALS

Molar concentration taken for the solution	Molar concentration present in the crystal
0.5	0.42
0.9	0.93

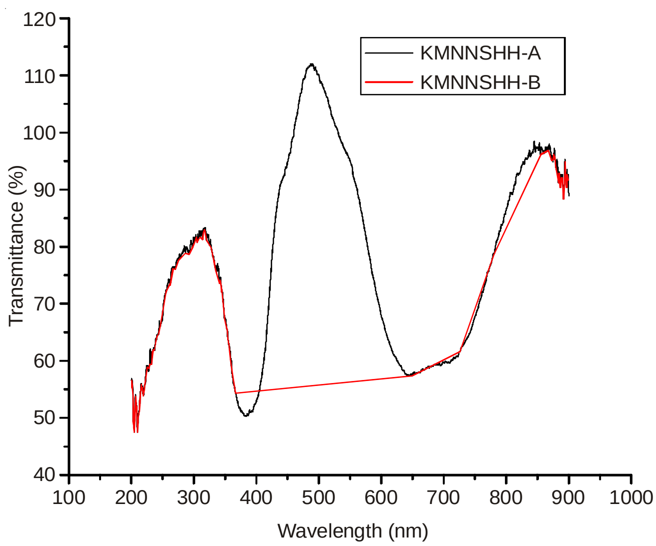

Fig. 3. Transmission spectra of KMNNSHH-A and KMNNSHH-B

The vibration frequencies of the grown crystals are presented in the Table-3. The stretching vibrations of the water molecule are expected in the region 3600-3000 cm^{-1} [10]. The broad vibrational band observed at 3230 cm^{-1} (KMNNSHH-A) and 3244 cm^{-1} (KMNNSHH-B) and is attributed to the symmetric stretching mode of water molecule. The medium band noticed at 1663 cm^{-1} (KMNNSHH-A) and 1699.2 cm^{-1} (KMNNSHH-B) is attributed to the bending vibrational mode of water molecules. The band observed at 759 cm^{-1} (KMNNSHH-A) and 755 cm^{-1} (KMNNSHH-B) is assigned to the liberation mode of water molecules (Fig. 4).

TABLE-3
VIBRATIONAL FREQUENCY ASSIGNMENTS OF GROWN CRYSTALS

FT-IR ν (cm^{-1})		Assignments
KMNNSHH-A	KMNNSHH-B	
3230	3244	Symmetric O-H stretching
1663	1699.2	Bending mode of H_2O
759	755	Liberation mode of H_2O
984.59	984	ν_1 SO_4^{2-}
419	458	ν_2 SO_4^{2-}
1099	1084	ν_3 SO_4^{2-}
632	631	ν_4 SO_4^{2-}

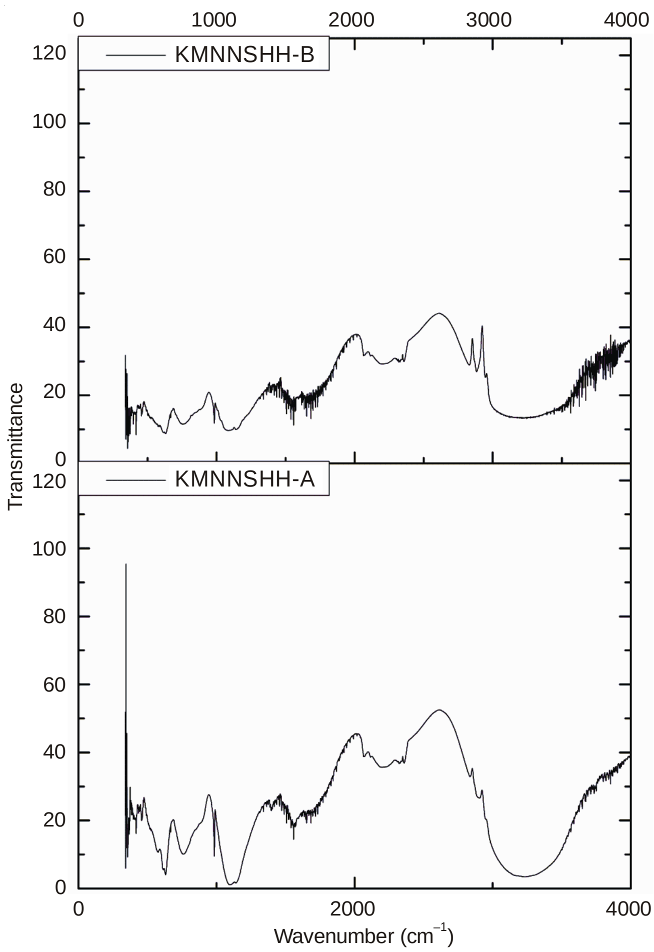

Fig. 4. FTIR spectrum of KMNNSHH-A and KMNNSHH-B crystals

According to the selection rules for T_d symmetry, the IR spectrum of SO_4^{2-} ion has two absorption bands ν_3 which correspond the asymmetric stretching vibrations of the S-O bonds and ν_4 which correspond to the bending vibrations of O-S-O. Each of these frequencies are triply degenerated. These two bands triply degenerated vibrations (ν_3 and ν_4) are observed in the IR absorption spectrum nearly at 1100 cm^{-1} and 630 cm^{-1}. Since the symmetry of SO_4^{2-} in solution is nearly tetrahedral [11,12], with a totally symmetric S-O stretching vibration at 980 cm^{-1} (ν_1) and an asymmetric, triply degenerate, S-O stretching vibration at 1100 cm^{-1} (ν_4). The deformation and combination vibrations (ν_2 and ν_4) for S-O occur at lower energy. The band observed nearly at 450 cm^{-1} is assigned to the doubly degenerate (ν_2) SO_4^{2-}.

In the spectrum of (KMNNSHH-A), the ν_1, ν_2, ν_3 and ν_4, modes are assigned to have frequencies at 984.6, 419, 1099 and 632 cm^{-1}, respectively. In the spectrum of (KMNNSHH-B), the ν_1, ν_2, $\nu_3$and ν_4, modes are assigned to have frequencies at 984, 458, 1084 and 631 cm^{-1}, respectively. The above assignments are in good agreement with the already reported sulphate group in triglygine sulphate (TGS) [13].

Thermal analysis: The grown crystals were crushed into fine powder and The TGA/DTA are recorded up to 800 °C using a Perkin-Elmer thermal analyzer STA409PC module with heating rate of 10 °C/min in the presence of nitrogen atmosphere to study the weight loss and thermal stability of KMNNSHH crystals. The thermo grams recorded for the grown crystals are presented in Fig. 5a and 5b.

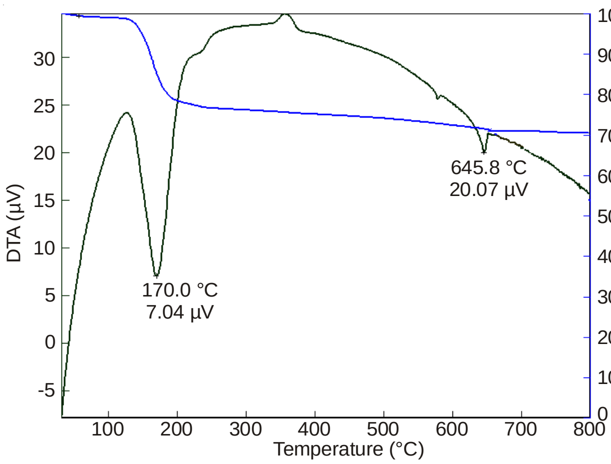

Fig. 5a. Thermogram of KMNNSHH-A crystals

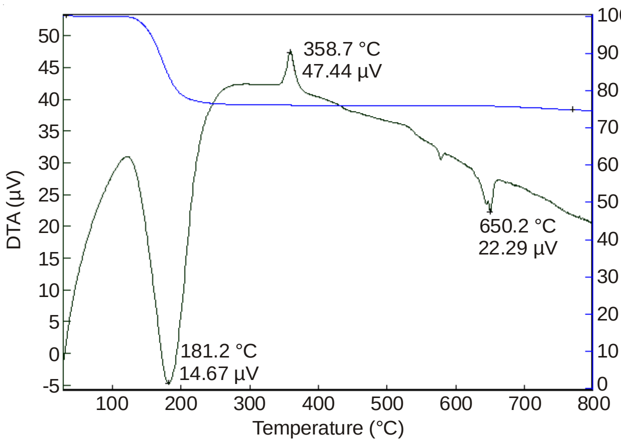

Fig. 5b. Thermogram of KMNNSHH-B crystals

For the mixed crystals, the analysis of thermograms reveal that the loss of weight in the temperature range of 150-180 °C correspond to the elimination of water of hydration equivalent to $6H_2O$ molecules.

The compound KMNNSHH-A is found to be thermally stable up to 131.6 ºC. The inflection occurring between 150-200 °C with a weight loss of 27.03 % corresponds to the evolution of 6 water molecules.. In the temperature range 150-200 °C inflections correspond to the following reactions:

$$K_2Mn_{0.5}Ni_{0.5}(SO_4)_2{\cdot}6H_2O \rightarrow K_2Mn_{0.5}Ni_{0.5}(SO_4)_2\uparrow + 6H_2O$$

Formula weight: 434.815; Theoretical weight losses: 24.838; Experimental weight loss: 27.03

The compound KMNNSHH-B is found to be thermally stable up to 129.4 °C. The inflection occurring between 150-200 °C with a weight loss of 25.2 % corresponds to the evolution of 6 water molecules.

The following decomposition pattern is formulated:

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

Formula weight: 433.38; Theoretical weight losses: 24.88; Experimental weight loss: 25.2

The slight variations in the percentage in both may be attributed to the isomorpous substitution.

The thermal stability of both the crystals KMNNSHH-A and KMNNSHH-B is very high compared to undoped potassium nickel sulphate hexa hydrate [9]. The addition of Mn probably is responsible for the increase in the thermal stability.

SEM and EDX measurement: Energy dispersive X-ray spectroscopy was employed on the broken solid sample to obtain the information on the mineral elements of calculi. The crystal was mounted on aluminium stub using carbon tape and the calculi of mineral elements was observed by scanning electron microscope.

The SEM photograph of the KMNNSHH-A and KMNNSHH-B crystal is shown in Fig. 6a and 6b, respectively. The SEM images of the crystal reveal the well formation of the faces of the crystal.EDX spectrum of the crystal is shown in Fig. 7a and 7b. The peak confirms the presence of manganese in the KMNNSHH-A& KMNNSHH-B crystals.

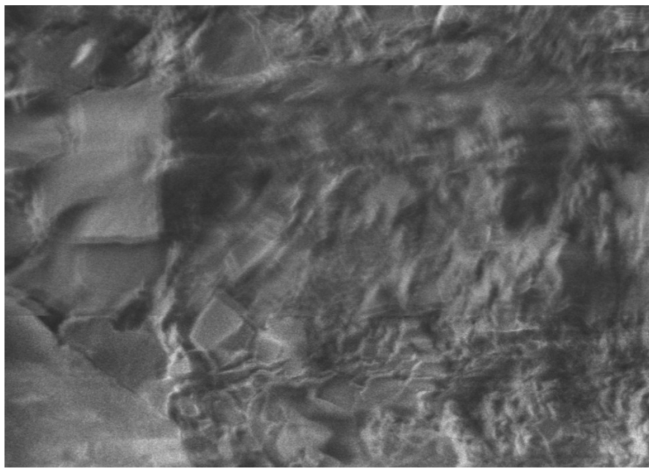

Fig. 6a. SEM Photograph of KMNNSHH-A crystals

Energy dispersive X-ray spectra labeled with all possible elemental compositions are also presented. Colored elemental mapping are also recorded for both the crystals are presented in Fig. 8a and 8b.

Conclusion

The mixed crystals KMNNSHH-A and KMNNSHH-B have been grown by the slow evaporation method at room temperature. The powder XRD reveals the crystallinity of the grown crystals.The cell parameters of grown crystals are in close agreement with the KNSH crystals. The FTIR studies confirm that the presence of sulfate and water molecules. The atomic

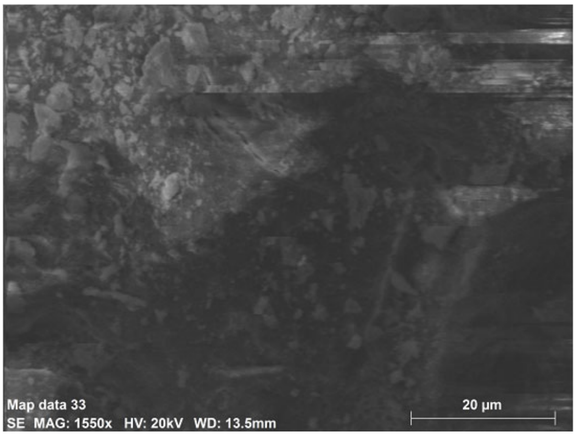

Fig. 6b. SEM Photograph of KMNNSHH-B crystals

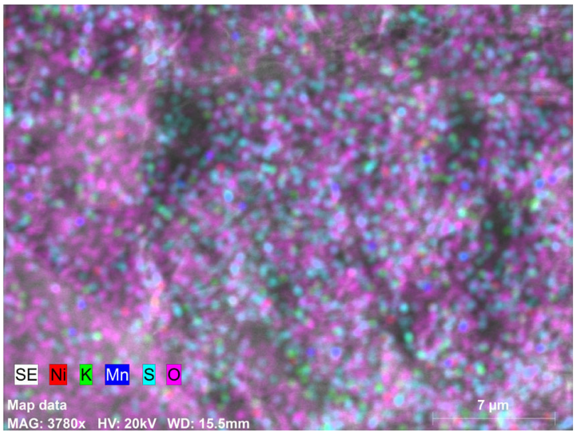

Fig. 7a. Colored elemental map of KMNNSHH-A crystals

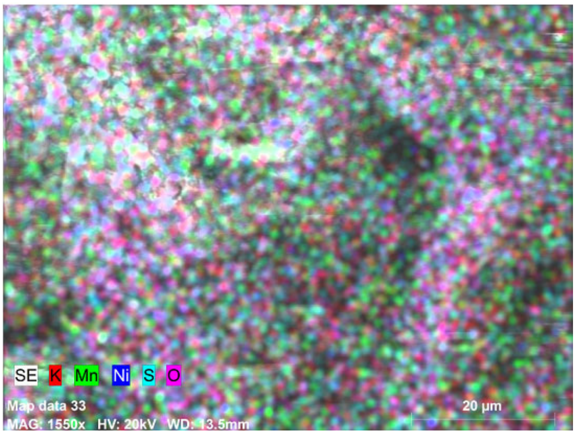

Fig. 7b. Colored elemental map of KMNNSHH-B crystals

absorption spectroscopy study reveals the expected concentration of dopants. The result obtained from AAS is confirmed by EDAX and both of them are in close agreement. The discontinuous spectral characteristic mainly arises from the absorption of hydrated transition metal ions $Ni(H_2O)_6$. The higher Ni concentration of the grown crystals is observed to be a good candidate for UV filters.The thermo grams were used to formulate the decomposition pattern of the compound. From TGA

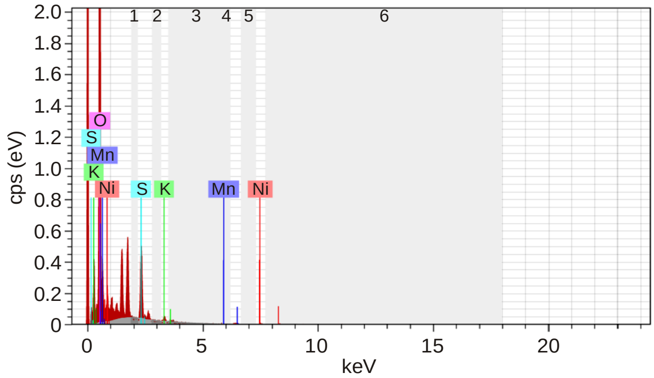

Fig. 8a. EDAX OF KMNNSHH-A crystals

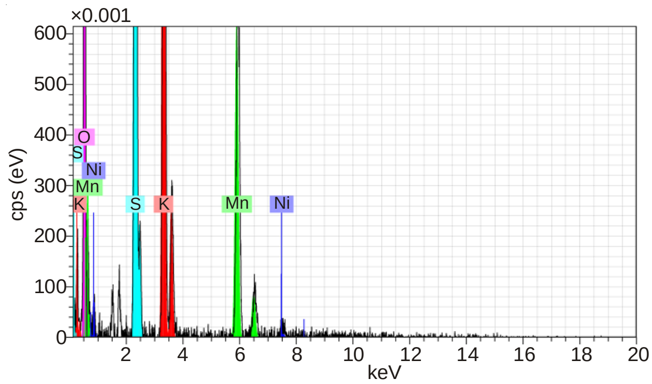

Fig. 8b. EDAX OF KMNNSHH-B crystals

studies, it is confirmed that there are six water molecules of crystallization. The higher concentration of Mn leads the present crystal as thermally more stable compared to earlier reported potassium nickel sulphate hexahydrate.

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