Research Article

Growth and Analysis of NSH and KMNSH Crystals by Slow Evaporation Technique

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Nickel sulphate hexahydrate (NSH) and potassium magnesium nickel sulphate hexahydrate (KMNSH) single crystals were grown by slow evaporation method. The grown NSH crystal was found to crystallize in tetragonal system with space group $P4_1 2_1 2$ and KMNSH in monoclinic system with space group $P12_1/c$. The optical band gap energies of the grown crystals using UV-Vis spectral results for the doped and undoped NSH crystals were calculated. The presence of various functional groups in the crystal was identified by FTIR analysis. The thermal behaviour of the grown crystal has been studied by TGA/DTA analysis.

1. Introduction

Ultraviolet (UV) light filters are used in missile approach warning systems which locate and track UV energy emitting sources and are used as sensors for helicopters or transport aircraft. Commercially available nickel sulphate hexahydrate crystals are widely used as sensors. The biggest problem for these sensors arises due to low thermal stability of nickel sulphate crystals which is 76°C . The potassium nickel sulphate hexahydrate (KNSH) crystals which have higher thermal stability as 97°C are used in missile approach warning systems and as sensors in spaceships [1, 2]. Several other crystals such as cesium nickel sulphate hexahydrate (CNSH) [3], iron nickel sulphate twelvehydrate (FNSH) [4], rubidium nickel sulphate hexahydrate (RNSH) [5], and ammonium cobalt nickel sulphate hexahydrate (ACNSH) [6] are also reported as UV filter materials. Similar research work carried out on potassium sulphate [7, 8], potassium cobalt nickel sulphate hexahydrate (KCNSH) [9, 10], bis thiourea magnesium sulphate (BTMS) [11], and magnesium sulphate heptahydrate [12] crystals is also reported. In the search of newer crystalline materials with better filter transmission property and higher thermal stability, the growth of potassium magnesium nickel sulphate crystal has been carried out in this research work.

2. Experimental Procedure

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, K_2SO_4 , and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ of AR grade (purity $> 98.0\%$) were used. Approximate molar ratio of materials was taken using digital balance and dissolved in double distilled water. The solution of pH value 5 was stirred for nearly 2 hours with magnetic stirrer to ensure homogeneity. Heating the solution to 60°C is carried out to promote the reaction and then is cooled to 40°C slowly. An abduction is formed according to the reaction given as follows:

The homogenised solution was filtered twice using Whatman filter paper number 1 and then allowed to evaporate at 40°C temperature using a constant temperature bath. Then the solution is transferred to the petridish and allowed to evaporate without disturbance. Optically good quality NSH, KMNSH single crystals have been grown within a period of 11 days and 8 days, respectively, and are shown in Figures 1(a) and 1(b).

FIGURE 1: (a) Photography of the grown NSH crystal and (b) photography of grown KMNSH crystal.

TABLE 1: Lattice parameters of NSH and KMNSH crystals.

Parameter	NSH crystal	KMNSH crystal
Crystal system	Tetragonal	Monoclinic
Space group (Z)	$P4_1 2_1 2, Z = 2$	$P_1 2_1/c, Z = 4$
a (Å)	6.6787	6.137
b (Å)	6.6787	12.190
c (Å)	18.2990	9.005
α	90°	90°
β	90°	105°
γ	90°	90°

3. Results and Discussion

X-ray diffraction studies of grown crystal were carried out with PANalytical X-ray diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.54060$ a.u.) radiation. The FTIR spectrum of both crystals was recorded in the range $400\text{--}4000\text{ cm}^{-1}$ using SHIMADZU IR AFFINITY-1 spectrometer by KBr pellet technique. Optical properties of the crystals were studied using UV-Visible spectrophotometer. Thermal analysis for the grown crystals was also carried out.

3.1. Powder X-Ray Diffraction. The grown NSH and KMNSH crystals were crushed to a uniform fine powder and subjected to powder X-ray diffractometer to identify the reflecting planes. Lattice parameters obtained from XRD data are listed in Table 1. It is observed that structure of KMNSH is monoclinic with space group $P_1 2_1/c$ and NSH is tetragonal with space group $P4_1 2_1 2$. The lattice parameters of KMNSH crystal agree well with the reported value of Vanitha et al. [13]. The powder XRD pattern of the grown crystals is shown in Figures 2(a) and 2(b), respectively.

3.2. UV-Vis Spectroscopy. The UV-Visible transmittance spectrum of the grown crystal was carried out using UV-1700 series UV-Vis spectrophotometer in the wavelength range from 200 nm to 800 nm. The UV-Visible spectra of NSH and KMNSH crystals are shown in Figures 3(a) and 3(b), respectively. In general majority of the crystals show continual optical transmission from UV to near IR wavelength range.

Only very few crystals show discontinuity. For both NSH and KMNSH crystal transmission efficiency is observed in a small narrow range. The discontinuous spectral characteristics can be due to the absorption of hydrated transition metal ions $\text{Ni}(\text{H}_2\text{O})_6$. The absorption spectra of NSH and KMNSH show lower cutoff wavelength around 228 nm and 226 nm, respectively. Similar result has been reported for thiourea potassium magnesium sulphate crystal [14] also. Using the formula $E_g = hc/\lambda$, optical band gap energy values were found as 3.405 eV and 3.435 eV for NSH and KMNSH crystals, respectively.

3.3. FTIR Spectroscopy. The FTIR spectroscopy studies are used to analyze qualitatively the presence of functional groups in the synthesized crystal. The spectrum was recorded in the wavelength range $400\text{--}4000\text{ cm}^{-1}$. The stretching vibration of the water molecule is observed for KMNSH at 3162 cm^{-1} . The medium broadband noticed around 1581 cm^{-1} is assigned to the vibrational mode of water molecules. The band observed at 763 cm^{-1} is assigned to librational mode of water molecules. In general free SO_4^{2-} ion has 4 fundamental vibrations, namely, a nondegenerate mode at 987 cm^{-1} and a doubly degenerated mode and a triply degenerated vibration at 1149 cm^{-1} and 632 cm^{-1} , respectively, [15]. FTIR studies also confirm the presence of water molecule and sulphate. The FTIR Spectrum of NSH and KMNSH is shown in Figures 4(a) and 4(b), respectively. The observed frequencies and their assignments are listed in Table 2.

3.4. TGA/DTA. The decomposition, phase transition, melting point, and weight loss of the grown crystal were determined by thermogravimetric analysis (TGA). The thermogram of NSH and KMNSH was recorded between 50°C and 400°C , using Perkin Elmer TGA/DTA instrument at a heating rate of $10^\circ\text{C}/\text{min}$ in the nitrogen atmosphere. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the crystal were carried out to understand the thermal stability of the crystal because it is an important factor for crystals that are to be used as Ultraviolet light filter. The thermogram of the NSH and KMNSH indicates a major weight loss at temperatures 76°C and 94°C as shown in Figures 5(a) and 5(b), respectively. It may be due to the expulsion

FIGURE 2: (a) Powder X-diffraction of NSH crystal and (b) powder X-diffraction of KMNSH crystal.

FIGURE 3: (a) UV transmittance spectrum for NSH crystal and (b) UV transmittance spectrum for KMNSH crystal.

FIGURE 4: (a) FTIR spectrum for NSH crystal and (b) FTIR spectrum for KMNSH crystal.

FIGURE 5: (a) TGA/DTA analysis of NSH crystal and (b) TGA/DTA analysis of KMNSH crystal.

TABLE 2: Assignment of vibrational frequencies in the FTIR spectra of NSH and KMNSH crystal.

NSH crystal	KMNSH crystal	Assignment
	3162	OH stretching, water trace
2245	2229	Ni-S stretching
1627		O-H symmetric stretching
	1581	H ₂ O stretching
1149	1141	SO ₄ asymmetric stretching
	1087	SO ₄ deformation
987	979	O-H bends
763	763	O-H op bending
632	632	Deformation of asymmetric SO ₄
462	462	Deformation of strong SO ₄

of physically adsorbed water molecules. The grown potassium magnesium nickel sulphate hexahydrate crystals have higher

thermal stability up to 94°C and hence are used in missile approach warning systems and as sensors in spaceships. The dehydration temperature of the potassium magnesium nickel sulphate hexahydrate (KMNSH) is more than pure nickel sulphate hexahydrate by 18°C. Youping He et al. [16] have also observed dehydration temperature of potassium nickel sulphate hexahydrate (KNSH) crystal to be higher than that of nickel sulphate hexahydrate (NSH) by 24°C. DTA curves of both pure NSH and KMNSH crystal show an endothermic dip at 107°C and 136°C, respectively. This endothermic dip represents the decomposition of crystals.

4. Conclusion

Good quality single crystals of NSH and KMNSH have been grown by slow evaporation solution growth technique. The crystalline nature of the grown crystals was verified by powder X-ray diffraction analysis. The crystal system of NSH

and KMNSH is tetragonal and monoclinic, respectively. The FTIR analysis confirmed the presence of water molecules and sulphate. The UV-Visible absorption spectra of the NSH and KMNSH crystals show lower cutoff wavelength around 226 nm and 228 nm, respectively. Thermogravimetric analysis reveals that both grown crystals remain thermally stable up to 76°C and 94°C, respectively. From TGA studies, it is confirmed that there are six water molecules of crystallization. Hence, the grown KMNSH crystal is a potential material for Ultraviolet light filter.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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