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Synthesis, thermal, XRD and spectroscopic studies characterization of Tutton salt $K_2M(SO_4)_2 \cdot 6H_2O$ (M = Mg, Ni)

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ABSTRACT

Tutton's salts $K_2M(SO_4)_2 \cdot 6H_2O$ (M = Mg, Ni) have been synthesized by the slow evaporation method at room temperature. A complete structural characterization has been carried out by means of powder X-ray diffraction (XRD). The results indicate that the structure of these salts is monoclinic system with the space group $P2_1/a$ (Z = 2). IR and Raman spectra of KMS6 (M = Mg,Ni) have been recorded and analyzed. From the spectra, the vibrations due to SO_4^{2-} ion, the complex $[M(H_2O)_6]^{2+}$ and the water molecules have been identified. Thermogravimetry, differential thermal analysis and XRD at high-temperature investigations show that the dehydration of these salts occurs between 300 and 500 K. This indicates the removal of all water molecules around 426 K.

1. Introduction

Recently our scientific interest and efforts have been concentrated on Tutton salts, scince these compounds can be considered as potential proton conductors due to the existence of comparatively strong hydrogen bands determined by the strong proton acceptor capabilities of the sulfate.

Tutton salts represent a large family of isomorphous crystals [1] with the general formula.

$M_2M'(SO_4)_2 \cdot 6H_2O$ where M represents a univalent cation (K^+, NH_4^+, Rb^+, Cs^+,Na^+, or Tl^+) and M′ is a bivalent cation (Ni^{2+}, Co^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}). Doping of divalent metal impurities on Tutton's salts has been studied for many years [2,3]. These salts are of historic importance because they are obtainable in high purity and served as reliable reagents and spectroscopic standards. The unit cell dimensions and molecular structures of the crystals of this family are very similar and they crystallize in the monoclinic system with space group $P2_1/a$ [4]. The applications of these compounds in pure salts and doped with transition metals have a very high added value. Detailed studies on vibrational patterns of NH_4^+ and SO_4^{2-} ions in Tutton's salts have been carried out [5–9]. Crystal growth, structural, thermal, and dielectric characterization of Tutton salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ crystals have been reported [10]. EPR of VO(II)-doped magnesium potassium Tutton's salt has been study [11].

In the present work, we are reporting the synthesis and structure of $K_2M(SO_4)_2 \cdot 6H_2O$ (M = Mg, Ni), characterized by FT-IR, Raman spectra, XRD, SEM, EDS, and thermal studies of $K_2Ni(SO_4)_2 \cdot 6H_2O$ to clarify their decomposition process.

2. Experimental

2.1. Synthesis of $K_2M(SO_4)_2 \cdot 6H_2O$ (M = Mg, Ni)

$K_2M(SO_4)_2 \cdot 6H_2O$ (M = Mg, Ni) potassium double sulfate crystals were synthesized by the slow evaporation method from double deionized aqueous solutions of K_2SO_4 (CHEMIPHARMA, 99%) and $MSO_4 \cdot xH_2O$ (NENTECH, 99%), taken in an equimolar ratio 1:1. The solution is magnetically stirred and heated on a plate at 333 K for 5 min to ease the reaction and obtaining of a homogenous and transparent liquid. This solution is evaporated at room temperature. $K_2M(SO_4)_2 \cdot 6H_2O$crystals were collected from the 7th to the 15th evaporation day by filtering. The grown crystals of $K_2M(SO_4)_2 \cdot 6H_2O$ salts have a prismatic morphology, a good crystallinity and their color is depending to the bivalent metal M, green

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color for those containing Ni and colorless for those with Mg (Fig. 1). Hereafter these crystals are going to be labeled as KMS6 (M = Mg, Ni).

2.2. Characterization techniques

For the X-ray diffraction and the spectral measurements the crystals were crushed with an agate mortar and the resulting powder was filtered by means of a 60 μm sieve in order to ensure a homogeneous size distribution. The powder X-ray diffraction at room temperature was carried out using a PANalyticalX'Pert PRO diffractometer with CuKα1 radiation(1.5406 Å) in the angular range $10° < 2\theta < 70°$, with a step size of 0.02° and a counting time of 5 s per step.

The Raman analyses were achieved in MacroMode by Horiba-JY Induram with a Raman head BWTEC BAC100 excited under at 532 nm with an exposition of 3 s and 30 accumulations.

The Fourier transform infrared spectrum was recorded using a Nicolet IR 200 FT-IR spectrometer in the 4000–400 cm^{-1} range.

The surface morphologies were observed on a JEOL JSM 6300 LV SEM with the resolution of 3.0 nm, an accelerating voltage 20 kV and maximum magnification 5000X–20.000X. Energy-dispersive spectroscopy (EDS) is a chemical microanalysis technique performed in conjunction with a scanning electron microscope (SEM). This method can detect elements from Na upward in the Periodic Table.

Both thermogravimetric and differential thermal analyses (TG/DTA) of powder samples were performed with a Perkin-Elmer Pyris Diamond instrument under dynamic regime and N_2 atmosphere, in a heating cycle from 298 to 1073 K at a rate of 10 K min^{-1}.

3. Results and discussion

3.1. Structural and morphological characterization

3.1.1. X-ray diffraction

The powder XRD patterns of the prepared salts KMS6 (M = Mg, Ni) are shown in Fig. 2. They are in a good agreement with the ICDD No. 99-100-9596 reference pattern and clearly confirm the purity of the synthesized phases. The XRD pattern did not indicate presence of the constituents K_2SO_4 (ICDD No.99-202-7338), $MgSO_4{\cdot}7H_2O$ (ICCD No. 99-200-4271) or $NiSO_4{\cdot}6H_2O$ (ICCD No.01-081-1048). From this fact, XRD patterns have been fitted with a monoclinic unit cell and space group $P2_1/a$ [4].

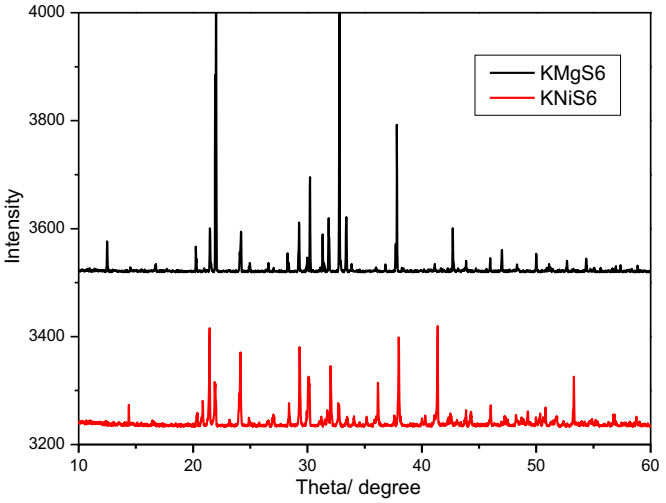

Fig. 2. XRD patterns of Tutton's salt KMS6 (M = Mg, Ni).

3.1.2. Raman and infrared structural analysis

The Raman spectrum of KMS6 (M = Mg, Ni) is shown in Fig. 3 and its analyses should be done considering the internal modes

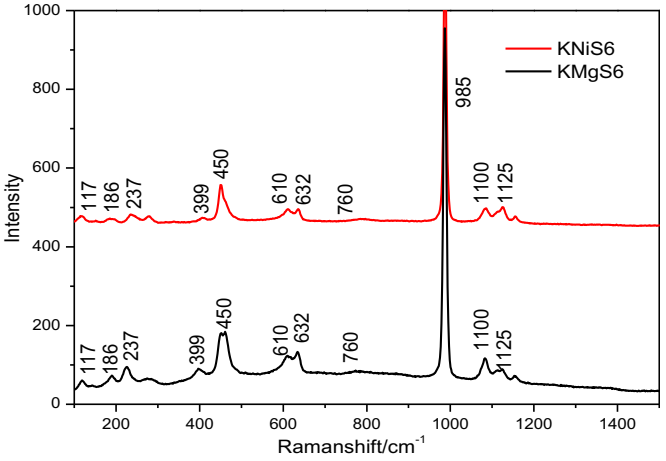

Fig. 3. Raman spectrum of KMS6 (M = Mg, Ni).

(a) **(b)**

Fig. 1. Photographs of KMgS6 (a) and KNiS6(b) crystals.