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Synthesis, characterization and thermal analysis of $K_2M(SO_4)_2.6H_2O$ (M= Mg, Co, Cu)

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ABSTRACT

Synthesis, characterization and thermal behavior for Tutton's salts $K_2M(SO_4)_2.6H_2O$ (M = Mg, Co, Cu) are reported. These double salts crystallize in the monoclinic system, with the space group $P2_1/a$ (Z = 2). The unit-cell parameters were affined with "affma" software. The IR spectrums reveal also the characteristic vibrational of water and sulfates. Thermogravimetry (TGA), differential thermal analysis (DTA) and XRD at high temperature investigations show that the dehydration of these salts occurs between 70 and 200°C. This indicates the removal of all water molecules around 200°C. Schemes of their decomposition are proposed. While $K_2M(SO_4)_2.6H_2O$ (M = Mg, Co, Cu) salts are isostructural, they do not exhibit the same decomposition steps.

Keywords: Tutton's salts crystals growth, FTIR spectroscopy, Thermal analysis, XRD at Height Temperature, phase transition.

INTRODUCTION

Tutton's salts are an isomorphous series of monoclinic crystals P_{2_1}/a with the general formula $M_2^{\ I} M^{II}(SO_4)_2.6H_2O$ and containing two octahedral hexahydrate complexes $[M^{II}(H_2O)_6]^{2+}$ in the crystal unit cell, where M^{II} is a divalent cation and M^1 is a monovalent cation [1]. Doping of divalent metal impurities on Tutton's salts has been studied for many years [2, 3]. Tutton salts have played a significant role in physics and chemistry; considerable attention is currently focused on the development of materials suitable for strong energy absorbed by solar collectors.

The unit cell dimensions and molecular structures of the crystals of this family are very similar, they crystallize in the monoclinic system with space group $P2_1/a$. The unit cell contains two M^{II} each surrounded by six water molecules forming an octahedron. The divalent atoms in the unit cell are located at (0, 0, 0) and (1/2, 1/2, 0), while all other atoms are in general positions.

The interesting properties of Tutton salts have been studied with many methods in recent years. However, the thermodynamic properties and the complete decomposition scheme of KMS6 crystals have not previously been reported.

In this paper we report the study of the thermal behavior of KMS6 (M = Mg, Cu, Co) to clarify their decomposition process.

MATERIALS AND METHODS

The powders X-ray diffraction (XRD) analysis has been carried out using a BRUKER D8-advance diffractometer with CuK_{α} radiation ($\lambda = 1.5406$ Å). X-ray diffraction data have been collected over of 10–70° 2θ range, with a 0.02° step size, the dectector is a LynxEye type and a counting time of 12 *s*. Crystalline phases detected in XRD patterns have been identified using the International Centre for Diffraction Data (ICDD) powder diffraction files. Cell parameters have been refined with the "Affma" program.

The thermogravimetry and differential thermal analysis were recorded in a $STAR^e$ system : METTLER TOLEDO instrument in nitrogen atmosphere at a heating and couling rates of 5°Cmin⁻¹ in the temperature range from 25 to 610°C and flux : 100mL min⁻¹: 70 µL. A1₂O₃ was used as reference sample.

The Fourier transform infrared spectrum was recorded using a Nicolet IR 200 FTIR 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 300, 000 times. 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.

 $K_2M(SO_4)_2.6H_2O$ (M = Mg, Cu, Co) (noted KMS6) single crystals were grown by using the slow evaporation method from an aqueous solution containing stoichiometric amounts of K_2SO_4 and $MSO_4.xH_2O$ (1:1). Transparent crystals appeared after about ten days under the experimental conditions. The resulting crystals are recovered from the solution by filtration and washing with an organic solvent (acetone) and then drying in air.

RESULTS AND DISCUSSION

Crystal morphology

The grown crystals of KMS6 salts have a prismatic morphology, a good crystallinity and their color is depending to the bivalent metal M (Figure 1).

The crystal sizes for the prepared samples were approximately $1 \times 1 \times 0.5 \text{ cm}^3$. They have well defined external faces.



Fig.1 Photographs of KMS6 crystals (M = Mg, Co, Cu).

SEM and EDS studies

The dispersion at the surface and morphology on the micrometer scale of the crystalline seeds constituents of each double hexahydrated salt are represented in Figure 2. The Table 1 presents chemical analysis of the KMS6 salts determined from EDS spectra.



Fig.2 SEM image of KMS6 double salts (M = Mg, Co, Cu)

Salt	Element	Weight %	Atomic %
	K	38.87	24.36
	S	19.53	15.73
KMgS6	0	32.46	47.88
	Mg	9.14	12.03
	Totals	100.00	100.00
	K	23.20	15.78
	S	17.90	14.84
KCoS6	0	35.74	59.40
	Co	23.16	9.98
	Totals	100.00	100.00
	K	23.77	18.54
	S	18.70	17.78
KCuS6	0	25.29	48.21
	Cu	32.23	15.47
	Totals	100.00	100.00

Table 1 EDS data of KMS6 crystals

X-ray diffraction

The powder XRD patterns of the prepared salts KMS6 (M = Mg, Co, Cu) are shown in Figure 4. They are in a good agreement with those of the ICDD data base and clearly confirm the purity of the synthesized phases [4]. From this fact, XRD patterns have been fitted with a monoclinic unit cell and space group $P2_1/a$ (Table 2) using the "Affma" sofware.



Fig.3 XRD patterns of double salts KMgS (a), KCoS6 (b) and KCuS6 (c)

Table 2 Lattice Parameters of KMS6 crystals

Parametres	KMgS6	<u>KMgS6[*]</u>	KCoS6	KCoS6*	KCuS6	KCuS6*
a (Å)	9.056	9.095	9.053	9.060	9.057	9.044
b (Å)	12.195	12.248	12.209	12,215	12,099	12.221
c (Å)	6.094	6.133	6.155	6,158	6.143	6.159
β (°)	104.815	104.880	104.800	105,047	104.549	104.775
V (Å ³)	650.77	660.38	657.89	650,56	651.64	658.33



Fig.4 FTIR spectrum of Tutton's salt KMS6 (M= Mg, Co, Cu)

Vibrational Infrared 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 - 4000 cm⁻¹ (Figure 4). The stretching vibrations of the water molecule are expected in 3000-3600 cm⁻¹. The broad vibrational band observed around 3220 cm⁻¹, is attributed to symmetric stretching mode of water molecule [5]. The medium broadband noticed around 1560 cm⁻¹ is assigned to the vibrational mode of water molecules. The band observed at 763.8 cm⁻¹ is assigned to liberational mode of water molecules. In general free SO₄²⁻ ion has Td symmetry and has four fundamental vibrations namely a non degenerate mode (v_1) at 984.6cm⁻¹, and a doubly degenerated mode (v_2) and a triply degenerated vibrations (v_3 and v_4) at 1142 cm⁻¹ and 631.8 cm⁻¹ respectively [6]. The peak observed at 1142 cm⁻¹ is attributed to triply

degenerate symmetric stretching mode (v_3) of $SO_4^{2^2}$. The band observed at 459 cm⁻¹ is assigned to the doubly degenerate $(v_2) SO_4^{2^2}$ mode. The peak appeared at 984.6 cm⁻¹ is reasonably assigned to the $(v_I) SO_4^{2^2}$ non degenerate mode. The mode at 631.6 cm⁻¹ is assigned to the triply degenerate vibrations $(v_4) SO_4^{2^2}$. The above assignment agrees with the one reported by G. Ramasamy [7] and D. Marinova [8]. Table 3 shows the different bands observed and their frequencies allocated.

FT-IR v/cm ⁻¹	Assignments
3220 s br	O-H sym str., H ₂ O Trace
1560	v H ₂ O
1437m	O-H i.p bending
1142 vs.	$v_{\rm as}({\rm SO}_4)$
984 s	$v_{\rm s}({\rm SO}_4)$
763	O-H o.p bending
632 s	$\delta_{\rm as}({ m SO}_4)$
459	$\delta_{\rm s}({ m SO}_4)$

 Table 3 FTIR Peak Assignments

 v_s =very strong; s=strong; δ =deformation or in plane bending; v=stretching; s=symmetric; as=asymmetric

Thermal behavior of KMS6 (M = Mg, Co, Cu)

The TG and DTA thermograms of KMS6 salts (M = Mg, Co, Cu) from room temperature to 700°C are given in figures 5-6. In the TG curves, the weight loss can be divided into five, three and two areas respectively for KMgS6, KCoS6 and KCuS6 salts. The total weight loss in 50-200°C temperature range is in agreement with the calculated value corresponding to the loss of six water moles for each salt. Every one of weight loss is accompanied by an endotherm peaking in the DTA curve. The dehydration of KMS6 salts (M=Mg, Co, Cu) and the number of molecules of water losses in each step are given in Table 4.



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Table 4 Dehydration of double salts KMS6 (M=Mg,Co,Cu)

Double salt	Température (°C)	Total loss of the water molecules	Product formulas
KMgS6	70	1.14	$K_2Mg(SO_4)_2.5H_2O(s)$
	128	3.29	K ₂ Mg(SO ₄) ₂ .1.5H ₂ O(s)
	145	0.37	$K_2Mg(SO_4)_2$. $H_2O(s)$
	180	1.07	$K_2Mg(SO_4)_2(s)$
KCoS6	101	2.80	K ₂ Co(SO ₄) ₂ .3 H ₂ O(s)
	116	1.11	K ₂ Co(SO ₄) ₂ .2H ₂ O(s)
	198	2.09	$K_2Co(SO_4)_2(s)$
KCuS6	81	3.94	$K_2Cu(SO_4)_2.2H_2O(s)$
	153	2.06	$K_2Cu(SO_4)_2(s)$



Fig.6 TG-DTA curves of KCoS6



Fig.7 TG-DTA curves of KCuS6

After 200°C, The DTA curves of KMS6 compounds presented different other endotherm and exotherm peaking nonaccompanied by weight loss. In order to identify the degradation products of these salts, a heat treatment was followed by X-ray diffraction at high temperature.

XRD at Height Temperature

The evolution of X-ray diffraction patterns at high temperature was followed in heating and cooling. Therefore we choose to record the diffraction patterns at the following temperature: ambient, 230, 330, 430 and 600°C (Figures 8.a-b, 9.a-b and 10.a-b). The selected temperatures are slightly higher than onset of peaks observed on the DTA curves of KMS6 compounds.

Result of KMgS6

X-ray powder diffraction patterns of KMgS6 product after heating at 40, 220, 320, 430 and 600°C (Figure 9.a-b) show the formation of a crystalline compound. After heating at 220°C, the X-ray pattern shows the formation of the anhydrous salt $K_2Mg(SO_4)_2$ (KMgS). The X-ray patterns of the product after 320 and 430°C, show the formation of $K_2Mg_2(SO_4)_3$ (K2MgS) and β -K₂SO₄ (β -KS). The Langbeinite (K2MgS) is present with (α -KS) in the X-ray

patterns of the product heated at 600°C. All the X-ray pattern recorded in cooling are identical and correspond to a mixture of β -KS and langbeinite.



Fig. 8 XRD patterns at height temperature of KMgS6 ; (a) : Heating , (b) Cooling

Taking into account these results, the scheme of KMgS6 decomposition can be represented by the following steps:

$K_2Mg(SO_4)_2.6H_2O$	$\longrightarrow K_2Mg(SO_4)_2.5H_2O + H_2O$	25-70°C
$K_2Mg(SO_4)_2.5H_2O$	$> K_2Mg(SO_4)_2.1.5H_2O + 3.5H_2O$	70-128°C
$K_2Mg(SO_4)_2.1.5H_2O$	$\longrightarrow K_2Mg(SO_4)_2.H_2O + 0.5H_2O$	128-145°C
$K_2Mg(SO_4)_2.H_2O$	\longrightarrow K ₂ Mg(SO ₄) ₂ + H ₂ O	145-180°C
$2K_2Mg(SO_4)_2$	$ \longrightarrow K_2 Mg_2(SO_4)_3 + \beta - K_2 SO_4 $	302°C
\Box -K ₂ SO ₄	\longrightarrow α -K ₂ SO ₄	577°C

Results of KCoS6

After calcinations at 230°C the heated product shows an DRX spectrum similar to anhydrous salt $K_2Co(SO_4)_2$. The X-ray patterns of the product after 320 and 430°C, show the formation of $K_2Co_2(SO_4)_3$ (K2CoS) and β -K₂SO₄ (β -KS). At 430°C it shows a better crystallinity than at 320°C. Poorly crystallized phase is formed when the product is heated at 580°C. It may be attributed to K2CoS salt. In the cooling, we observed again the crystallization of β -KS and K2CoS salt.

So the decomposition of KCoS6 can be represented by the following steps:

$K_2Co(SO_4)_2.6H_2O$	$\longrightarrow K_2Co(SO_4)_2.3H_2O + 3$	H_2O	$25-101^{\circ}C$
$K_2Co(SO_4)_2.3H_2O$	$\longrightarrow K_2Co(SO_4)_2.2H_2O + 1$	H ₂ O	101 – 116°C
K ₂ Co(SO ₄) ₂ .2H ₂ O	$\longrightarrow K_2 Co(SO_4)_2 + 2H_2O$		116 – 198°C
$2K_2Co(SO_4)_2$	\longrightarrow (K2CoS + β -KS)	amorphous	280°C
(K2CoS + β -KS) amorphous	\longrightarrow (K2CoS + β -KS)	crystallized	380°C
β -K ₂ SO ₄	$\longrightarrow \alpha - K_2 SO_4$		567°C



Results of KCuS6

Dehydration steps of this salt are different from those of its isomorphic salts KMgS6 and KCoS6.

Results obtained through X ray diffraction at high temperature are shown in this following decomposition scheme:

$K_2Cu(SO_4)_2.6H_2O$	$\longrightarrow K_2Cu(SO_4)_2.2H_2O + 4H_2O$	25-81°C
$K_2Cu(SO_4)_2.2H_2O$	$\longrightarrow K_2Cu(SO_4)_2 + 2H_2O$	81-153 ° C
$2K_2Cu(SO_4)_2$	\longrightarrow Unidentified phase + β -KS	300°C
β -K ₂ SO ₄	\longrightarrow α -K ₂ SO ₄	528°C



Fig. 10 XRD patterns at height temperature of KCuS6 ; (a) : Heating , (b) Cooling

CONCLUSION

Tutton's salts KMS6 (M = Mg, Co and Cu) were grown by slow evaporation solution growth technique using an equimolar aqueous solution of K_2SO_4 and $MSO_4.xH_2O$ and characterized by different technical FT-IR, SEM, EDS, XRD powder.

The decomposition of these salts was followed by the thermal analysis DTA / TGA and XRD high temperature and shows that these compounds are dehydrated before 200°C. After dehydration, they transformed into a mixture of Langbeinte (K2MS)-and β -K₂SO₄ (M = Mg, Co and Cu). The transition phase of K₂SO₄ is observed around 560°C.

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