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SYNTHESIS AND CHARACTERIZATION OF A NEW SULFATE $K_4H_2(SO_4)_3$

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The formation of a new sulfate compound $K_4H_2(SO_4)_3$ is obtained by evaporation at 25°C of an aqueous solution, which was formed by a mixture of K_2SO_4 and H_2SO_4. The characterization of this solid is carried out by X-ray diffraction, thermal and infrared analyzes. The heat treatment was carried out in interval 25–700°C; the end product of the thermal evolution is K_2SO_4. The vibration bands relating to SO_4 and OH groups were highlighted by the infrared spectroscopy. Moreover, one study of ionic conductivity on this solid compound was carried out according to the temperature in interval 25–80°C. Its activation energy is 0.47 eV. The X-ray intensities collection obtained on a monocrystal of $K_4H_2(SO_4)_3$ gives the following cell parameters: a=7.035(5), b=19.751(4), c=23.466(2) Å, β=95.25(1)°.

Keywords: *ionic conductivity, potassium, sulfate*

Introduction

The physical properties and the phase transitions from sulfated compounds of type $A_xB_y(SO_4)_z$ (*A* and *B* represent Li, Na, K, NH_4 and H) aroused the interest of several researchers. Thus, one finds in the bibliography of the studies on electric conductivity [1–5], thermoluminescence [6–8], the Raman diffusion spectroscopy [9–11] and IR [11–13], AFM [14], just as the properties dielectric, pyroelectric and piezoelectric [5, 15–17]. Thermal studies on sulfates of various cations, primarily mono- and bivalent were largely studied (Ni, Co, ...) [10, 18–24]. However, we did not raise any work of investigation on the compound $K_4H_2(SO_4)_3$.

This work concerns the synthesis and the characterization of the new potassium hydrogenosulfate $K_4H_2(SO_4)_3$; this compound is obtained by evaporation, with 25°C, starting from a mixture of K_2SO_4 and H_2SO_4. The characterization of this solid is carried out chemically, by X-ray diffraction, thermal analyzes (DTA and TG) and IR spectroscopy.

With an aim of a possible use of this material in the energy field (battery), a study of ionic conductivity was also carried out at various temperatures.

Experimental

By applying the ternary diagram H_2SO_4–K_2SO_4–H_2O [25] with Janaké co-ordinates (Fig. 1), the new sulfated compound is synthesized. Indeed, the evaporation of the mixture P, of co-ordinates Z_{H_2O}=550, Y_K=37.92% and Y_H=62.08%, in a controlled thermostated bath at 25°C (±0.1°C) gives the title product. The drying of this last was carried out at the ambient temperature.

The atomic absorption spectrometry (AAS Vario-6), the gravimetric method and acido-basic titration by pH-metry were used for the determination of the chemical formula of the compound. Moreover, X-rays diffraction (X'PERTPANalytical, $CuK_{\alpha_1\alpha_2}$ = 1.54060, 1.54443 Å) IR spectrometry (Nicolet Magna IR560), thermogravimetric analysis and differential thermal analyzis coupled (TG-ATD92, Setaram) were used to characterize this compound.

In addition, a study of electric conductivity was carried out. Indeed, the sample being presented in pellet form is obtained starting from the crushed solid, compressed under a pressure of 7–8 t cm^{-2} using a manual hydraulic press then sintered under air. The

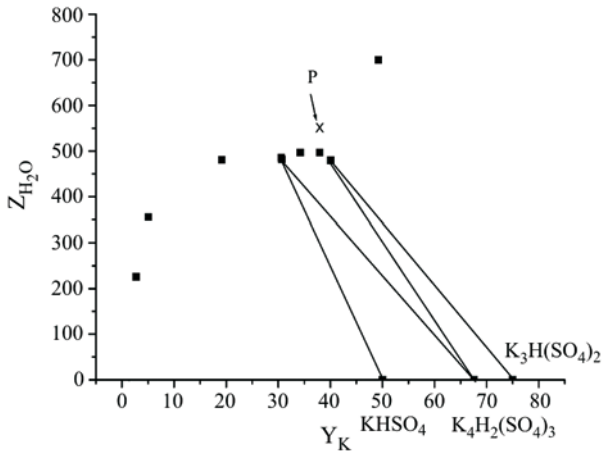

Fig. 1 Part of the (K_2SO_4–H_2SO_4–H_2O) diagram in Janaké co-ordinates at 25°C

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platinum electrodes are fixed on the faces of the pellet by a layer of silver lacquer. The measurement technique used is the spectroscopy of impedance. For all measurements, the impedance measures (HP 4192A) was used in a frequency band ranging between 10 and 500 KHz. Measurements of electric conductivity were taken under air. The temperature of the furnace is fixed and ordered by a regulation system.

Results

Chemical analysis

The chemical analyses of the elements constituting the solid are summarized in Table 1. Except for the experimental errors, the molar ratio $r=n_i/n_H$ (i is K or SO_4) makes it possible to deduce that the chemical formula of the compound is $K_4H_2(SO_4)_3$.

Table 1 Chemical analysis

Ion	K^+	H^+	SO_4^{2-}
n/mmol	4.63	2.29	3.34
Mass/%	35.94	0.45	63.75
r	2.02	1.00	1.46

X-ray diffraction

The interplanar (*h k l*) distances and the ratio I/I_0 are summarized in Table 2. X-ray pattern of $K_4H_2(SO_4)_3$ is represented on Fig. 2.

In addition, a collection of X-ray intensities (Enraf-Nonius, Mach 3 goniometer) carried out on a $K_4H_2(SO_4)_3$ monocrystal made it possible to deduce that it crystallizes in the monoclinic system. The cell parameters are: a=7.035(5), b=19.751(4), c=23.466(2) Å, β=95.25(1)°. The determination of the crystalline structure is in hand.

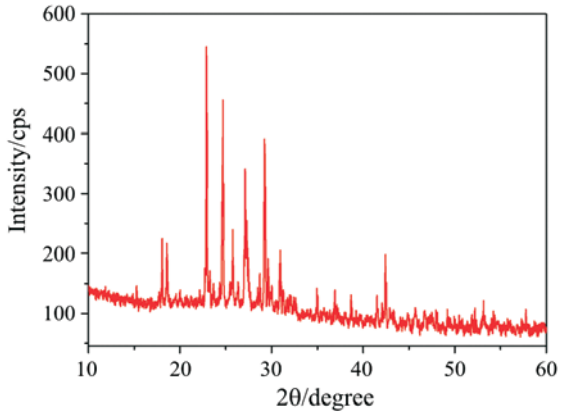

Fig. 2 X-ray pattern of $K_4H_2(SO_4)_3$ at 25°C

Table 2 Examination of X-ray diffractogram of $K_4H_2(SO_4)_3$

d(*hkl*)	I/I_0
5.803	3
4.909	13
4.782	12
4.434	2
3.885	100
3.823	6
3.607	41
3.455	9
3.381	3
3.288	36
3.245	8
3.109	5
3.055	49
3.015	8
2.895	8
2.860	3
2.787	2
2.752	1
2.564	2
2.434	4
2.327	3
2.175	3
2.128	12
2.107	1
2.017	1
1.985	2
1.945	1
1.762	1
1.751	2
1.722	1
1.594	2
1.389	2
1.377	1
1.258	2

Infrared spectroscopy

The FTIR absorption spectrum of $K_4H_2(SO_4)_3$ is represented on Fig. 3. The frequencies vibration bands ranging between 550 and 1250 cm^{-1} correspond to SO_4 groups. It is as to announce as the frequencies located in the vicinities of 1640 and 3500 cm^{-1} are characteristic of the deformation vibrations H–O–H and valence O–H.

Thermal analysis

The thermal analysis curves obtained with a heating rate of 10°C min^{-1}, are schematized for $K_4H_2(SO_4)_3$ on Fig. 4. We note endothermic peaks located at temperatures 165, 204, 226, 251 and 577°C. An exothermic peak is announced at 564°C during the cooling of the sample. Two losses of mass (A→B, B→C) are noted on curve TG with respective percentages 17.86 and 8.91. The residue obtained after the first 4 endothermic peaks presents a pasty aspect and does not lend itself to the analyses by X-ray diffraction and IR study. The final residue is K_2SO_4 (Fig. 5). We can then deduce that the peaks endo and exo located respectively at 577 and 564°C correspond to the reversible transition α-$K_2SO_4 \leftrightarrow \beta$-$K_2SO_4$ and that the total thermal transformation can be schematized by the following equation:

$$K_4H_2(SO_4)_3 \rightarrow 2K_2SO_4(sd)+SO_3(g)+H_2O(g)$$

This decomposition diagram is confirmed by the value of the total percentage of loss of mass between the points A and C which is 26.77. The theoretical value being 27.22.

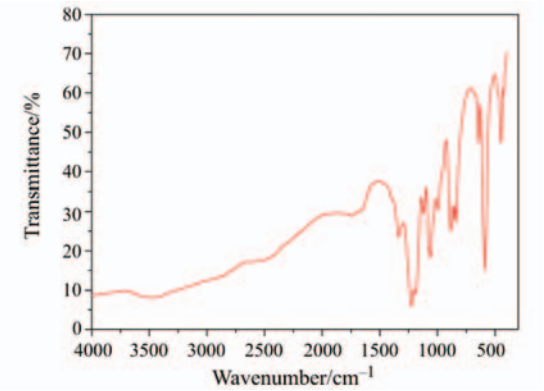

Fig. 3 FTIR spectrum of $K_4H_2(SO_4)_3$

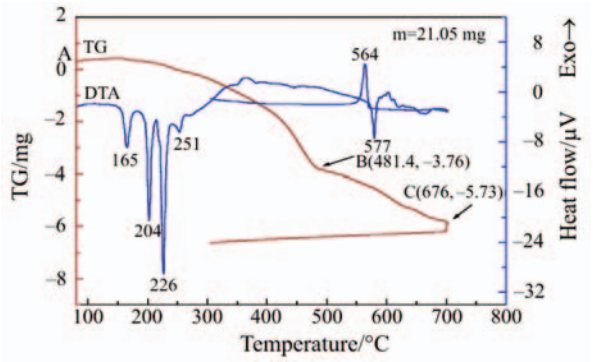

Fig. 4 DTA and TG curves of $K_4H_2(SO_4)_3$

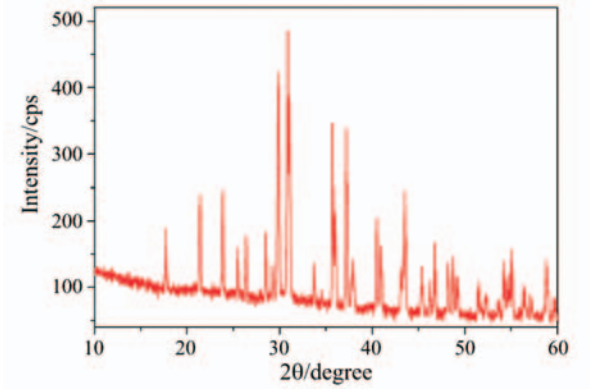

Fig. 5 X-ray pattern of $K_4H_2(SO_4)_3$ heated at 600°C

Ionic conductivity

Measurements of electric conductivity were given in the temperature range 25–80°C. It should be noted that the impedance diagrams complexes are arcs of circle for any temperature; This type of curve characterize the voluminal properties of the sample. An example of these diagrams is represented on Fig. 6.

The chart (Fig. 7) in Arrhenius co-ordinates of σT (σ being the electric conductivity of material at the absolute temperature T) highlights only one line whose slope is the energy of activation E_a=0.47 eV. This value is low and probably represents the energy of migration without creation of a specific defect [26].

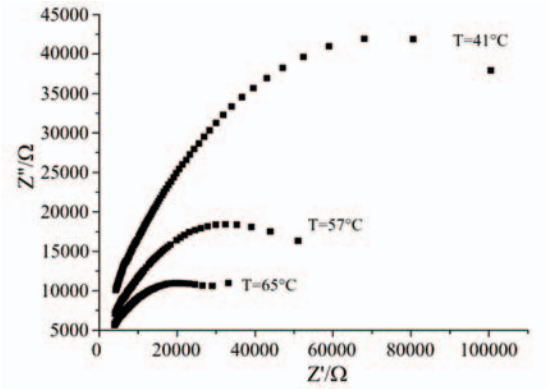

Fig. 6 Impedance diagrams obtained at various temperatures for $K_4H_2(SO_4)_3$

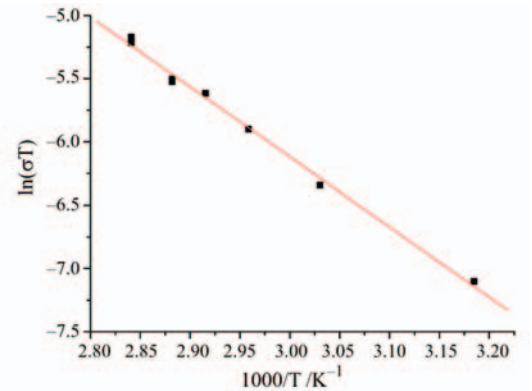

Fig. 7 Variation of σT in Arrhenius co-ordinates for $K_4H_2(SO_4)_3$

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