

Original Article

Crystal Growth, Structure, and Thermal Analysis of $K_2Cu(SO_4)_2 \cdot 6H_2O$ Tutton Salt

A.M. Abdulwahab¹, *M.A. Gaffar², and A. Abu El-Fadi²

¹ Physics Department, Faculty of Applied Science, Thamar University, Dhamar 87246, Yemen.

² Physics Department, Faculty of Science, Assiut University, Assiut 71516, Egypt.

*Corresponding author: at Physics Department, Faculty of Applied Science, Thamar University, Dhamar 87246, Yemen, Tel.: +967770612913, Fax: +9676425058, E-mail: abduhabdulwahab@yahoo.com (A.M. Abdulwahab)

Received: 2 May 2024. Received (in revised form): 29 May 2024. Accepted: 2 June 2024. Published: 26 June 2024.

Abstract

By using aqueous solutions of K_2SO_4 and $CuSO_4 \cdot 5H_2O$ with equal molecular ratios (1:1) light blue single crystals of $K_2Cu(SO_4)_2 \cdot 6H_2O$ (KCUSH) were prepared and grown by the slow evaporation technique of supersaturated aqueous solution at 309 K. X-ray diffraction measurements revealed the monoclinic structure, space group $P2_1/a$ and $Z = 2$ for KCUSH crystal which is the structure of all Tutton salts family. The DTA and TGA measurements revealed that the evolution of the six water molecules of KCUSH takes place in two steps (two after four) at 351 K and 426 K respectively. It was found also that the two exothermic peaks at the end of DTA thermogram (792 K and 822 K) related to the material of the crucible (aluminum) in addition to the existence of Cu in our material KCUSH. By using platinum crucible, the two exothermic peaks disappeared and instead there is an endothermic peak at 796 K which refers to the melting process.

Keywords: Potassium copper sulfate hexahydrate; Tutton salts; Crystal structure; Thermal analysis; Dehydration process

1. Introduction

Potassium copper sulfate hexahydrate, which is abbreviated as KCUSH and has the chemical formula $K_2Cu(SO_4)_2 \cdot 6H_2O$, is one of the complexes in the family called Tutton salts. Tutton salts are aqua complexes having general formula $M^I_2M^{II}(XO_4)_2 \cdot 6(H_2O)$, where M^I is a univalent cation, K^+ , NH_4^+ , Rb^+ , Cs^+ , etc., M^{II} is a divalent cation, Ni^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , Zn^{2+} , Fe^{2+} , etc., and X stands for S, Se or Cr. They are all isostructural and they crystallize in the monoclinic system with the space group $P2_1/a$, and $Z = 2$ [1, 2]. The unit cell dimensions of members of Tutton salts family are in the ratio $a:b:c = 3.4:2$ and the monoclinic angle β lies in the $103\text{--}107^\circ$ range [3].

The hydrogen bonding interaction was found to be the most important parameter that can affect the switching of $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ from Cu-O(7) to Cu-O(8) at low temperatures [4]. Because of their interesting paramagnetic properties, as they can be used as an element for cooling to very low temperatures, Tutton salts have been the subject of numerous studies [5-9].

Augustyniak and Krupski [10] found that hydrostatic pressure changes the volume and packing of the $(ND_4)_2Cu(SO_4)_2 \cdot 6D_2O$ (ACUSD) crystal and at low temperatures, a new phase with a new system of hydrogen bonds is created. Composing the IR of hydrated Tutton salts and dehydrated one, Campbell et al. [11] were able to prove that the dehydration process can be achieved during sample preparation by mulling and pressing, similar to the dehydration process by heating. Doping the ACUSD crystal with Zn to substitute Cu with a concentration of 1.3-3.4% change the structure from low-density dimorph to the high-density dimorph. This change is accompanied by a switch in the direction

of the Jahn-Teller distortion [12]. Cesium copper Tutton salt $Cs_2Cu(SO_4)_2 \cdot 6H_2O$ was investigated in a study by Gómez-Salces et al. [13], where they studied the coordination geometry of copper (II) ions in aqueous solution through absorption intensity. The electronic properties and vibrational spectra of ammonium copper Tutton salt $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ were studied by Ghosh et al. [14].

Potassium copper sulfate hexahydrate $K_2Cu(SO_4)_2 \cdot 6H_2O$ (KCUSH) crystal has been studied widely because of its interesting properties and important applications. The most interesting properties are the structure and thermal analysis, primarily due to the direct relation between these properties and the use of this crystal in important applications such as thermochemical heat storage material. Thermal analysis of KCUSH crystal has been investigated in several studies [15-17]. It was found that KCUSH crystal loses its six water molecules in two steps. Four water molecules are lost in the first step while the remaining two water molecules are lost in the second step [15-17].

Recently, the KCUSH crystal has been studied in many publications [18-21] because of its interesting properties and important applications. The electronic structure of the KCUSH crystal alongside some other Tutton salts was studied by Colaneri and Vitali [18]. Peets et al. [19] grew single crystal of the KCUSH Tutton salt and investigated its structural and magnetic properties. They found that the magnetic response is fully consistent with free Cu^{2+} spins. Neto et al. [20] synthesized and studied novel mixed Tutton salts with the chemical formulas $K_2Mn_{0.03}Ni_{0.97}(SO_4)_2(H_2O)_6$ and $K_2Mn_{0.18}Cu_{0.82}(SO_4)_2(H_2O)_6$. They found that, both samples had the potential for use in thermochemical heat storage devices due to their high energy density. Smith et al. [21] studied the dehydration

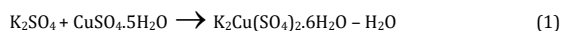
performance of some mixed Tutton salts as thermochemical heat storage materials. One of these Tutton salts is potassium copper sulfate hexahydrate mixed with potassium zinc sulfate hexahydrate. They concluded that, increasing the copper content leads to a nearly linear decrease in the onset dehydration temperature. Souamti *et al.* [15] found that the dehydration process of the KCUSH crystal occurs in two steps. Four water molecules are lost at 354 K and the remaining two water molecules are lost at 426 K. Smith *et al.* [21] reported that the two steps of the dehydration process for the KCUSH crystal are at 353 K and 423 K respectively.

The previous works studied some properties of the KCUSH crystal but without details on the dehydration process and phase transitions of the material. Also, the thermal stability and its importance for using the material in some applications were not studied carefully. Although $K_2Cu(SO_4)_2 \cdot 6H_2O$ (KCUSH) Tutton salt is very important as a thermochemical heat storage material, the studies on this crystal are limited as far as our knowledge. The existence of the six water molecules in the structure of $K_2Cu(SO_4)_2 \cdot 6H_2O$ is the cause of most of the interesting properties of this crystal. The evolution of these water molecules by heat treatment changes the properties of this material. Also, temperature stability is very important for using the material in some applications. In this work, we prepare KCUSH as single crystal, characterize its structure and study its thermal behavior in detail to clarify the dehydration process and other reactions at different temperatures. These studies will show the range of temperatures where the material remains stable and suitable for using in its applications.

2. Experimental Details

2.1. Synthesis and Crystal Growth

The compound $K_2Cu(SO_4)_2 \cdot 6H_2O$ (KCUSH) was synthesized by a complex reaction of K_2SO_4 (99% purity) with $CuSO_4 \cdot 5H_2O$ (99% purity) in an equal molecular ratio (1:1) as shown in the following equation:



It was prepared as an aqueous solution by dissolving the two sulfates in double-distilled water in a suitable beaker.

To evaporate the excess amount of water slowly at a constant room temperature, the beaker was kept in a steady place (the temperature changes very slowly with the weather throughout the day). Therefore, we obtained a supersaturated aqueous solution slowly, and small crystals (seeds) were produced due to spontaneous nucleation after about 5 days. A clear seed with high quality was chosen to be used for growing a single crystal of KCUSH. The slow evaporation of the supersaturated aqueous solution was used in the crystal growth process at a fixed temperature of 309 K. To allow the crystal to grow uniformly from all sides, the seed was suspended in the supersaturated aqueous solution using a nylon thread. The apparatus which used for crystal growth was described in our published paper [22]. After about 45 days, single crystal with a light blue color and dimensions of $2 \times 1.5 \times 1 \text{ cm}^3$ was obtained. Figure 1 displays a photograph of the grown KCUSH single crystal. From the figure, it is clear that the crystal has a regular shape and low transparency.

2.2. Samples Preparation

The samples were used as powder for X-ray diffraction and thermal measurements. A sample was cut from the single crystal and ground thoroughly in an agate mortar and pestle for analysis and testing. Then, a small amount of the obtained fine powder was taken to be used in each measurement.

2.3. Powder X-ray Diffraction Measurements

Powder X-ray diffraction measurements were performed for KCUSH using a Philips (PW1710) diffractometer, which is equipped with a curved graphite crystal monochromator, an automatic divergence slit, a vertical goniometer (PW1050) with an automatic sample changer, and a Xenon proportional detector. The measurements were taken from $2\theta = 4^\circ$ to $2\theta = 80.02^\circ$ with a step size of 0.06° , using a copper target at 40 kV, 30 mA, a scanning speed of $0.06^\circ/\text{min}$ and an incident wavelength $\lambda_{K\alpha_1} = 1.5405 \text{ \AA}$.



Figure 1: Photograph of the grown $K_2Cu(SO_4)_2 \cdot 6H_2O$ single crystal.

2.4. Thermal Measurements

The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were measured for KCUSH by using the differential thermal analyzer (DTA-60, Shemadzu, Japan). Powder sample of mass 5.046 mg was used for these measurements between 295 K and 875 K. Both DTA and TGA were recorded simultaneously at a heating rate of 10 K/min. The atmosphere was the nitrogen gas which was flowing at a rate of 40 ml/min. The reference material was aluminum oxide (Al_2O_3) and the output of DTA was in μV .

3. Results and Discussion

3.1. Crystal Structure

Figure 2 displays the X-ray powder diffraction pattern of $K_2Cu(SO_4)_2 \cdot 6H_2O$ (KCUSH) crystal. The obtained data from the X-ray measurement were processed, and the unit cell dimensions were calculated using the FullProf program and the Rietveld method. Refinement of the X-ray data confirmed that the structure of the KCUSH crystal has a monoclinic system with a space group of $P2_1/a$ and $Z = 2$. This is the structure of all Tutton salts, of which this crystal is a member. It is clear from Figure 2 that the diffraction peak values match very well with the values of the peaks reported for the KCUSH crystal in the ICDD card [PDF No. 70-1570].

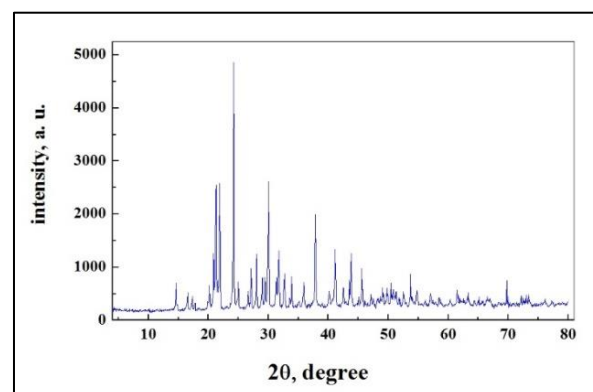


Figure 2: X-ray powder diffraction pattern of $K_2Cu(SO_4)_2 \cdot 6H_2O$ crystal.

The unit cell dimensions of KCUSH obtained in this work are in very good agreement with those in the same card, as shown in Table 1. Additionally, the unit cell dimensions calculated in this work for the KCUSH crystal are in very good agreement with those reported by Colaneri and Vitali [18] and Peets *et al.* [19]. Although there are some

differences in the contents, such as K replaced by ND_4 and H_2O replaced by D_2O , the unit cell dimensions of KCUSH calculated in this work are nearly similar to those of the ACUSD reported by Schultz et al. [12].

Table 1: A comparison between unit cell dimensions in the present study and that in the ICDD card of $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystal.

Parameter	Present work	Card (70-1570)
$a, \text{\AA}$	9.0730 ± 0.0002	9.066
$b, \text{\AA}$	12.1058 ± 0.0002	12.13
$c, \text{\AA}$	6.1560 ± 0.0001	6.149
$\beta, ^\circ$	104.4485 ± 0.0018	104.40
$V, \text{\AA}^3$	654.757 ± 0.023	654.96

3.2. Thermal Analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) thermograms of the KCUSH crystal are shown in Figure 3. In the DTA thermogram, there are two large endothermic peaks. The first peak starts at 325 K and its maximum intensity occurs at 351 K. In the same range of temperatures, a weight loss of approximately 16.5% is detected, as it is clear in TGA thermogram. This weight loss corresponds to the molar weight of four water molecules as a ratio of the total compound molar weight. Therefore, this peak represents the escape of only four water molecules from the lattice.

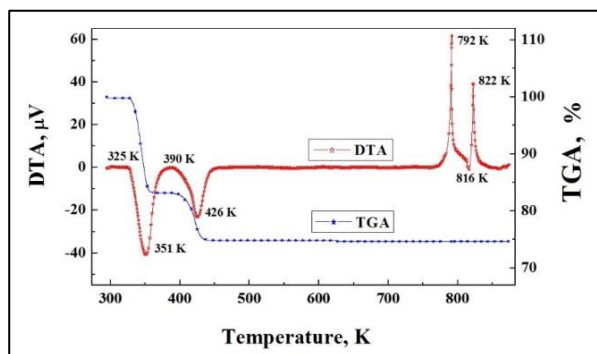
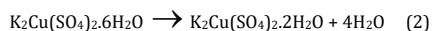
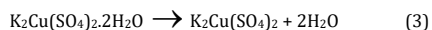


Figure 3: DTA and TGA thermograms of $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystal.

The second peak starts at 390 K and its maximum intensity occurs at 426 K. In the same range of temperatures, a weight loss of approximately 8.5% is detected, as is evident in the TGA thermogram. This weight loss corresponds to the molar weight of two water molecules as a ratio of the total compound molar weight. Therefore, this peak indicates that the remaining two water molecules leave the structure. The evolution of the six water molecules (dehydration process) takes place in two steps (two after four) as follows:



Then:



These results are in very good agreement with previous works [15–17] where it was found that the KCUSH crystal loses its six water molecules in two steps. Four water molecules are lost in the first step, while the remaining two water molecules are lost in the second step. For the two peaks, the maximum intensities occur at the temperatures 351 K and 426 K respectively as shown in Table 2. These two values are in very good agreement with those in the literatures [15, 21]. They were detected at 354 K and 426 K respectively, by Souami et al. [15], while Smith et al. [21] detected them at 353 K and 423 K respectively. The evolution of water molecules (dehydration process), which occurs in two steps, was also detected in other materials such as potash alum [23, 24].

Table 2: The temperatures of starting, maximum dehydration process and the two exothermic reactions in the DTA thermogram of $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystal.

Starting Dehydration, K		Maximum dehydration, K		1 st strong exo. peak, K	2 nd strong exo. peak, K
Step 1	Step 2	Step 1	Step 2		
325	390	351	426	792	822

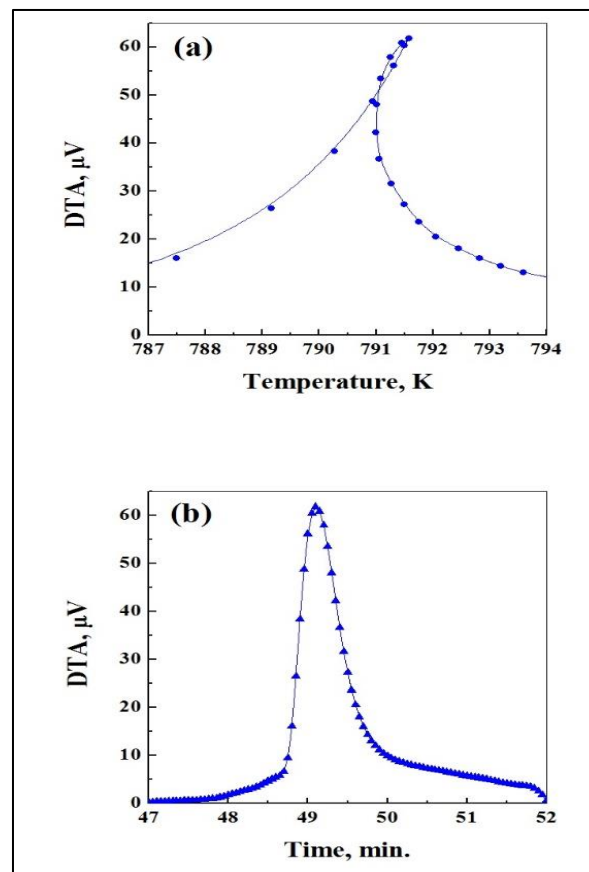


Figure 4: The DTA signal: (a) temperature and (b) time dependence of the exothermic reaction peak at 792 K of the $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystal.

It is clear in Figure 3 that there are two strong exothermic peaks at 792 K and 822 K (DTA thermogram) without loss in weight (TGA thermogram). The amount of heat associated with the reaction at 792 K is so high that it accelerates the sensor temperature, causing a loop to be observed in the DTA signal. We did not find these two exothermic peaks in the literature, so we attempted to explain them by conducting some additional procedures.

Figure 4 shows the DTA of the first of these two peaks, plotted once against temperature and once again against time. The figure indicates a significant amount of heat is released at a rate higher than that of heating during the reaction. The DTA-time curve shows a nearly symmetric peak with a broad area. Similar behavior was not observed for the second peak at 822 K. A sample of KCUSH that was previously heated to 363 K for four hours was subjected to DTA measurement.

Figure 5 confirms the evolution of the four water molecules and the inset shows the TGA thermograms as another confirmation of this observation. A shift of approximately 3 K, a decrease in the DTA signal height, and a disappearance of the thermal loop were also observed for the peak at 792 K. However, the peak at 822 K shows an increase in the peak height and the presence of a thermal loop. It is noteworthy that Figure 6 contains two DTA thermograms for the KCUSH with two different heating rates, namely 5 and 10 K/min. The difference in the peak temperature and the change in the broadening of the peak due to the change in the heating rate confirm that this peak represents a thermally activated process.

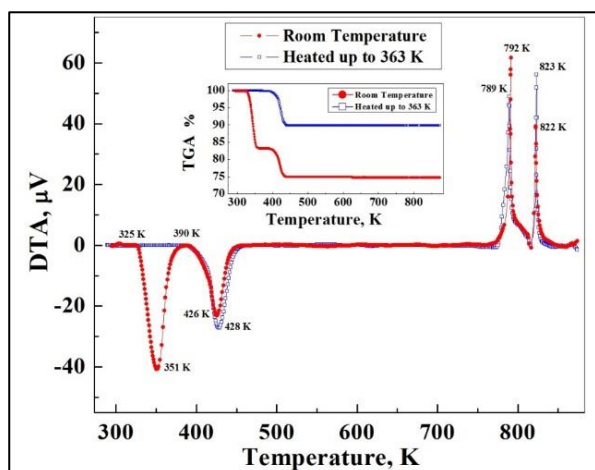


Figure 5: The thermograms of hydrated and partially dehydrated sample of the $K_2Cu(SO_4)_2 \cdot 6H_2O$ crystal.

The last procedure conducted to find out the reason for the existence of the two strong exothermic peaks involved changing the crucible material. The DTA of KCUSH was repeated using a platinum crucible instead of aluminum crucible used in the previous measurements. The resultant thermograms for the two crucibles are shown in Figure 7. When the platinum crucible was used, the two exothermic peaks disappeared and instead there was an endothermic peak nearly at the same position (exactly at 796 K). This endothermic peak was detected at 801 K by Souamti *et al.* [15]. They explained this peak as a phase transition where β - K_2SO_4 transformed to α - K_2SO_4 while β - K_2SO_4 was obtained from the decomposition of $K_2Cu(SO_4)_2$ at the exothermic peak at 573 K. The exothermic peak at 573 K is not observed in this work, and we can explain the endothermic peak at 796 K as the melting process.

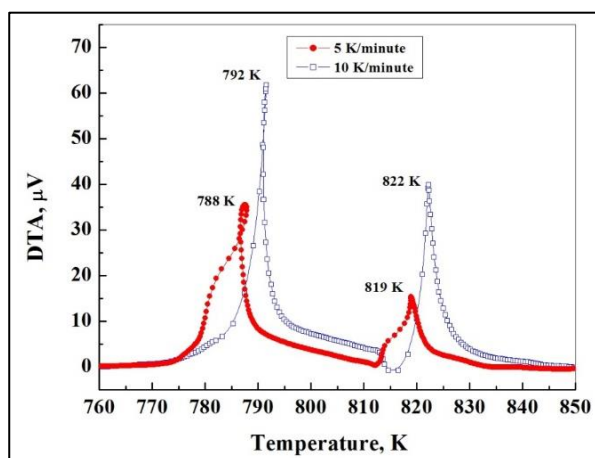


Figure 6: The DTA thermograms of $K_2Cu(SO_4)_2 \cdot 6H_2O$ crystal with two different heating rates.

From this result one could conclude that the two strong exothermic peaks are directly related to the material of the crucible in addition to the existence of Cu in our material. It is noteworthy that this process was not observed in the case of nickel or cobalt Tutton salts [25].

What happens is that Al atom transfers its outer electrons to Cu ions because of the higher position of Al in the electrochemical series relative to Cu. The following equation represents this transfer:



Approaching the melting point, the electron transfer process started partially while the material was still in the solid state. This electron transfer is associated with the evolution of a significant amount of heat, which appeared in the form of the first exothermic peak. Then the material melted rapidly due to the high amount of heat generated, which masked the appearance of the endothermic peaks associated with melting. The melting process enhanced the electron transfer process, leading to the appearance of a second peak indicating this process.

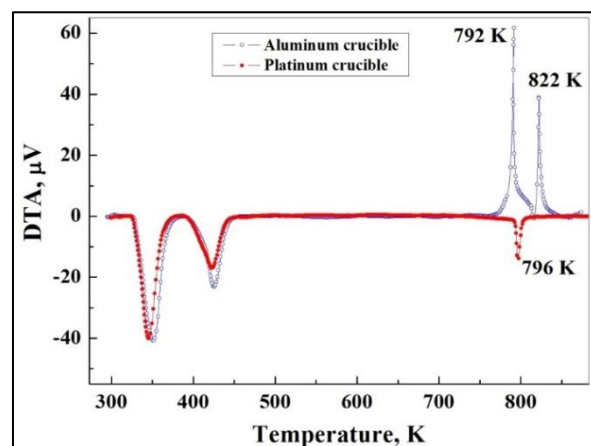


Figure 7: The DTA thermograms of $K_2Cu(SO_4)_2 \cdot 6H_2O$ crystal using two different crucibles.

To confirm this idea, pure Al powder was added to the KCUSH powder in a platinum crucible with weight ratios of 1:1, 1:4 and 1:20 respectively. The DTA indicated the same exothermic reaction but with a single broad peak. The amount of heat per gram increased with decreasing Al weight. This is because only part of the higher Al weight used reacts with Cu-ion according to the given equation.

4. Conclusions

In this study, single crystal of $K_2Cu(SO_4)_2 \cdot 6H_2O$ (KCUSH) was grown by the slow evaporation technique of a supersaturated aqueous solution at 309 K. It has a light blue color, monoclinic structure, space group $P2_1/a$ and $Z = 2$.

The dehydration process of the KCUSH crystal occurs in two steps (two after four). Four water molecules are lost in the first step, while the remaining two water molecules are lost in the second step. The two steps occur at 351 K and 426 K respectively.

The two exothermic peaks at 792 K and 822 K are directly related to the material of the crucible (aluminum) in addition to the presence of copper in KCUSH. When a platinum crucible was used for thermal measurements instead of aluminum crucible used in the previous measurements, these two exothermic peaks disappeared, and an endothermic peak was detected at 796 K, which refers to the melting process of the KCUSH crystal.

Dedication

The authors dedicate this paper to Prof. Dr. M.A. Gaffar, a member of the authoring team, who passed away before this paper was sent for publication.

Data Availability

The datasets used and analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.

References

- [1] Euler, H., Barbier, B., Klumpp, S., Kirfel, A. (2000) Crystal structure of Tutton's salts, $Rb_2[M^{II}(H_2O)_6](SO_4)_2$, $M^{II} = Mg, Mn, Fe, Co, Ni, Zn$, *Zeitschrift für Kristallographie - New Crystal Structures* **215**: 473-476.
- [2] Ivanovski, V., Petruševski, V.M., Gunde, M.K. (2005) The IR reflectance spectra of the $\nu_3(SO_4^{2-})$ and $\nu_4(SO_4^{2-})$ band regions of some Tutton salts using polarized radiation: testing the model dielectric function, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **61**: 67-76.

- [3] Narasimhulu, K.V., Rao, J.L. (1997) A single crystal EPR study of VO_2^{2+} ions doped in $\text{Cs}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ Tutton salt, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **53**: 2605-2613.
- [4] Figgis, B.N., Sobolev, A.N., Simmons, C.J., Hitchman, M.A., Stratemeier, H., Riley, M.J. (2000) Bonding effects and the crystal structures of $(\text{NH}_4)_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ and its H_2^{18}O substituted form at 9.5 K, *Acta Crystallographica Section B* **56**: 438-443.
- [5] Lubbers, J., Miedema, A.R., Huiskamp, W.J. (1965) Cooling by means of anisotropic hyperfine structure coupling; Orientation and relaxation of nuclear spin systems in strong magnetic fields, *Physica* **31**: 153-192.
- [6] Fujii, Y., Wakana, H., Shigi, T. (1981) Thermal boundary resistance between liquid ^3He and copper potassium tutton salt, *Physica B+C* **108**: 921-922.
- [7] Fisher, R.A., Brodale, G.E. (1981) Thermal resistance between the electronic spin system of $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (powder) and ^4He -II from 0.7 to 1.8K to magnetic fields of 15 kG¹, *Physica B+C* **108**: 911-912.
- [8] Fisher, R.A., Brodale, G.E. (1982) Thermal resistance between the electronic spin system of $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (powder) and ^4He II below 1.8 K to magnetic fields of 15 kG, *The Journal of Chemical Physics* **76**: 3699-3712.
- [9] Fujii, Y., Shigi, T. (1987) Thermal resistance between liquid ^3He and copper potassium tutton salt, *Journal of Low Temperature Physics* **66**: 69-84.
- [10] Augustyniak, M.A., Krupski, M. (1999) The temperature dependence of the pressure switching of Jahn-Teller deformation in the deuterated ammonium copper Tutton salt, *Chemical Physics Letters* **311**: 126-130.
- [11] Campbell, J.A., Ryan, D.P., Simpson, L.M. (1970) Interionic forces in crystals—II. Infrared spectra of SO_4 groups and "octahedrally" coordinated water in some alums, Tutton salts, and the double salts obtained by dehydrating them, *Spectrochimica Acta Part A: Molecular Spectroscopy* **26**: 2351-2361.
- [12] Schultz, A.J., Cowan, J.A., Hitchman, M.A., Stratemeier, H. (2005) Single-crystal neutron-diffraction study of 3.4% Zn-doped $(\text{ND}_4)_2[\text{Cu}(\text{D}_2\text{O})_6](\text{SO}_4)_2$ at 20 K, *Acta Crystallographica Section C* **61**: m234-m236.
- [13] Gómez-Salces, S., Aguado, F., Valiente, R., Rodríguez, F. (2012) Unraveling the Coordination Geometry of Copper(II) Ions in Aqueous Solution through Absorption Intensity, *Angewandte Chemie International Edition* **51**: 9335-9338.
- [14] Ghosh, S., Ullah, S., de Mendonça, J.P.A., Moura, L.G., Menezes, M.G., Flôres, L.S., Pacheco, T.S., de Oliveira, L.F.C., Sato, F., Ferreira, S.O. (2019) Electronic properties and vibrational spectra of $(\text{NH}_4)_2\text{M}''(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (M = Ni, Cu) Tutton's salt: DFT and experimental study, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **218**: 281-292.
- [15] Souamti, A., Zayani, L., Palomino, J.M., Cruz-Yusta, M., Vicente, C.P., Hassen-Chehimi, D.B. (2015) Synthesis, characterization and thermal analysis of $\text{K}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (M = Mg, Co, Cu), *Journal of Thermal Analysis and Calorimetry* **122**: 929-936.
- [16] Morales, A.C., Cooper, N.D., Reisner, B.A., DeVore, T.C. (2018) Variable temperature PXRD investigation of the phase changes during the dehydration of potassium Tutton salts, *Journal of Thermal Analysis and Calorimetry* **132**: 1523-1534.
- [17] Morales, A., Cooper, N., Reisner, B.A., DeVore, T.C. (2022) Enthalpies of formation and standard entropies for some potassium Tutton salts, *Chemical Thermodynamics and Thermal Analysis* **8**: 100085.
- [18] Colaneri, M.J., Vitali, J. (2021) Effect of the Lattice Field on the Electronic Structure and Dynamics of Copper-Hexahydrate in Tutton Salts, *The Journal of Physical Chemistry A* **125**: 3268-3278.
- [19] Peets, D.C., Avdeev, M., Rahn, M.C., Pabst, F., Granovsky, S., Stötzer, M., Inosov, D.S. (2022) Crystal Growth, Structure, and Noninteracting Quantum Spins in Cyanochroite, $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, *ACS Omega* **7**: 5139-5145.
- [20] de Oliveira Neto, J.G., Viana, J.R., Lima, A.D.d.S.G., Lopes, J.B.O., Ayala, A.P., Lage, M.R., Stoyanov, S.R., dos Santos, A.O., Lang, R. (2023) Assessing the Novel Mixed Tutton Salts $\text{K}_2\text{Mn}_{0.03}\text{Ni}_{0.97}(\text{SO}_4)_2(\text{H}_2\text{O})_6$ and $\text{K}_2\text{Mn}_{0.18}\text{Cu}_{0.82}(\text{SO}_4)_2(\text{H}_2\text{O})_6$ for Thermochemical Heat Storage Applications: An Experimental-Theoretical Study, *Molecules* **28**: 8058.
- [21] Smith, J., Weinberger, P., Werner, A. (2024) Dehydration performance of a novel solid solution library of mixed Tutton salts as thermochemical heat storage materials, *Journal of Energy Storage* **78**: 110003.
- [22] Abdulwahab, A.M. (2012) Influence of temperature on the optical properties of zinc tris-thiourea sulfate (ZTS) single crystal, *Optical Materials* **35**: 146-154.
- [23] Abdulwahab, A.M., Al-magdashy, Y.A.A., Meftah, A., Al-Eryani, D.A., Qaid, A.A. (2019) Growth, structure, thermal, electrical and optical properties of potassium aluminum sulfate dodecahydrate (potash alum) single crystal, *Chinese Journal of Physics* **60**: 510-521.
- [24] Abdulwahab, A.M., Al-Dhabyani, K.M., Ahmed, A.A.A., Al-Hada, N.M., Qaid, A.A. (2022) The effect of lithium doping on structural, thermal, optical and electrical properties of potash alum single crystals, *Inorganic Chemistry Communications* **145**: 109985.
- [25] Abdulwahab, A.M., Gaffar, M.A., El-Fadl, A.A. (2023) Crystallization and characterization of $\text{K}_2\text{Ni}_x\text{Co}_{1-x}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ mixed crystals for ultraviolet light filters and sensors, *Solid State Sciences* **143**: 107261.