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# On the Formation of Solid Solutions with Blödite and Kröhnkite-Type Structures. II. Structural and Thermal Investigations of Solid Solutions $Na_2Zn_{1-x}Cu_x(SO_4)_2{\cdot}4H_2O (0 < x < 0.14)$

**D. Marinova[1], M. Georgiev[2], Tsv. Bancheva[2], D. Stoilova[1*]**

*[1]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[2]Department of Inorganic Chemistry, University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

## ABSTRACT

Structural and thermal investigations of solid solutions $Na_2Zn_{1-x}Cu_x(SO_4)_2{\cdot}4H_2O$ ($0 < x < 0.14$) of a blödite-type structure are reported in the present paper. The replacement of the zinc ions by copper ones in the crystals of the blödite-type structure do not change considerably the lattice parameters and the volumes of the unit cells of the solid solutions due probably to the buffer effect of the sodium cations. However, the degree of distortion of the $[M(H_2O)_4(SO_4)_2]$ clusters in the solid solutions is larger than that in $Na_2Zn(SO_4)_2{\cdot}4H_2O$ as deduced from the single crystal X-ray diffraction due to the Jahn-Teller effect (DI has value of 0.011 and 0.018 for the neat zinc blödite and solid solutions, respectively).

On the basis of TG-DTA-DSC methods combined with X-ray powder diffraction at elevated temperature, it has been found that the dehydration of blödite phases occurs stepwise, thus forming intermediate dehydrate (at about 130 ºC) and two polymorphic modifications of anhydrous compounds. The form (I) of $Na_2Zn(SO_4)_2$ and $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2$ is stable in the temperature interval of about 200–280 ºC and the from (II) – in the temperature interval of about 330–380 ºC. The incorporation of copper ions in the zinc blödite results in increasing in the values of $\Delta H_{deh}$ and decreasing in the values of $\Delta H_f$ with increasing in the copper content. The water molecule in the kröhnkite compound $Na_2Cu(SO_4)_2{\cdot}2H_2O$ are separated in one step (the dihydrate is stable up to 250 ºC) and after heating at higher temperature it transforms into an anhydrous compound (300–380 ºC). Additionally, the anhydrous $Na_2Zn(SO_4)_2$, $Na_2Cu(SO_4)_2$ and $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2$ were characterized structurally using both X-ray diffraction and spectroscopic techniques. The infrared spectroscopic experiments add an additional information about the structural properties of the anhydrous compounds. For example, the sulfate tetrahedra in the anhydrous compounds are distorted in a higher degree in comparison to those in the hydrated ones.

**Keywords:** $Na_2Zn_{1-x}Cu_x(SO_4)_2{\cdot}4H_2O$ solid solutions; X-ray powder diffraction; Enthalpy of dehydration; Enthalpy of formation; Infrared spectra.

## I. INTRODUCTION

In a previous paper we provided for the first time results on the synthesis and spectroscopic investigations (infrared, Raman and EPR) of solid solutions $Na_2Zn_{1-x}Cu_x(SO_4)_2{\cdot}4H_2O$ ($0 < x < 0.14$) [1]. The preparation procedure – crystallization from mixed sodium copper zinc solutions using the method of isothermal decrease of supersaturation guarantees the homogeneity of the solid phases obtained. The other advantage of the method used is the possibility to prepare solid solutions with a desired amount of copper ions incorporated in the zinc blödite structure. The main conclusion of these studies is the finding that the copper ions are included isodirmorphously in the crystals of the zinc blödite up to 14 mol%, thus forming solid solutions of a blödite-type structure. Contrary, as the solubility diagram of the

$Na_2Zn(SO_4)_2$–$Na_2Cu(SO_4)_2$–$H_2O$ system at 25 ºC and the EPR spectra show $Na_2Cu(SO_4)_2{\cdot}2H_2O$ crystallizes free of zinc ions in a wide concentration range – from the binary saturated solution of the sodium copper sulfate up to solutions containing 25.27 mass% sodium zinc sulfate and 10.00 mass% sodium copper sulfate. The formation of the title solid solutions means that the copper ions are able to accept the coordination environment of the zinc ions in the blödite structure, thus forming $[Cu(H_2O)_4(SO_4)_2]^{2-}$ clusters. At concentrations of copper ions larger than 14 mol% the cooperative Jahn-Teller effect results in the interruption in the series of the solid solutions, thus leading to the crystallization of $Na_2Cu(SO_4)_2{\cdot}2H_2O$ free of zinc ions, i.e. the zinc ions are not able to replace the copper ions in the strongly distorted $[Cu(H_2O)_2(SO_4)_4]$octahedra in the kröhnkite-type structure.

The crystal structures of the zinc blödite and copper kröhnkite are described in detail in the first part of our investigations [1]. Here, we will mark briefly only these structural properties of the both compounds, which are necessary to explain the experimental results reported in this paper. The monoclinic structure of the zinc blödite (SG $P2_1/a$) consists of slightly distorted $[Zn(H_2O)_4(SO_4)_2]^{2-}$ clusters which form electrostatic bonds with sodium ions [2-6]. Additionally, the zinc clusters are interlinked by hydrogen bonds of different strength depending on both the Zn–$OH_2$ intermolecular interactions (*synergetic* effect) and the proton acceptor capability of the sulfate oxygen acceptors, thus forming 3D structure. The hydrogen bond lengths ($H_2O{\cdots}O$ bonds) of the water molecules linking to the $Zn^{2+}$cations via shorter Zn–$OH_2$ bond distances (2.065 Å) have values of 2.704 and 2.745 Å, while those of the water molecules linking to the $Zn^{2+}$cations via longer Zn–$OH_2$ bond distances (2.132 Å) have values of 2.868 and 2.926 Å. The zinc blödite is isomorphous with the tetrahydrate of the sodium magnesium, cobalt and nickel sulfates [5].

$Na_2Cu(SO_4)_2{\cdot}2H_2O$ is a member of a large series of natural and synthetic compounds built up of kröhnkite-type octahedral-tetrahedral chains (it crystallizes in the monoclinic space group $P2_1/c$) [7]. According to the classification scheme proposed by M. Fleck *at all*.$Na_2Cu(SO_4)_2{\cdot}2H_2O$ belongs to the structural type D [8,9]. The $[Cu(H_2O)_2(SO_4)_4]$octahedra are strongly distorted with respect to the Cu–O bond lengths as a result of the Jahn-Teller effect (the shortest and the longest Cu–O bond lengths have values of 1.937 and 2.462 Å, respectively). The copper ions are linked to the water molecules via the shortest bonds in the octahedra. The respective hydrogen bonds distances have value of 2.626 and 2.699 Å [7].

The strength of the hydrogen bonds formed in the compounds of blödite-type structure and those of kröhnkite-type structure as deduced from the wavenumbers of $\nu_{OD}$ of matrix-isolated HDO molecules is discussed in Refs. [1,5,10,11]. According to Novak [12] the hydrogen bonds in the zinc blödite could be classified as hydrogen bonds of middle strength and weak and those in the copper kröhnkite as comparatively strong.

With this contribution we made an attempt to solve several tasks: (i) To analyze the influence of the included copper ions on the structural characteristics of the zinc blödite and the anhydrous sodium zinc sulfate. (ii) In order to understand whether the homogeneity of the solid solutions is maintained after heating we monitor the behavior of the solid solutions by means of X-ray powder diffraction at elevated temperature. (iii) The other purpose of the present paper is to study the thermal behavior and phase transitions of the zinc blödite, copper kröhnkite and solid solutions using thermal gravimetric, differential thermal analyses and differential scanning calorimetry methods combined with X-ray powder diffraction. The infrared spectra of the anhydrous compounds are also presented and discussed with respect to the normal vibration of the sulfate anions.

## II. METHODS AND MATERIAL

Solid solutions$Na_2Zn_{1-x}Cu_x(SO_4)_2{\cdot}4H_2O$ ( where $x$ = 0.03, 0.05, 0.09 and 0.14) were prepared by crystallization from mixed sodium zinc copper solutions using the method of isothermal decrease of supersaturation. The experimental procedure used for the preparation of the double salts, $Na_2Zn(SO_4)_2{\cdot}4H_2O$ and $Na_2Cu(SO_4)_2{\cdot}2H_2O$, as well as the solid solutions was described in detail in Ref. [1]. Additionally, anhydrous sulfates were prepared by heating of the crystal hydrates for several hours at different temperatures - 200, 280, 330 and 380 ºC (zinc compound) and 300 ºC (copper compound).

The X-ray powder diffraction spectra were collected within the range from 5° to 60° 2θ with a step 0.02° 2θ and counting time 35 s/step on Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector. The X-ray powder diffraction measurements at elevated temperature (temperature interval 25–380 °C) were performed using a PANalytical Empyrean equipped with a multichannel detector (Pixel 3D) using Cu Kα (45 kV-40 mA) radiation in the 10–100° 2θ range, with a scan step of 0.01° for 24 s. The high temperature X-ray diffraction measurements were carried out by means of an ANTON PAAR HT-16 camera with a sample directly heated with a heating filament. All experiments were conducted on air at 5$^o$ C per minute. The lattice parameters of the solid solutions were determined using the program LSUCR.

The thermal properties and phase transitions of the double sulfates and solid solutions were investigated by thermogravimetric analysis, differential thermal analysis and differential scanning calorimetry. Simultaneous TG-DTA curves were obtained applying a computerized combined apparatus for thermal analysis LABSYSEvo, SETARAM Company, France, at atmospheric pressure in a flow of synthetic air (MESSER CHIMCO GAS - OOH 1056, ADR 2, 1A) in the temperature range 25–400 $^o$C. Corundum crucibles with a volume of 100 µl were used. The sample weight in all tests was 50-60 mg. The experiments were carried out in dynamic mode, with heating rates of 5 $^o$C min$^{-1}$ and oxidizing gas flow rates of 20 ml.min$^{-1}$. The DSC measurements were recorded on STA PT1600 (TG-DTA/DSC Simultaneous Thermal analysis) instrument in air up to 400 °C at a heating rate of 5 °C min$^{-1}$ using standard corundum crucibles (sample mass about 18 mg).

The infrared spectra were recorded on a Nicolet iS5 Fourier transform interferometer (resolution <2 cm$^{-1}$) at ambient temperature. The spectra were obtained using KBr discs as matrices. Ion exchange or other reactions with KBr have not been observed (infrared spectra using Nujol mulls were also measured).

## III. RESULTS AND DISCUSSION

### A. Structural properties of the solid solutions

The copper ions are reported to change the crystal structures of the host orthorhombic compounds $ZnSO_4·7H_2O$ and $MgSO_4·7H_2O$ and to transform the orthorhombic solid solutions $Zn_{1-x}Cu_xSO_4·7H_2O$ and $Mg_{1-x}Cu_xSO_4·7H_2O$ into monoclinic ones [13]. A similar interesting phenomenon was observed even in the case of formation of solid solutions between the isostructural formates $M(OCOH)_2·2H_2O$ (M = Mg, Mn, Co, Zn) and $Cu(OCOH)_2·2H_2O$. For example, the isostructural manganese and coper formates, respectively zinc and copper formates form two series of solid solutions [14,15], while the cobalt and magnesium formates form even three series of solid solutions with the copper compound [16-18]. These findings are explained with the properties of the Jahn-Teller copper ions which cause strong distortions of the $MO_6$octahedra of the host compound.

X-ray powder diffraction patterns of $Na_2Zn_{1-x}Cu_x(SO_4)_2·4H_2O$ solid solutions are presented in Fig. 1 (the lattice parameters of the solid solutions are listed in Table 1). The Fig. 1 reveals that the solid solutions crystallize in a blödite-type structure, thus confirming the results obtained from the investigation of the crystallization processes in the $Na_2Zn(SO_4)_2$–$Na_2Cu(SO_4)_2$–$H_2O$ system[1]. Furthermore, the included copper ions do not influence on the values of the lattice parameters, which are not changed considerably with increasing in the chemical compositions of the solid solutions (see Table 1).

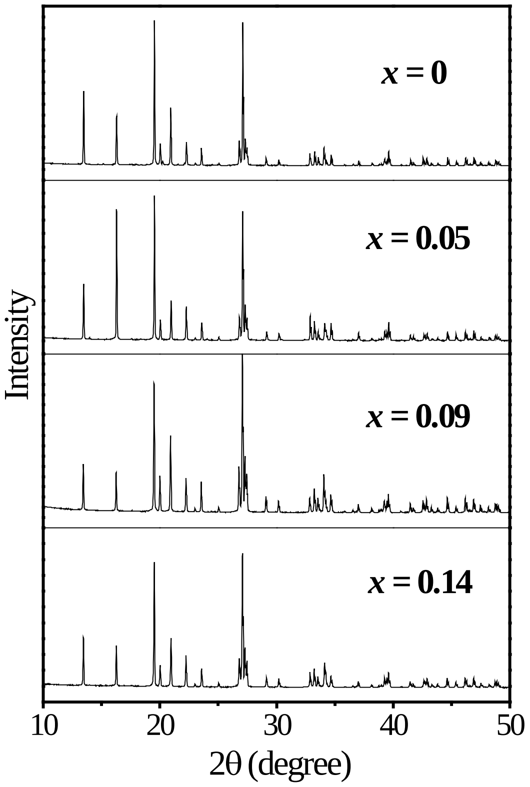

**Figure 1:** X-ray powder diffraction patterns of solid solutions $Na_2Zn_{1-x}Cu_x(SO_4)_2·4H_2O$.

TABLE I
LATTICE PARAMETERS OF THE SOLID SOLUTIONS $NA_2ZN_{1-x}CU_x(SO_4)_2{\cdot}4H_2O$

| **Compositions** | ***a*, Å** | ***b*, Å** | ***c*, Å** | ***β*, °** | ***V*, Å$^3$** |
|---|---|---|---|---|---|
| ***x* = 0**<br>**single crystals [5]** | 11.081(1) | 8.258(1) | 5.538(1) | 100.20(1) | 498.8 |
| ***x* = 0** | 11.0752(1) | 8.2515(9) | 5.5315(7) | 100.182(8) | 497.5 |
| ***x* = 0.05** | 11.070(3) | 8.255(2) | 5.534(1) | 100.110(2) | 497.9 |
| ***x* = 0.09** | 11.067(2) | 8.256(2) | 5.531(3) | 100.09(2) | 497.5 |
| ***x* = 0.14** | 11.0653(9) | 8.2580(7) | 5.5308(5) | 100.084(6) | 497.6 |

To extract more information for the impact of the copper ions on the first coordination sphere around the metal ions in the solid solutions single crystals were prepared from a solution containing about 26 mass% sodium zinc sulfate and 9 mass% sodium copper sulfate. The single crystal was measured by Prof. Manfred Wildner from Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum (Althanstr. 14, A-1090 Wien, Austria) and the results are politely provided to us. This solid phase crystallizes in the monoclinic space group $P2_1/a$ with lattice parameters: $a$ = 11.0430 Å, $b$ = 8.2721 Å, $c$ = 5.5305 Å and $\beta$ = 99.92 °. The measurements show that the inclusion of the copper ions in the blödite-type structure leads to decreasing in the M–O5 bond distance going from the neat zinc blödite to the solid solution (2.065 and 2.039 Å, respectively) and to increasing in the M–O3 and M–O6 bond distances (2.105 and 2.110 Å, and 2.132 and 2.141 Å, respectively). The O5 and O6 oxygen atoms belong to water molecules and O3 to sulfate tetrahedra, respectively (for the labeling of all atoms in the zinc blödite see also Ref. [5]). The changes in the bond lengths demonstrate the influence of the Jahn-Teller copper ions on the degree of deformation of the $[M(H_2O)_4(SO_4)_2]$ clusters. As a measure of the extent of deformation the values of DI are used (the calculations are described in Ref. [19]). Thus, the value of DI is 0.011 for $Na_2Zn(SO_4)_2{\cdot}4H_2O$ and 0.018 for the solid solution. It is worth mentioning that the bond lengths S–O and Na–O in the sulfate tetrahedra and sodium octahedra, respectively, are not influenced by the included in the host blödite-type structure copper ions.

### B. Thermal behavior of the neat compounds and solid solutions

Cot and Tiesi reported that the heating of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ leads to the formation of an intermediate dihydrate and four different polymorphic modifications of the anhydrous sodium zinc sulfate. These modifications are stable in different temperature intervals, as follows: the form (I) is stable in the interval of 170–270 ºC. The form (II) exists between 270 and 330 ºC, the form (III) is obtained at temperature larger than 330 ºC, and the form (IV) is obtained after cooling the form (III). At room temperature the form (IV) transform into the form (I). The authors provide also data on $d$-spacing for all compounds obtained by heating the tetrahydrate [20]. A stepwise water-loss mechanism of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ and the existence of $Na_2Zn(SO_4)_2{\cdot}2H_2O$ and $Na_2Zn(SO_4)_2$ is commented also in Ref. [2]. Berg and Thorup reported the crystal structure of $Na_2Zn(SO_4)_2$ obtained as a result of the reaction between ZnO and $Na_2S_2O_7$ (the anhydrous sodium zinc sulfate crystallizes in monoclinic SG $P2/n$ with lattice parameters: $a$ = 8.648(3) Å, $b$ = 10.323(3) Å, $c$ = 15.103(5) Å, $\beta$ = 90.879(6)º; $Z$ = 8) [21]. The data reported by Berg and Thorup ($d$-spacings) coincide with those of form (II) mentioned by Cot and Tiesi. The zinc ions in the 3D structure of $Na_2Zn(SO_4)_2$ (two crystallografically different kinds) are coordinated by five oxygen atoms, thus forming trigonalbipyramids. The sulfate ions (four structural types) are slightly distorted with respect to the S–O bond lengths. All atoms adopt general positions. Surprisingly, the structure of $Na_2Zn(SO_4)_2$ is different from those of $Na_2Co(SO_4)_2$ and $Na_2Ni(SO_4)_2$, irrespective of the isostructureness of the tetrahydrates [22].

Our experimental results of the dehydration of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ and the solid solutions are presented in Fig. 2. According to the TG and DTA curves the dehydration process of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ occurs stepwise in the temperature interval of 107–270 ºC, thus forming an anhydrous salt (see Fig. 2a). The mass loss calculation (TG curve) shows that two water molecules are separated in the temperature interval of about 107–126 ºC, thus producing $Na_2Zn(SO_4)_2{\cdot}2H_2O$. The latter begins to decompose almost immediately and the temperature interval of stability of the dihydrate could not be determine unambiguously ($\Delta m_{exp}$ = 9.50 mass% at about 130 ºC; $\Delta m_{cal}$ = 9.59 mass%). The strong endothermic effect centered at 120 ºC on the DTA curve corresponds to the escape of the first two water molecules. The slope of the TG curve shows that the dihydrate obtained loses rapidly a large part of the remaining two water molecules in the interval of about 134–180 ºC ($\Delta m_{exp}$ = 18.4 mass% at about 170 ºC). However, a very small decrease in the mass of the sample occurs at temperature larger than 230 ºC corresponding to the separation of the last small amount of water (probably occluded in the crystals of the anhydrous compound). The second strong peak at 153 ºC on the DTA curve is related to the second stage of dehydration. The separation of the four water molecules corresponds to 19.10 mass% ($\Delta m_{cal}$ = 19.18 mass%). The DSC curve also consists of two well distinguished endothermic effects – the first one is centered at 116 ºC and corresponds to the separation of two water molecules ($\Delta H_{deh}$ = 397.2 kJ mol$^{-1}$) and the second one at 141 ºC is related to the separation of the remaining two water molecules ($\Delta H_{deh}$ = 354.9 kJ mol$^{-1}$). Thus, the total enthalpy of dehydration of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ has value of 752.1 kJ mol$^{-1}$).

The stepwise dehydration process of the zinc blödite is well understandable if the structural detail of the $[Zn(H_2O)_4(SO_4)_2]^{2-}$ clusters and the interactions between them are taken into consideration. On the other hand, it is well known that the hydrogen bond strength plays a significant role in the process of dehydration. Thus, the water molecules $H_2O(2)$ linking to the $Zn^{2+}$cations via longer Zn–$OH_2$ bond lengths form weak hydrogen bonds and as a result they are separated easily at lower temperatures. Contrary, the water molecules $H_2O(1)$ linking to the $Zn^{2+}$cations via shorter Zn–$OH_2$ bond lengths form hydrogen bonds of middle strength and they escape at a relatively higher temperature (for the strength of the hydrogen bonds formed in the zinc blödite as deduced from the $\nu_{OD}$ modes of matrix-isolated HDO molecules see Ref. [1,5]).

Taking into account the mass loss calculation from the TG curve and the corresponding endothermic peaks registered on the DTA curve we propose the following scheme of phase transitions of $Na_2Zn(SO_4)_2{\cdot}4H_2O$:

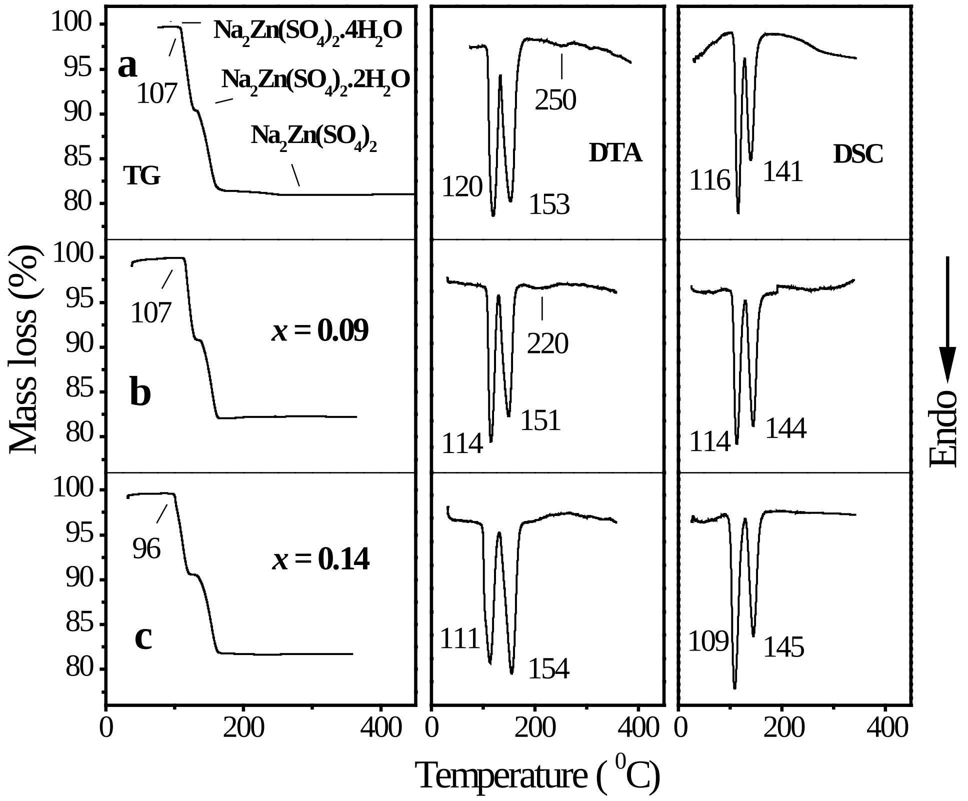

**Figure 2:** TG, DTA and DSC curves of: a, $Na_2Zn(SO_4)_2{\cdot}4H_2O$; b, c, $Na_2Zn_{1-x}Cu_x(SO_4)_2{\cdot}4H_2O$.

$$Na_2Zn(SO_4)_2{\cdot}4H_2O \xrightarrow{107-126℃} Na_2Zn(SO_4)_2{\cdot}2H_2O \xrightarrow{135-180℃} Na_2Zn(SO_4)_2 \text{ (form I)} \xrightarrow{220-270℃} Na_2Zn(SO_4)_2 \text{ (form II)}$$

Using the data for $\Delta H_f$ of the simple salts (the data are taken from Ref. [23] as well as the values of $\Delta H_{deh}$ obtained from the DSC measurements the enthalpy of formation of the tetrahydrate and dihydrate have been calculated: $\Delta H_f$of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ is -4089.2 kJ $mol^{-1}$ and $\Delta H_f$of $Na_2Zn(SO_4)_2{\cdot}2H_2O$ is -3208.4 kJ $mol^{-1}$.

Fig. 2b and c show that the inclusion of copper ions in the crystals of the zinc tetrahydrate does not change considerably the shape of the respective thermal curves and the positions of the endo effects. The beginning of the dehydration process of the sample $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2{\cdot}4H_2O$ occurs at about 96 ºC. One interesting feature of the TG curve of the sample containing 14 mol% copper ions is the finding that the temperature interval of stability of the dihydrate seems to be slightly larger as compared to that of $Na_2Zn(SO_4)_2{\cdot}4H_2O$. The same phenomenon is observed in the case of mixed $Na_2Ni_{1-x}Cu_x(SO_4)_2{\cdot}4H_2O$ and $Na_2Co_{1-x}Cu_x(SO_4)_2{\cdot}4H_2O$ crystals (these data will be provided in the forthcoming paper). Fig. 2b and c show that the endothermic effect corresponding to the first stage of dehydration of the solid solution $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2{\cdot}4H_2O$ appears on the DTA and DSC curves at slightly lower temperature as compared to the neat zinc compound. The calculated values of $\Delta H_{deh}$ for the two stages of dehydration increase with increasing in the concentration of the included copper ions: 438. 9 and 409.7 kJ $mol^{-1}$ ($x$ = 0.09) and 490.1 and 433.8 kJ $mol^{-1}$ ($x$ = 0.14).The total enthalpies of dehydration of $Na_2Zn_{0.91}Cu_{0.09}(SO_4)_2{\cdot}4H_2O$ and $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2{\cdot}4H_2O$ have values of 848.6 and 923.9 kJ $mol^{-1}$. The respective enthalpies of formation ($\Delta H_f$) have values of -4186.7 and -4261.0 kJ $mol^{-1}$.

To obtain further insight into the dehydration process, we monitored the evolution of the XRD patterns as a function of the temperature (temperature interval 25–380 ºC). The X-ray diffraction patterns are shown in Fig. 3 (a, $Na_2(SO_4)_2{\cdot}4H_2O$ and b, $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2{\cdot}4H_2O$). Since the samples obtained as a results from X-ray diffraction at elevated temperature are of poor crystallinity we heated the hydrate sulfates at 200, 280, 330 and 380 ºC for several hours in order to determine the *d*-spacings of different intermediate products. The close inspection of the XRD patterns leads to several findings.

(i) The roentgenograms on the left and right sides are identical, thus indicating the isostructureness of the products obtained by heating the neat sodium zinc sulfate and those obtained by heating the solid solution $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2{\cdot}4H_2O$.

(ii) The *d*-spacing values for the phase at 130 ºC (see Table 2) are very close to those for $Na_2(SO_4)_2{\cdot}2H_2O$ reported by Cot and Tiesi [20].

(iii) Fig. 3 shows that two structurally different anhydrous compounds are formed as a result of heating $Na_2Zn(SO_4)_2{\cdot}4H_2O$ and the solid solutions $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2{\cdot}4H_2O$. One form is stable in the temperature interval of about 200–280 ºC and the other – in the temperature interval of about 330–380 ºC. Consequently, the endo effect on the DTA curve at 250 ºC is related to the phase transition of the anhydrous sodium zinc sulfates. According to the experiments of the X-ray powder diffraction at elevated temperature the lower temperature form exists at 280 ºC, while the phase transition from the lower temperature form into the higher temperature one occurs at about 250 ºC according to DTA curve (compare Fig. 2 and Fig. 3). In our opinion this contradiction is due to some kinetic reasons. To confirm this claim $Na_2Zn(SO_4)_2{\cdot}4H_2O$ was heated at 280 ºC for two hours – the roentgenogram resembles that of the sample obtained in the interval of 330–380 ºC at elevated temperature. The *d*-spacing values for the higher temperature form of $Na_2Zn(SO_4)_2$ correspond well to both the Debye-Scherrer pattern for the form (II) [20] and to the single crystal measurements [21]. The phase transformation from the structure of the tetrahydrate into an anhydrous structure is shown in Fig. 4.

(iv) Our results for the lower temperature form differ considerably from those reported for the form (I) reported in Ref. [20].

(v) All samples of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ heated at temperatures higher than 200 ºC accept rapidly a moisture in air, thus converting into a hydrated form, which differ from tetrahydrate as deduced from the infrared spectroscopic measurements. We assume that this hydrated phase is formed on the surface of the samples, since the X-ray measurements do not show any changes in the diffraction patterns.

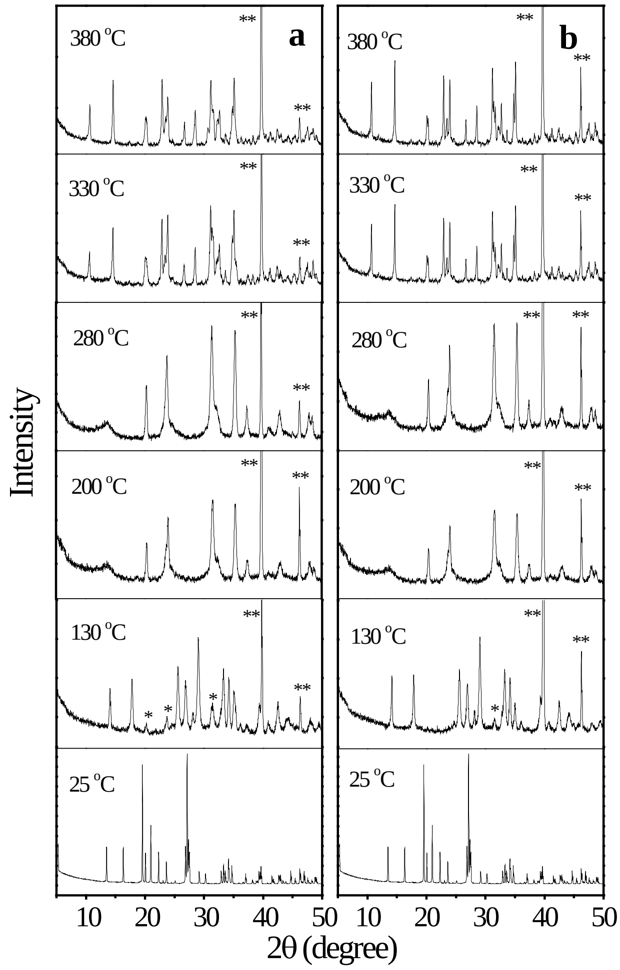

**Figure 3:**X-ray powder diffraction patterns at elevated temperature: a, $Na_2Zn(SO_4)_2\cdot 4H_2O$; b, $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2\cdot 4H_2O$ (*, reflections due probably to an anhydrous compound; **, platinum).

According to Silber and Cot the dehydration of $Na_2Cu(SO_4)_2\cdot 2H_2O$ in air leads to the formation of two polymorphic modification of the anhydrous sodium copper sulfate – the low temperature form is stable in the interval of 210–470 ºC and the high temperature form in the interval of 470–510 ºC. The authors provided also *d*-spacings for the both forms [24]. On the basis of TG-DTA curves Nagase and Yokobayashi reported that the dehydration of $Na_2Cu(SO_4)_2\cdot 2H_2O$ occurs stepwise, thus forming a monohydrate as an intermediate product [25].

TABLE II

*HKL*, *D*-SPACING AND RELATIVE INTENSITIES FOR $NA_2ZN(SO_4)_2\cdot 2H_2O$ ($NA_2ZN(SO_4)_2\cdot 4H_2O$ HEATED AT 130 ºC).

| $d_{exp}$, Å | $I/I_0$ | $d_{exp}$, Å | $I/I_0$ |
|---|---|---|---|
| 6.2926 | 50 | 2.2900 | 33 |
| 4.9839 | 61 | 2.2100 | 17 |
| 4.4025 | 11 | 2.1268 | 17 |
| 3.4840 | 72 | 2.0500 | 17 |
| 3.3236 | 55 | 2.0104 | 11 |
| 3.1725 | 22 | 1.8435 | 11 |
| 3.0778 | 100 | 1.8179 | 17 |
| 2.6948 | 67 | 1.7809 | 11 |
| 2.6270 | 61 | 1.7485 | 22 |
| 2.5561 | 44 | 1.7187 | 28 |
| 2.4829 | 11 | 1.6624 | 33 |
| 2.4140 | 11 | | |

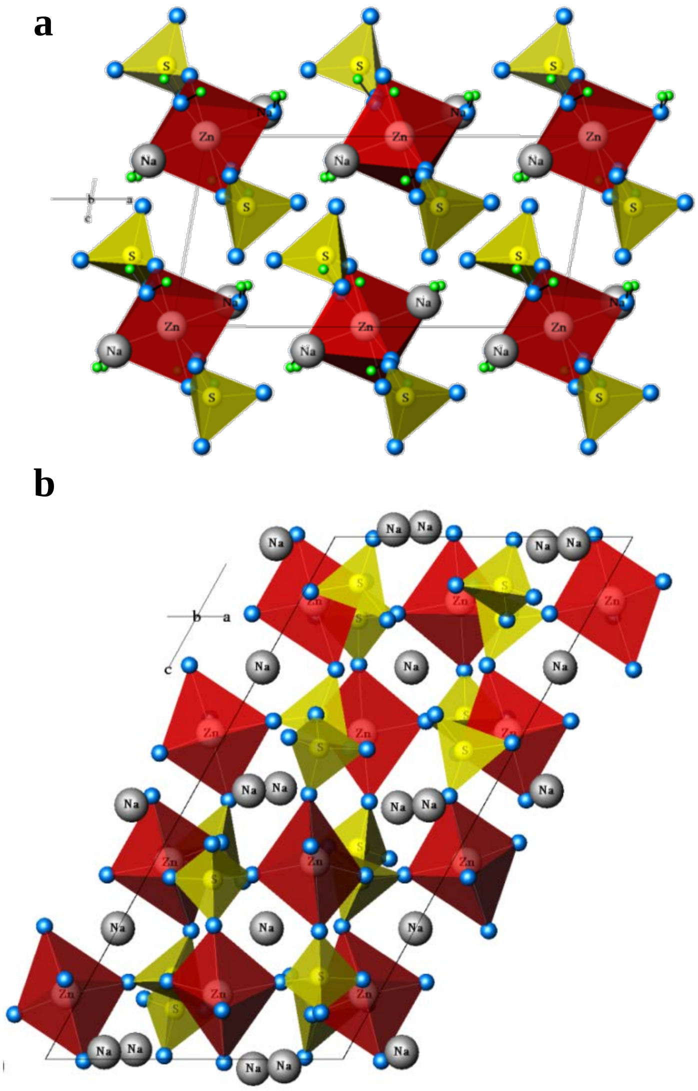

**Figure 4:** Transformation of the crystal structure of $Na_2Zn(SO_4)_2\cdot 4H_2O$ (a) into $Na_2Zn(SO_4)_2$ (b).

No inflections are observed on TG curve of $Na_2Cu(SO_4)_2{\cdot}2H_2O$ (see Fig. 5). The experimental mass loss ($\Delta m_{exp}$ = 9.78 mass%) is in good agreement with the theoretical one ($\Delta m_{cal}$ = 10.66 mass%). However, the dehydration process is registered on DTA and DSC curves with two strong endothermic effects at 190 and 206 ºC, and 180 and 194 ºC, respectively, which are close in intensity. To throw more light on the process of dehydration we performed X-ray diffraction study of the sodium copper sulfate dihydrate at elevated temperature (the X-ray patterns are shown in Fig. 6). It is seen that the copper dihydrate retains its structure up to 250 ºC and at temperatures higher than 300 ºC it converts into an anhydrous salts. Hence, the endo effects on the DTA and DSC curves are related to the simultaneously separation of the water molecules. The calculated enthalpy of dehydration of $Na_2Cu(SO_4)_2{\cdot}2H_2O$ has value of 354.0 kJ mol$^{-1}$ and that of formation -2996.5 kJ mol$^{-1}$. In Table 3 *d*-spacings and intensities of the peaks of the anhydrous sodium copper sulfate obtained by heating the dihydrate at 300 ºC for several hours are provided. The *d*-spacings coincide well with those reported by Silber and Cot for the low temperature form [24].

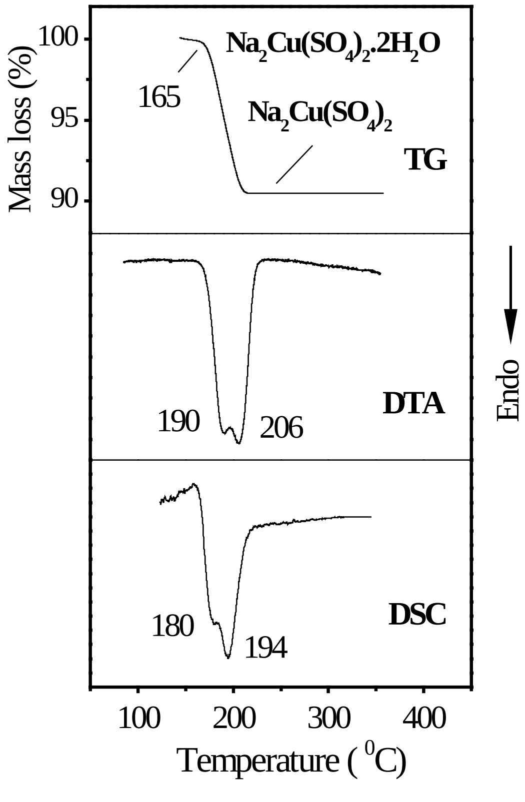

**Figure 5:**TG, DTA and DSC curves of $Na_2Cu(SO_4)_2{\cdot}2H_2O$.

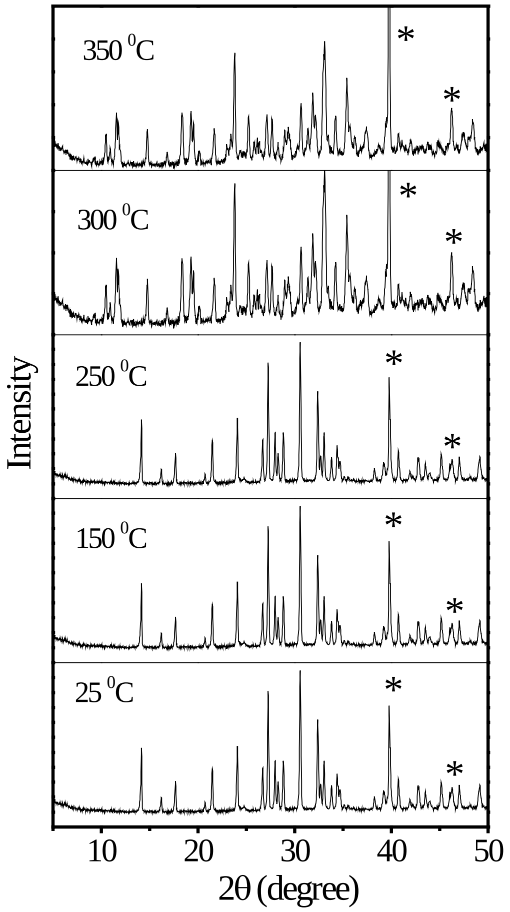

**Figure 6:** X-ray powder diffraction patterns of $Na_2Cu(SO_4)_2{\cdot}2H_2O$ at elevated temperature.

TABLE III

*HKL*, *D*-SPACING AND RELATIVE INTENSITIES FOR $Na_2Cu(SO_4)_2$ ($Na_2Cu(SO_4)_2{\cdot}2H_2O$ HEATED AT 300 °C).

| $d_{exp}$, Å | $I/I_0$ | $d_{exp}$, Å | $I/I_0$ | $d_{exp}$, Å | $I/I_0$ |
|---|---|---|---|---|---|
| 9.6773 | 26 | 4.5616 | 43 | 3.0858 | 22 |
| 8.5483 | 74 | 4.4254 | 13 | 3.0435 | 17 |
| 8.2219 | 39 | 4.1138 | 26 | 2.9564 | 9 |
| 7.7529 | 100 | 3.8800 | 13 | 2,9188 | 39 |
| 7.6081 | 87 | 3.8106 | 22 | 2.8529 | 17 |
| 7.4919 | 30 | 3.7492 | 96 | 2.8065 | 43 |
| 6.8297 | <5 | 3.5346 | 39 | 2.7889 | 17 |
| 6.0537 | 56 | 3.4578 | 13 | 2.7798 | 22 |
| 5.3006 | 13 | 3.4184 | 13 | 2.7201 | 52 |
| 4.8675 | 43 | 3.3890 | 13 | 2.7027 | 78 |
| 4.8451 | 35 | 3.2923 | 30 | 2.6790 | 13 |
| 4.6474 | 17 | 3.2273 | 30 | 2.6201 | 26 |
| 4.6213 | 48 | 3.1595 | 9 | 2.5333 | 43 |

### C. Infrared spectroscopic study of $Na_2Zn(SO_4)_2$ and $Na_2Cu(SO_4)_2$

Infrared spectroscopic study is expected to give an additional information about the structural properties of the anhydrous salts. Generally, the librations of the coordinated water molecules in crystal hydrates appear in the spectral region below 1000 $cm^{-1}$ and the corresponding bands are expected to disappear in their vibrational spectra after their complete dehydration.

Raman spectra of $Na_2Zn(SO_4)_2$ are reported in Ref. [21] and the infrared spectrum of $Na_2Cu(SO_4)_2$ is briefly discussed in Ref. [25]. Our infrared spectroscopic measurements of the anhydrous double salts are shown in Fig. 7 (see also Table 4). For a sake of clarity, the spectra of the respective hydrated salts are also shown (the spectra of the crystal hydrates are taken from Ref. [1]). The wavenumbers of the water librations (rocking and wagging) in the crystal hydrates $Na_2Zn(SO_4)_2{\cdot}4H_2O$ and $Na_2Cu(SO_4)_2{\cdot}2H_2O$ are marked in the spectra (see Fig. 7).

According to the structural data the monoclinic unit cell of $Na_2Zn(SO_4)_2$ (Z = 8; factor group symmetry $C_{2h}$) contains 104 atoms with 312 zone-center degrees of freedom. All atoms adopt $C_1$ sites [21]. The sulfate ions contribute 144 internal modes to the 312 optical zone-center modes (each tetrahedral ion is characterized with nine normal vibrations; four crystallographically different sulfate ions). The low site symmetry of the $SO_4^{2-}$ ions leads to a removal of the degeneracy of both the doubly degenerate $\nu_2$ modes and the triply degenerate $\nu_3$ and $\nu_4$ modes (the non-degenerate $\nu_1$ mode is activated). According to the site symmetry analysis nine internal modes of each type of sulfate tetrahedra are predicted (all of A symmetry): one mode for the symmetric stretching vibrations ($\nu_1$), two modes for the symmetric bending vibrations ($\nu_2$), and three modes for both asymmetric stretching and bending vibrations ($\nu_3$ and $\nu_4$).

Additionally, under the factor group symmetry $C_{2h}$ each species of A symmetry split into four components – Ag + Bg + Au + Bu (related to interactions of identical oscillators, correlation field effect, see Fig. 8). Consequently, the 144 optical modes for the $SO_4^{2-}$ ions are subdivided into 36Ag + 36Bg + 36Au + 36Bu modes. The 168 external modes are distributed between the translational and librational lattice modes. The unit cell theoretical treatment for the translational ($Zn^{2+}$, $Na^{+}$, $SO_4^{2-}$) and librational lattice modes ($SO_4^{2-}$) yields: 48 librations (12Ag + 12Bg + 12Au + 12Bu) and 120 translations (30Ag + 30Bg + 30Au + 30Bu).

Then the 312 vibrational modes of the unit cell decompose according to the following representation:

$\Gamma$= 78Ag + 78Bg + 78Au + 78Bu; where 1Au + 2Bu are translations (acoustic modes).

The species of *u*-symmetry are active in the infrared spectra, while those of *g*-symmetry in Raman spectra (mutual exclusion principle).

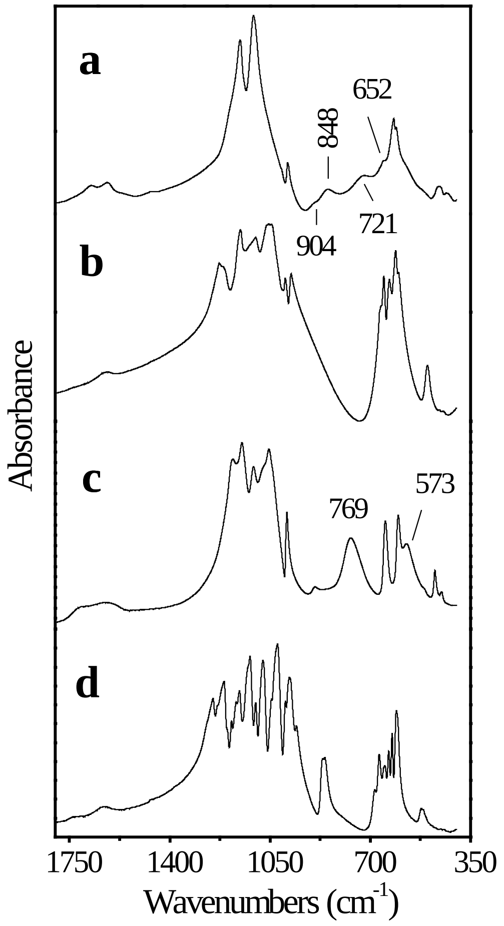

**Figure 7:**Infrared spectra of hydrated and anhydrous compounds: a, $Na_2Zn(SO_4)_2{\cdot}4H_2O$; b, $Na_2Zn(SO_4)_2$: c, $Na_2Cu(SO_4)_2{\cdot}2H_2O$; d, $Na_2Cu(SO_4)_2$.

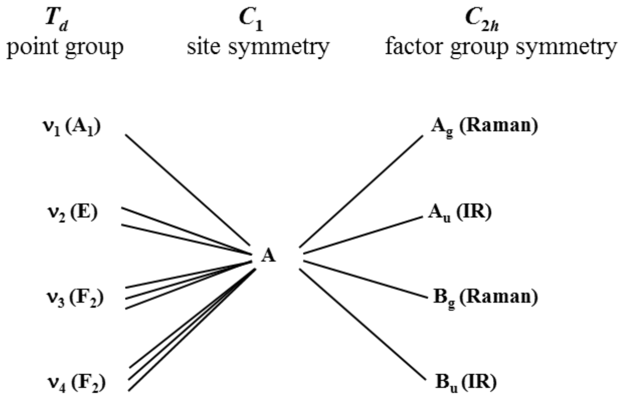

**Figure 8:**Correlation diagram between $T_d$ point symmetry, $C_1$ site symmetry and $C_{2h}$ factor group symmetry (sulfate ions in the anhydrous zinc compound).

The bands at higher wavenumbers 904 and 848 cm$^{-1}$, and those at lower wavenumbers 721 and 652 cm$^{-1}$ correspond to rocking and wagging modes of the two structurally different water molecules in $Na_2Zn(SO_4)_2\cdot4H_2O$, respectively. The water molecules in $Na_2Cu(SO_4)_2\cdot2H_2O$ exhibit two bands at 769 and 573 cm$^{-1}$ related to rocking and wagging modes (for additional comments see also Ref. [1]). As expected, these bands disappear in the spectra of the anhydrous sulfates, thus indicating a complete dehydration of the crystal hydrates (see Fig. 7).

The groups of very strong bands spread in the wide spectral ranges of 1226–1044 cm$^{-1}$ (bands at 1226, 1212, 1153, 1119, 1102, 1063 and 1044 cm$^{-1}$) and 1251–1024 cm$^{-1}$ (bands at 1251, 1234, 1211, 1200, 1184, 1167, 1158, 1128, 1120, 1099, 1075, 1064, 1024 cm$^{-1}$) correspond to the asymmetric stretching vibrations of the sulfate ions in the zinc and copper compounds, respectively. The positions of these bands point to existence of S–O bonds of different lengths. Thus, the bonds of larger lengths contribute in a higher degree to bands detected at highest frequencies. On the other hand, the appearance of bands at large wavenumbers (1251 and 1234 cm$^{-1}$) shows the existence of longer S–O bonds in the copper compounds in comparison to those in the zinc one (the highest frequency bands appear at 1226 cm$^{-1}$). According to the site group analysis the four structurally different sulfate ions in $Na_2Zn(SO_4)_2$ are expected to exhibit four infrared bands corresponding to the $\nu_1$ modes of the sulfate tetrahedra. Instead of this expectation two bands only at 998 and 978 cm$^{-1}$ are seen in the spectrum (see Fig. 7b). The corresponding Raman bands are observed at 1029, 1002 and 980 cm$^{-1}$ [21]. In the vicinity of the lowest wavenumbered component of $\nu_3$ of the sulfate ions in the coper compound three very strong bands are detected – bands at 995, 982 and 957 cm$^{-1}$, which are attributed to the symmetric stretches $\nu_1$ (Fig. 7d). However, the bands at 995 and 982 cm$^{-1}$ could not be assigned unambiguously – they could due either to the crystal field effect (frequency difference is only 13 cm$^{-1}$) or to $\nu_1$ of two different sulfate tetrahedra (as was commented above in the text the crystal structure of the copper salt is not known). Taking into account the numbers of the bands related to $\nu_3$ and their positions we assume that more than two crystallographically different sulfate tetrahedra exist in the structure of the anhydrous copper compound.

The analysis of the infrared spectra in the region of the stretching modes reveals that the sulfate tetrahedra in both anhydrous compounds are strongly distorted – the $\nu_3$splittings have very large values (227 cm$^{-1}$ for the copper compound and 182 cm$^{-1}$ for the zinc one) and the bands corresponding to $\nu_1$ are of very strong intensities. It is known that the high intensities of the bands corresponding to $\nu_1$ reflect both the strong distortion of the sulfate ions in the sulfate compounds [1,26,27] and the strong coupling between $\nu_1$ and $\nu_3$ of the anions [28,29].

The asymmetric bending modes $\nu_4$ are distributed over the comparatively narrow frequency intervals of 663–601 cm$^{-1}$ (zinc compound) and 653–608 cm$^{-1}$ (copper compound) (see Table 4). When the values of $\Delta\nu_3$ and $\Delta\nu_4$ are compared it is seen that the former are larger than the latter ones – 182 and 62 cm$^{-1}$, and 227 and 45 cm$^{-1}$ for the zinc and copper compound, respectively. This spectroscopic finding is the reason to claim that the tetrahedra are stronger distorted with respect to the S–O bond lengths than to the O–S–O bond angles. The bands at 500 cm$^{-1}$ (zinc compound) and 521 and 516 cm$^{-1}$ (copper compound) arise from the symmetric bending modes $\nu_2$ of the tetrahedra. The band position in the ranges below 700 cm$^{-1}$ evidence that the metal cation nature do not influence on the bending modes of the sulfate ions.

TABLE IV

*ASSIGNMENTS OF THE IR BANDS TO VIBRATIONAL MODES IN THE REGION OF 1600–400 CM$^{-1}$ (NORMAL VIBRATIONS OF THE SULFATE TETRAHEDRA).*

| **$Na_2Zn(SO_4)_2$** | **$Na_2Cu(SO_4)_2$** | **Modes** |
|---|---|---|
| 1226 1212<br>1153 1119<br>1102 1062 | 1251 1234 1211<br>1200 1184 1167<br>1158 1128 1120<br>1099 1075 1064<br>1024 | **$\nu_3(SO_4)$** |
| | | |
| 998 978 | 996 982 957 | **$\nu_1(SO_4)$** |
| | | |
| | 867 859 | **$\nu$(Cu–O)** |
| | | |
| 663 652<br>633 612<br>601 | 653 650 636<br>625 608 | **$\nu_4(SO_4)$** |
| | | |
| 500 | 521 516 | **$\nu_2(SO_4)$** |

It is interesting to note that the very weak band at 892 $cm^{-1}$ in the spectrum of $Na_2Cu(SO_4)_2{\cdot}2H_2O$ splits into two comparatively strong bands at 867 and 859 $cm^{-1}$ in the spectrum of $Na_2Cu(SO_4)_2$ – these bands are attributed to Cu–O bond vibrations. The higher intensity of these bands reflects the existence of different sulfate ions on one hand, and on the other - the extent of covalency of the Cu–O bonds. Thus, we could conclude that stronger interactions between the $Cu^{2+}$ ions and the sulfate tetrahedra occur in the anhydrous compound as compared to those in the hydrate salt. Additionally we want to add that the spectrum of the anhydrous copper sulfate resembles too much to that presented in [25].

## IV. CONCLUSION

Several conclusions could be made on the basis of the experiments described in the present paper: (i) Owing to the buffer effect of the sodium cations the lattice parameters and volumes of the unit cells of the solid solutions are not changed considerably as compared to those of the unit cell of the zinc blödite. The hydrogen bonds in the blödite phases are also assumed to undertake the strain caused by the isodimorphously included copper ions. (ii) The degree of distortion of the $[M(H_2O)_4(SO_4)_2]$ clusters in the solid solutions increases as compared to that in the zinc blödite structure as deduced from the X-ray measurements of the single crystals due to the Jahn-Teller effect. (iii) The TG-TDA-DSC analyses reveal two steps of dehydration of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ and $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2{\cdot}4H_2O$. The dihydrates obtained at about 130 ºC convert into two polymorphic modifications of the anhydrous phases at temperatures higher than 200 ºC. (iv) The six-coordinated $Zn^{2+}$ ions forming distinct structural motives $[Zn(H_2O)_4(SO_4)_2]$ in the blödite phases transform into five-coordinated ones forming trigonalbipyramids, which are linked in 3D structure (higher temperature form). (v) In the course of dehydration the solid solution $Na_2Zn_{0.86}Cu_{0.14}(SO_4)_2{\cdot}4H_2O$ retains the crystal structures of the products of dehydration of $Na_2Zn(SO_4)_2{\cdot}4H_2O$ as deduced from the X-ray diffraction studies at elevated temperature. (vi) Contrary, no intermediate crystal hydrates are obtained after dehydration of $Na_2Cu(SO_4)_2{\cdot}2H_2O$. (vii) The large numbers of bands distributed over much wide frequency ranges point to the existence of more than two crystallographically different tetrahedra building up the structures of the anhydrous phases. These spectroscopic findings indicate widely different sorts of strong and weak bands between the copper ions and the sulfate anions. (viii) The spectroscopic experiments indicate that the tetrahedra in the anhydrous salts exhibit stronger distortion with respect to the S–O bond lengths as compared to that with respect to O–S–O bond angles. (ix) The Cu–O interactions in the anhydrous sodium copper sulfate are assumed to be stronger than those in the kröhnkite.

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