SYNTHESIS AND CHARACTERIZATION OF LIMITED MIXED SODIUM MANGANESE - SODIUM COPPER SULFATE DIHYDRATES WITH A KRÖHNKITE-TYPE STRUCTURE AND THEIR ANHYDROUS ANALOGUES

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ABSTRACT

The investigations reported in this contribution were carried out with respect to the possible application of the title solid solutions as precursors for the preparation of energy storage materials owing to their ability to store and transport sodium ions. On the basis of the solubility data combined with X-ray powder diffraction, it has been found that kröhnkite and Mn-kröhnkite form limited solid solutions, irrespective of their isostructurness due to the different effective ionic radii of Cu²⁺ and Mn²⁺ ions, the difference in the lattice parameters of both kröhnkites, and the influence of the Jahn-Teller effect on the distortion of the MO₆ polyhedra. The solid solutions Na₂Cu₁₋ₓMnₓ(SO₄)₂·2H₂O were characterized by means of X-ray powder diffraction, vibrational spectroscopy, TG-DTA-DSC and SEM methods. A new method for the synthesis of anhydrous sodium manganese copper sulfates is proposed. Two types of anhydrous solid solutions Na₂Cu₁₋ₓMnₓ(SO₄)₂ and Na₂CuxMn₁₋ₓ(SO₄)₂ with saranchinaite and alluaudite-type structures, respectively, are obtained after heating the hydrated solid solutions at 350°C. Additionally to the anhydrous solid solutions unidentified solid phases are obtained.

Keywords: kröhnkite-type solid solutions, solubility diagram, vibrational spectroscopy, phase transitions, X-ray powder diffraction.

INTRODUCTION

This contribution is a part of our several-years research on the formation and properties of solid solutions among the three dimensional double sulfates of 3d-transition metals with blödite- and kröhnkite-type crystal structures. The results are reported in our previous papers, as follows: limited blödite-type solid solutions Na₂M₁₋ₓCuₓ(SO₄)₂·4H₂O (M = Co, Zn, Ni) are obtained by crystallization in the Na₂Cu(SO₄)₂-Na₂M(SO₄)₂-H₂O systems at 25°C [1-4]; a continuous series of blödite-type solid solutions Na₂Co₁₋ₓMgₓ(SO₄)₂·4H₂O is obtained by crystallization in the Na₂Co(SO₄)₂-Na₂Mg(SO₄)₂·4H₂O system at 25°C [5]; limited blödite- and kröhnkite-type solid solutions Na₂Ni₁₋ₓMnₓ(SO₄)₂·4H₂O and Na₂Mn₁₋ₓNiₓ(SO₄)₂·2H₂O are obtained by crystallization from the solutions containing manganese and nickel ions [6]. The compounds with blödite- and kröhnkite-type structures are attractive for scientists since they are considered to be used as precursors for the preparation of energy storage materials owing to their ability to store and transport alkali ions [7-11 and Refs. therein]. For example, Marinova et al. reported that the alluaudite phase Na₂Mn₂₋₄SO₄·2H₂O prepared from Na₂Mn(SO₄)₂·2H₂O demonstrates better electrochemical properties than the lithium manganese phospho-olivine LiMnPO₄ [9].

Na₂Cu(SO₄)₂·2H₂O (kröhnkite) and Na₂Mn(SO₄)₂·2H₂O (Mn-kröhnkite) belong to a large family of natural and synthetic compounds built up of kröhnkite-type octahedral-tetrahedral chains. According to the classification scheme proposed by Fleck et al. both salts crystallize in the structural type D [12, 13]. Recently, we have re-
ported the crystal structure of synthetic kröhnkite [4]. Na$_2$Cu(SO$_4$)$_2$·2H$_2$O and Na$_2$Mn(SO$_4$)$_2$·2H$_2$O crystallize in the monoclinic SG $P2_1/c$ ($Z = 2$) with the following lattice parameters: Na$_2$Cu(SO$_4$)$_2$·2H$_2$O - $a = 5.812(1)$ Å, $b = 12.650(3)$ Å, $c = 5.516(2)$ Å, $\beta = 108.38(1)^\circ$, $V = 384.9$ Å$^3$; Na$_2$Mn(SO$_4$)$_2$·2H$_2$O - $a = 5.824(1)$ Å, $b = 12.999(1)$ Å, $c = 5.497(1)$ Å, $\beta = 106.05(1)^\circ$, $V = 399.9$ Å$^3$ (the structure of the manganese salt is reported in a previous paper of one of the authors (DS) [14]). The structures consist of MO$_4$(H$_2$O)$_2$ octahedra which share four corners with sulfate tetrahedra, thus forming chains [M(SO$_4$)$_2$(H$_2$O)$_2$] along [001]. The chains are linked by Na$^+$ ions and hydrogen bonds, thus forming layers. Additionally, the latter form 3D structure through Na$^+$ ions and hydrogen bonds. The SO$_4$ tetrahedra act as polydentate ligands – they are involved in metal–oxygen bonds including Na$^+$ and M$^{2+}$ cations. Both metal octahedra are distorted with respect to the M–O bond lengths (the distortion parameters $\Delta_{\text{oct}}$ have values of 0.01261 for kröhnkite and 0.00038 for Mn-kröhnkite; calculations are made according to Ref. [15]). The water molecules are linked to M$^{2+}$ ions via the shortest M–O bond distances (bond lengths Cu–OH$_2$ and Mn–OH$_2$ have values of 1.9386 and 2.145 Å, respectively). The different M–O bond lengths in both compounds are responsible for the formation of hydrogen bonds of different strength due to the different metal–water interaction, i.e. to the different synergetic effect of the M$^{2+}$ ions. The hydrogen bond strength as deduced from $v_{\text{OD}}$ of the matrix-isolated HDO molecules is reported in a previous paper of one of the authors (DS) [16].

Crystal structure of kröhnkite is shown in Fig. 1.

The present paper aims at studying the formation of solid solutions Na$_2$Cu$_{1-x}$Mn$_x$(SO$_4$)$_2$·2H$_2$O between the isostructural kröhnkite and Mn-kröhnkite in a wide concentration range ($0 < x < 1$) as a first step for the preparation of anhydrous solid solutions – materials for sodium batteries. For this purpose we have studied the solubility in the system Na$_2$Cu(SO$_4$)$_2$–Na$_2$Mn(SO$_4$)$_2$–H$_2$O at 25°C [17]. The method of isothermal decrease of supersaturation was used to reach the equilibrium between the liquid and solid phases in the Na$_2$Cu(SO$_4$)$_2$–Na$_2$Mn(SO$_4$)$_2$–H$_2$O system at 25°C (the different experimental steps of the method are reported in Refs. [1, 18]. The method used guarantees the receipt of homogenous solid solutions. Saturated solutions containing different ratios of the salts were vigorously stirred for 3-4 days. The concentrations of the sodium copper and sodium manganese sulfates in the aqueous solutions and solid solutions were determined, as follows: the copper ion concentration was determined iodometrically. The total concentration of the sulfate ions was determined after precipitation as PbSO$_4$ with Pb(NO$_3$)$_2$. The precipitate was dissolved in complexon III and Pb$^{2+}$ were determined complexometrically at pH 5.5-6 using xylenol orange as indicator. The concentration of the sodium manganese sulfate was calculated by difference. The method of Trendafelov and
Balarew for an algebraic indirect identification of the solid phase compositions was applied to calculate the compositions of the completely dry solid solutions [19]. Anhydrous solid solutions were prepared by heating the hydrated samples at 350°C for two days. The reagents used were “p.a.” quality. The distribution coefficients, describing the partitioning of the Cu$^{2+}$ and Mn$^{2+}$ ions between the liquid and solid solutions were calculated according to the equations:

\[
\begin{align*}
D_{\text{Cu/Mn}} &= \frac{C_{\text{Cu(S)}}}{C_{\text{Mn(L)}}} \frac{C_{\text{Mn(L)}}}{C_{\text{Cu(S)}}} \\
D_{\text{Mn/Cu}} &= \frac{C_{\text{Mn(S)}}}{C_{\text{Cu(L)}}} \frac{C_{\text{Cu(L)}}}{C_{\text{Mn(S)}}}
\end{align*}
\]

where C are the concentrations in mass % of the copper and manganese ions in the liquid (L) and dry solid phases (S), respectively.

The infrared spectra were recorded on a Nicolet iS5 Fourier transform interferometer at ambient temperature over the frequency range of 4000 - 400 cm$^{-1}$ (resolution < 2 cm$^{-1}$). 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). The Raman spectra were recorded with a Horiba Jobin-Yvon LabRAM HR800 spectrometer using a 600 l/mm grating and a 633 nm He-Ne laser line for excitation. The samples were placed under the 50x achromatic objective of an Olympus BX41 microscope and measured in back scattering configuration. The laser power on the sample was kept below 5.54 mW so that no heating and dehydration effects on the powder sample could be observed.

The X-ray powder diffraction data were collected within the range from 5° to 80° 2θ (step 0.02° 2θ, counting time 35 s/step) on a Bruker D8 Advance diffractometer with CuKα radiation and LynxEye detector. The lattice parameters of the anhydrous solid solutions were determined using the powder pattern calculation program FullProf Suite v.3.00 (Rodríguez-Carvajal, J., Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr 1990, 127) and those of the anhydrous solid solutions with a program for least square unit cell refinements (LSUCR). The X-ray powder diffraction patterns at elevated temperature (temperature interval 25 - 400°C) were obtained using a PANalytical Empyrean equipped with a multichannel detector (Pixel 3D) using Cu Kα (45 kV-40 mA) radiation in the 10 - 100° 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 performed on air (heating rate 5°C per minute).

Simultaneous TG–DTA curves were obtained applying a computerized combined apparatus for thermal analysis LABSYS Evo, 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°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°C min$^{-1}$ and oxidizing gas flow rates of 20 ml min$^{-1}$. The DSC measurements were recorded on a 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 - 20 mg).

Scanning electron microscopy (SEM) of selected samples was performed on a JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with an ultrahigh resolution scanning system (ASID-3D) in regimes of secondary electron image (SEI). The accelerating voltage was 20 kV, I ~ 65 μA and the pressure was of the order of 10$^{-4}$ Pa. The samples were gold coated with coating times of ~40 sec. The particles size is additionally measured with program LINCE-Linear Intercept v.2.4.2.

RESULTS AND DISCUSSION

Solubility diagram of the three-component Na$_2$Cu(SO$_4$)$_2$-Na$_2$Mn(SO$_4$)$_2$-H$_2$O system at 25°C

The above system is studied from a saturated solution of the copper compound up to a saturated solution of the manganese one. The solubility diagram is shown in Fig. 2 and the experimental solubility data are summarized in Table 1. Two crystallization fields of solid phases are observed in the solubility diagram – a large crystallization field of solid solutions having kröhnkite as a matrix and a comparatively narrow crystallization field of solid solutions having Mn-kröhnkite as a matrix. The experiments show that the Mn-kröhnkite incorporates up to 16 mol % copper ions, while kröhnkite incorporates up to 8 mol % manganese ions. The solubility diagram
points a large miscibility gap extended from a solid solution Na$_2$Cu$_{0.92}$Mn$_{0.08}$(SO$_4$)$_2$·2H$_2$O to a solid solution Na$_2$Cu$_{0.16}$Mn$_{0.84}$(SO$_4$)$_2$·2H$_2$O. The distribution coefficient of the manganese ions between the liquid phases and solid solutions $D_{\text{Mn/Cu}}$ has a mean value 0.04, while $D_{\text{Cu/Mn}}$ has a mean value of 0.66. X-ray powder diffraction patterns of the solid solutions are presented in Fig. 3 and the respective lattice parameters of the solid solutions are given in Table 2.

The experimental results point that irrespective of their isostructurness both krohnkites form limited solid solutions owing to several reasons: (i) different effective ionic radii of Cu$^{2+}$ and Mn$^{2+}$ ions (0.73 Å vs. 0.83 Å); (ii) different lattice parameters $b$, $\beta$ and unit cell volumes $V$, and (iii) the influence of the Jahn-Teller effect on the strong distortion of the CuO$_6$ polyhedra.

### Table 2. Lattice parameters of solid solutions Na$_2$Cu$_{1-x}$Mn$_x$(SO$_4$)$_2$·2H$_2$O.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
<th>$\beta$, $^\circ$</th>
<th>$V$, Å$^3$</th>
</tr>
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<td>$x = 0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>single crystals [4]</td>
<td>5.812(1)</td>
<td>12.650(3)</td>
<td>5.516(2)</td>
<td>108.38(1)</td>
<td>384.9</td>
</tr>
<tr>
<td>this paper</td>
<td>5.818(1)</td>
<td>12.659(2)</td>
<td>5.510(2)</td>
<td>108.35(1)</td>
<td>385.3</td>
</tr>
<tr>
<td>$x = 0.05$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.820(2)</td>
<td>12.669(3)</td>
<td>5.512(1)</td>
<td>108.35(2)</td>
<td>385.7</td>
<td></td>
</tr>
<tr>
<td>$x = 0.07$</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>5.823(1)</td>
<td>12.673(3)</td>
<td>5.513(1)</td>
<td>108.36(1)</td>
<td>386.2</td>
<td></td>
</tr>
<tr>
<td>$x = 0.84$</td>
<td></td>
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<td></td>
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<tr>
<td>5.819(2)</td>
<td>12.954(1)</td>
<td>5.492(2)</td>
<td>106.28(1)</td>
<td>397.4</td>
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<tr>
<td>5.819(3)</td>
<td>12.969(2)</td>
<td>5.491(2)</td>
<td>106.19(2)</td>
<td>398.0</td>
<td></td>
</tr>
<tr>
<td>$x = 0.94$</td>
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<td></td>
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<tr>
<td>5.820(2)</td>
<td>12.983(3)</td>
<td>5.492(2)</td>
<td>106.12(2)</td>
<td>398.7</td>
<td></td>
</tr>
<tr>
<td>$x = 1$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>this paper</td>
<td>5.818(2)</td>
<td>12.990(1)</td>
<td>5.493(3)</td>
<td>106.08(1)</td>
<td>399.9</td>
</tr>
<tr>
<td>$x = 1$</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>single crystals [14]</td>
<td>5.824(1)</td>
<td>12.999(1)</td>
<td>5.497(1)</td>
<td>106.05(1)</td>
<td>399.9</td>
</tr>
</tbody>
</table>
\[ = 983 \text{ cm}^{-1}, \nu_2 = 450 \text{ cm}^{-1}, \nu_3 = 1105 \text{ cm}^{-1}, \nu_4 = 611 \text{ cm}^{-1} \]

In solids the internal vibrations of the sulfate ions are expected to shift to lower or larger wavenumbers due to the interactions with other entities in the structure.

Na\(_2\)Cu(SO\(_4\))\(_2\)·2H\(_2\)O and Na\(_2\)Mn(SO\(_4\))\(_2\)·2H\(_2\)O crystallize in the monoclinic space group (\(Z = 2\); factor group symmetry \(C_{2h}\)) with 38 atoms in the unit cell and are characterized with 114 zone-center degrees of freedom. The SO\(_4^{2-}\) ions (four SO\(_4^{2-}\) ions in the unit cell located on \(C_1\) sites) and the water molecules (four molecules in the unit cell located on \(C_1\) sites) contribute 48 internal modes to the 114 optical zone-center modes – 36 internal modes for the tetrahedral ions and 12 internal modes for the water molecules).

The low site symmetry of the sulfate ions causes 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 the nine internal modes of the tetrahedral ions are of A symmetry. Additionally, under the factor group symmetry \(C_{2h}\) each species of A symmetry splits into four components – Ag + Bg + Au + Bu (related to interactions of identical oscillators, correlation field effect; see correlation diagram in Fig. 4). Consequently, the 36 optical modes for the SO\(_4^{2-}\) ions are subdivided into 9Ag + 9Bg + 9Au + 9Bu modes. As was mentioned above the water molecules contribute 12 modes, as follows – 3Ag + 3Bb + 3Au + 3Bu.

The remaining 63 optical modes are distributed between the translational and librational lattice modes, as follows: 42 translations for (Na\(^+\), SO\(_4^{2-}\), H\(_2\)O – all in \(C_1\) site symmetry, Cu\(^{2+}\) – in \(C_1\) site symmetry; 9Ag + 9Bg + 12Au + 12Bu) and 24 librations (SO\(_4^{2-}\) and H\(_2\)O; 6Ag + 6Bb + 6Au + 6Bu).

Thus, the 114 vibrational modes of the unit cell decompose, as follows:

\[ \Gamma = 27Ag + 27Bg + 30Au + 30Bu; \text{ where } 1Au + 2Bu \text{ are translations (acoustic modes).} \]

Since the crystal structures of the kröhnkites are centrosymmetric, the Raman modes display g-symmetry,
and their IR counterparts display u-symmetry (mutual exclusion principle).

Raman and infrared spectra of Na$_2$Cu(SO$_4$)$_2$·2H$_2$O are commented briefly in Refs. [21 - 23] and those of Na$_2$Mn(SO$_4$)$_2$·2H$_2$O in Refs. [9, 16]. Fig. 5 shows infrared spectra of solid solutions Na$_2$Cu$_{1-x}$Mn$_x$(SO$_4$)$_2$·2H$_2$O in the region of the normal vibrations of the sulfate ions and water librations (for comparison the infrared spectra of the neat double hydrates are also given). Raman spectra of both kröhnkites are presented in Fig. 6. The assignments of the respective infrared and Raman bands are summarized in Table 3.

The analysis and the comparison of the vibrational spectra of the neat sulfate hydrates and solid solutions Na$_2$Cu$_{1-x}$Mn$_x$(SO$_4$)$_2$·2H$_2$O reveal:

(i) The ν$_3$ modes of the sulfate ions in both compounds are spread over wide spectral intervals thus indicating comparatively strong energetic distortions of the sulfate tetrahedra. ∆ν$_3$ calculated from the infrared spectra has values of 128 cm$^{-1}$ and 132 cm$^{-1}$ for the manganese and copper salts, respectively. This spectroscopic finding correlates with the geometric distortions of the tetrahedra – ∆r has values of 0.031 and 0.035 Å for the tetrahedra in the manganese and copper compounds, respectively (∆r is the difference between the longest and the shortest bond length in the respective sulfate tetrahedra [3, 14]).

(ii) One interesting feature of the infrared spectra of both compounds is the grouping of the bands in the ν$_3$ region, thus confirming the conclusion that the sulfate tetrahedra are strongly energetically distorted (the bonds of the shorter S–O bond lengths, i.e. the stronger bonds have a considerable contribution to the bands at larger wavenumbers).

(iii) Another evidence for the strong energetic distortion of the sulfate ions in both compounds is the high intensity of the infrared bands corresponding to ν$_1$ (see Fig. 5). According to Petruševski and Ćojprajanov the intensity of the bands corresponding to ν$_1$ reflects the degree of distortion of the sulfate ions in series of salts – the higher the intensity of these bands is the stronger the geometric distortion of the polyatomic ions is [24].

(iv) The values of ∆ν$_3$ are larger than those of ∆ν$_4$, thus pointing that the sulfate ions are stronger distorted with respect to the S–O bond lengths as compared to the O–S–O bond angles (see Table 3).

(v) The appearance of more infrared and Raman bands corresponding to ν$_1$ than three bands expected according to the site symmetry analysis is owing to the interactions between the identical sulfate oscillators (crystal field effect). The larger number of the bands and the appearance of two bands for ν$_1$ in the Raman spectrum of the copper salt is a sign for the stronger crystal field effect on the sulfate vibrations in kröhnkite than that in Mn-kröhnkite due to the smaller unit cell volume of the copper compound (384.9 Å$^3$(Cu) vs. 399.9 Å$^3$(Mn)).
(vi) It is important to mention that the most of the infrared and Raman bands appear at different frequencies due to the different energy of the g- and u-motions (see Table 3).

(vii) The water librations (rocking and wagging) appear in the spectral region below 1000 cm\(^{-1}\). The assignments of the bands are made by analogy to those for the Tutton compounds, M’M’’(XO\(_4\))\(_2\)·6H\(_2\)O (M’ = K, Rb, Cs; M’’ = Mg, Co, Ni, Cu, Zn; X = S, Se) [25 - 27]. Thus, the comparatively strong bands centered at 748 and 769 cm\(^{-1}\) and those at 582 cm\(^{-1}\) and 573 cm\(^{-1}\) originate from the rocking and wagging modes of the water molecules in the manganese and copper crystal hydrates, respectively. The appearance of the rocking modes for the copper compound at larger frequency as compared to those for the manganese one is an evidence for the formation of stronger hydrogen bonds in the former compound.

(viii) The hydrogen bonds in kröhnkite are stronger than those in Mn-kröhnkite as deduced from the bands corresponding to both the \(v_{\text{OH}}\) and the \(v_{\text{OD}}\) modes of matrix-isolated HDO molecules due to the stronger synergetic effect of the copper ions (see Table 3; the \(v_{\text{OD}}\) motions are taken from Ref. [21]). The data in Table 3 point also that the molecular symmetry of the water molecules in the manganese compound is close to \(C_{2v}\) (\(\Delta \nu\) is 16 cm\(^{-1}\)), while \(\Delta \nu_{\text{OD}}\) for the copper compound has a value of 53 cm\(^{-1}\), i.e. the water molecules in kröhnkite demonstrate a considerable deviation from \(C_{2v}\) symmetry.

(ix) The inclusion of Cu\(^{2+}\) ions in the structure of Mn-kröhnkite changes the shape of the spectrum of the neat manganese compound: a new band (shoulder) at 1170 cm\(^{-1}\) appears in the spectrum of Na\(_2\)Cu\(_{0.06}\)Mn\(_{0.94}\)(SO\(_4\))\(_2\)·2H\(_2\)O due to \(v_3\) of the sulfate ions coordinated to the included copper ions in [Cu–OSO\(_4\)] clusters. The lower frequency bands at 1057, 1080 and 1064 cm\(^{-1}\) (manganese compound) coalesce into two well-distinguished bands at 1098 and 1068 cm\(^{-1}\). When the concentration of the copper ions in the solid solutions increases up to 12 mol % (sample Na\(_2\)Cu\(_{0.12}\)Mn\(_{0.88}\)(SO\(_4\))\(_2\)·2H\(_2\)O) a new shoulder at 1054 cm\(^{-1}\) arises, which is also owing to the included copper ions. The inclusion of Mn\(^{2+}\) ions in the copper compound

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>(\text{Na}_2\text{Mn}(\text{SO}_4)_2\cdot2\text{H}_2\text{O})</th>
<th>(\text{Na}_2\text{Cu}(\text{SO}_4)_2\cdot2\text{H}_2\text{O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_{\text{Ow}})</td>
<td>3208 3082</td>
<td>2392 2376 2371 2318</td>
</tr>
<tr>
<td>(v_{1\text{Ow}})</td>
<td>1709 1623</td>
<td>1097 1080 1045 1023 1150 1108 1135 1120</td>
</tr>
<tr>
<td>(v_{3\text{Ow}})</td>
<td>984 989 990 992 984</td>
<td>748 769 750</td>
</tr>
<tr>
<td>(L_6(\text{H}_2\text{O}))</td>
<td>823 892</td>
<td>582 573 569</td>
</tr>
<tr>
<td>(L_6(\text{H}_2\text{O}))</td>
<td>647 630 606 648 633 620 647 603 658 649</td>
<td>639 633</td>
</tr>
<tr>
<td>(v_4(\text{SO}_4))</td>
<td>471 455 464 446 474 450 462 447</td>
<td>621 613</td>
</tr>
</tbody>
</table>
also changes the profile of the spectra in the region of the lower wavenumbered components of ν₃: the band at 1054 cm⁻¹ decreases in intensity and the bands at 1078 and 1108 cm⁻¹ transform into one intensive band at 1088 cm⁻¹ and a shoulder at 1004 cm⁻¹ (see the spectrum of the sample Na₂Cu₀.93 Mn₀.07 (SO₄)₂·2H₂O). The lower frequency parts of the spectra of the host compounds (regions of ν₄, ν₁ and water librations) are not influenced by the copper and manganese guest ions.

**Thermal behavior and phase transitions**

The anhydrous sodium manganese sulfate is reported to form two minerals known as alluaudite (Na₂Mn₂(SO₄)₃) and vanthoffite (Na₆Mn(SO₄)₄) [9, 28, 29]. The mass loss behavior of Mn-kröhnkite is commented briefly in a previous paper of one of the authors (DM). The thermal dehydration occurs stepwise, thus forming a monohydrate as an intermediate product at 1088 cm⁻¹ and a shoulder at 1004 cm⁻¹ (see the spectrum of the sample Na₂Cu₀.93 Mn₀.07 (SO₄)₂·2H₂O). The lower frequency parts of the spectra of the host compounds (regions of ν₄, ν₁ and water librations) are not influenced by the copper and manganese guest ions.

The anhydrous sodium manganese sulfate is reported to form two minerals known as alluaudite (Na₂Mn₂(SO₄)₃) and vanthoffite (Na₆Mn(SO₄)₄) [9, 28, 29]. The mass loss behavior of Mn-kröhnkite is commented briefly in a previous paper of one of the authors (DM). The thermal dehydration occurs stepwise, thus forming a monohydrate as an intermediate product with an alluaudite-type structure [9]. Na₆Mn(SO₄)₄ (M = Mg, Mn, Fe, Co, Ni, Zn) with a vanthoffite-type structure (monoclinic space group P2₁/c) are reported to crystallize from Na₂SO₄-MSO₄ systems. The copper analog was not synthesized [28]. Recently, Sharma et al. prepared single crystals of Na₆Mn(SO₄)₄ by crystallization from an aqueous solution containing a 3:1 molar ratio of Na₂SO₄ and MnSO₄·H₂O at 80°C and solved its crystal structure. It crystallizes in the monoclinic SG P2₁/c (a = 9.6910(5) Å; b = 9.281(5) Å; c = 8.258(5) Å; β = 113.124(5)°; V = 683.1(7) Å³; Z = 2) [29]. Alluaudite crystallizes in the monoclinic SG C2/c (a = 12.764(1) Å; b = 12.943(1) Å; c = 6.5871(6) Å; β = 115.780(3)°; V = 979.95(25) Å³; Z = 4) [9].

The literature data concerning the dehydration of kröhnkite are contradictory. According to Silber and Cot the dehydration of Na₂Cu(SO₄)₂·2H₂O occurs in one step, thus forming two polymorphic modifications of the anhydrous product [30]. Nagase and Yokobayashi reported that Na₂Cu(SO₄)₂·H₂O is obtained as an intermediate product [31]. Recently, the anhydrous sodium copper sulfate Na₂Cu(SO₄)₂ (mineral saranchinaite) has been found in sublimes of the Saranchinaitovaya fumarole, Naboko Scoria Cone, Tolbachik volcano, Kamchatka (Russia). It crystallizes in monoclinic space group P2₁ with lattice parameters: a = 9.0109(5) Å, b = 15.6355(8) Å, c = 10.1507(5) Å, β = 107.079(2)°, V = 1367.06(12) Å³, Z = 8. The authors provided results for the preparation of the anhydrous compound by heating kröhnkite at 200°C using a HTXRD method [32]. Testasicca et al. reported that kröhnkite is stable up to 150°C and forms a mixture of copper and sodium sulfates at higher temperature. The authors do not comment the formation of an anhydrous sodium copper sulfate [33]. Our previous experimental results from TG, DTA and DSC analyses show that the escape of the water molecules from kröhnkite occurs in one step. This finding was confirmed with X-ray diffraction at elevated temperature – kröhnkite exists up to 250°C according to our experiments and loses completely the water molecules at about 300°C. The enthalpy of dehydration of Na₂Cu(SO₄)₂·2H₂O has a value of 354.0 kJ mol⁻¹ and that of formation -2996.5 kJ mol⁻¹ [2].

TG–DTA–DSC curves of solid solutions Na₂Cu₁-x Mnₓ(SO₄)₂·2H₂O and neat double salts are shown in Fig. 7. Several inflexion points are observed on the TG curve of the manganese kröhnkite at about 168, 206 and 238°C. The first inflexion point corresponds to the loss of 6.48 % of the weight, the second to the 2.58 % and the third to 1.72 %. Thus, the total dehydration of the manganese compound completes at about 236°C (∆mᵦ = 10.94 mass %; ∆mₑp = 10.78 mass %). The process of dehydration is registered on the DTA curve with one intensive endoeffect at 160°C and two weak endoeffects at 204 and 233°C. At temperatures higher...
than 240°C a process of decomposition of the manganese kröhnkite probably begins. It is important to mention that all these processes occur continuously as TG curve shows (no intervals of stability of intermediate products are observed). DSC curve is characterized with two endoeffects at 160 and 229°C. $\Delta H_{\text{deh}}$ calculated for the first intensive effect has value of 363.6 kJ mol$^{-1}$. $\Delta H_{\text{deh}}$ for the two water molecules has value of 394.7 kJ mol$^{-1}$ and $\Delta H_q$ of Na$_2$Mn(SO$_4$)$_2$·2H$_2$O is -3368.3 kJ mol$^{-1}$. The included Cu$^{2+}$ ions in the crystals of Mn-kröhnkite

Table 4. X-ray powder diffraction data of saranchinaite prepared after heating kröhnkite at 350°C for two days (in Å for CuKα).

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change the profiles of the TG curve. The dehydro of Na$_2$Cu$_{0.12}$Mn$_{0.88}$(SO$_4$)$_2$·2H$_2$O begins at about 150ºC and completes at about 230ºC, thus forming an anhydrous solid solution. The first inflexion point on the TG curve of the sample Na$_2$Cu$_{0.12}$Mn$_{0.88}$(SO$_4$)$_2$·2H$_2$O at 177ºC corresponds to the loss of 7.86 mass %, thus producing Na$_2$Cu$_{0.12}$Mn$_{0.88}$(SO$_4$)$_2$·0.5H$_2$O (the theoretical mass loss is 8.21 mass %). The full separation of the crystallization water occurs at about 230ºC (theoretical mass loss is 10.94 mass%; experimental - 9.60 mass %). The process of dehydro is registered on the DTA curve with three endothermic peaks – one intensive peak centered at 165ºC related to the release of 1.5 water molecules and two weak endoeffects at 194 and 224ºC. DSC measurements show that the total $\Delta H_{deh}$ of Na$_2$Cu$_{0.12}$Mn$_{0.88}$(SO$_4$)$_2$·2H$_2$O is 402.2 kJ mol$^{-1}$ (372.5 kJ mol$^{-1}$ for the removal of 1.5 water molecules and 29.7 kJ mol$^{-1}$ for the separation of the last 0.5 water molecules). $\Delta H_f$ of Na$_2$Cu$_{0.12}$Mn$_{0.88}$(SO$_4$)$_2$·2H$_2$O has value of -3336 kJ mol$^{-1}$.

The sample Na$_2$Cu$_{0.93}$Mn$_{0.07}$(SO$_4$)$_2$·2H$_2$O displays a TG curve identical with that of kröhnkite. The two intensive peaks at 190 and 206ºC on the DTA curve of the copper salt coalesce into one peak at 198ºC on the DTA curve of the solid solution. According to DSC measurements (peak maximum at 193ºC) $\Delta H_{deh}$ and $\Delta H_f$ of Na$_2$Cu$_{0.93}$Mn$_{0.07}$(SO$_4$)$_2$·2H$_2$O have values of 329.6 kJ mol$^{-1}$ and -2987 kJ mol$^{-1}$, respectively, values which are close to those for the neat Na$_2$Cu(SO$_4$)$_2$·2H$_2$O (see above in the text).

Anhydrous solid solutions were prepared by heating the hydrates at 350ºC for two days. The X-ray diffraction patterns of anhydrous compounds prepared from Na$_2$Cu(SO$_4$)$_2$·2H$_2$O and Na$_2$Cu$_{1-x}$Mn$_x$(SO$_4$)$_2$·2H$_2$O (x = 0.05, 0.07) are shown in Fig. 8 (the pattern of saranchinaite according to [32] is also presented; see Fig. 8a). The pattern of the Na$_2$Cu(SO$_4$)$_2$·2H$_2$O heated at 350 ºC shows reflections of an unidentified phase (or phases) (reflections marked with asterisks; Fig. 8b) additionally to the saranchinaite-phase. The lattice parameters calculated for SG $P2_1$ have the following values: $a = 8.983(4)$ Å; $b = 15.552(7)$ Å; $c = 10.155(2)$ Å; $\beta = 107.07(3)^\circ$; $V = 1356.1$ Å$^3$. The sample Na$_2$Cu$_{0.95}$Mn$_{0.05}$(SO$_4$)$_2$·2H$_2$O exhibits a diffractogram identical to that of saranchinaite (Fig. 8c). New additional reflections appear in the diffraction pattern of this anhydrous sample (Fig. 8d). The lattice parameters of the anhydrous sample are: $a = 9.0224$ Å; $b = 15.5625$ Å; $c = 10.1601$ Å; $\beta = 107.43^\circ$; $V = 1361.1$ Å$^3$. The slight increase in the lattice parameters of the anhydrous solid solution as compared to those of pure saranchinaite is in agreement with the larger ionic radius of the guest manganese ions.

The phase transitions of the solid solutions having as a matrix the copper compound were monitored also by means of X-ray diffraction at elevated temperature (reflections of new phase are marked with asterisks). Fig. 9a shows that kröhnkite is stable up to 250ºC and at 300ºC it transforms into anhydrous compound with a saranchinaite-type structure. The solid solution Na$_2$Cu$_{0.93}$Mn$_{0.07}$(SO$_4$)$_2$·2H$_2$O preserves the crystal structure of kröhnkite up to 250ºC and of saranchinaite at higher temperature (Fig. 9b). The comparison of Figs. 8b and 9a, allows us to assume that the longer heating time favors the decomposition of kröhnkite.

The inclusion of Cu$^{2+}$ ions in the structure of Mn-kröhnkite yields anhydrous solid solutions with an alluaudite-type structure and a new phase (see Fig. 10). Marinova et al. reported that the solid solution Na$_2$Co$_{0.63}$Mn$_{0.37}$(SO$_4$)$_2$·4H$_2$O heated at 350 ºC for 40 h transforms into two phases - solid solutions Na$_2$(Co/Mn)$_2$(SO$_4$)$_3$ with an alluaudite-type structure and solid solutions Na$_6$(Co/Mn)(SO$_4$)$_4$ with a vanthoffite-type structure [11]. Thus, the new phase formed after heating the solid solutions reached in manganese is vanthoffite
Na$_2$Mn(SO$_4$)$_4$ (marked with asterisks). The lattice parameters of the solid solution with an alluaudite-type structure obtained by heating Na$_2$Cu$_{0.12}$Mn$_{0.88}$(SO$_4$)$_2$·2H$_2$O have values of: $a = 12.808(8)$ Å; $b = 12.951(7)$ Å; $c = 6.567(3)$ Å; $\beta = 115.91(5)^\circ$; $V = 980.1$ Å$^3$.

Fig. 9. Evolution of the X-ray patterns at elevated temperature of: a) Na$_2$Cu(SO$_4$)$_2$·2H$_2$O and b) Na$_2$Cu$_{0.93}$Mn$_{0.07}$(SO$_4$)$_2$·2H$_2$O (asterisks, unidentified phases).

Fig. 10. X-ray powder diffraction patterns of Na$_2$Mn(SO$_4$)$_3$ and Na$_2$Cu$_{1-x}$Mn$_x$(SO$_4$)$_2$ ($x = 0.94$ and $0.88$; asterisk, vanthoffite phase).

Fig. 11 shows the morphology of the kröhnkites (Fig. 11a, c) and of respective anhydrous compounds (Figs. 11b and d). The measurements reveal that the difference in the shape of the particles of the hydrated salts and the corresponding anhydrous analogs is negligible.

Fig. 11. SEM images of hydrated samples and their anhydrous analogs (a) Na$_2$Cu(SO$_4$)$_2$·2H$_2$O; b) Na$_2$Cu(SO$_4$)$_2$; c) Na$_2$Mn(SO$_4$)$_2$·2H$_2$O; d) Na$_2$Mn(SO$_4$)$_3$. 
All samples consist of isometric to slightly oval shaped particles. The particle size varies in a large range from 1.3 to 16.2 μm. The determination of the grain sizes is made by intercept line method (program Lince Liner Intercept 2.4.2e).

CONCLUSIONS

Two types of solid solutions of a kröhnkite-type structure are formed in the system kröhnkite – Mn-kröhnkite – water, irrespective of the isostructureness of the salts due to the different ionic radii of the metal ions (0.73(Cu) vs. 0.83(Mn)), different lattice parameters and the Jahn-Teller effect. The distribution coefficient of the manganese ions between the liquid phases and solid solutions $D_{Mn/Cu}$ has a mean value 0.04, while $D_{Cu/Mn}$ has a mean value of 0.66.

The vibrational spectra reveal that the $ν_3$ modes of the sulfate tetrahedra in both compounds are spread over wide spectral ranges, thus indicating a strong deviation of the sulfate ions from $T_d$ symmetry in agreement with the structural data. The stronger Cu–OSO$_3$ bonds and the smaller unit cell volume of the copper compound (384.9 Å$^3$ (Cu) vs. 399.9 Å$^3$ (Mn)) lead to a stronger sulfate ion distortion in the copper compound as compared to that of the sulfate tetrahedra in the manganese one. The hydrogen bonds in kröhnkite are stronger than those in Mn-kröhnkite due to the stronger Cu–O$_w$ interactions, i.e. to the stronger synergetic effect of the copper ions. The appearance of more vibrational bands corresponding to $ν_3$ than three bands expected according to the site symmetry analysis is owing to the strong crystal field effect.

TG-DTA-DSC analyses reveal that the thermal dehydration of the solid solution Na$_2$Cu$_{0.12}$Mn$_{0.88}$$(SO_4)_2$·2H$_2$O forms as an intermediate product Na$_2$Cu$_{0.12}$Mn$_{0.88}$(SO$_4$)$_2$·1.5H$_2$O, while the solid solution Na$_2$Cu$_{0.93}$Mn$_{0.07}$$(SO_4)_2$·2H$_2$O transforms directly into an anhydrous salt. Solid solutions having a copper compound as a matrix form after heating at 350ºC anhydrous solid solutions with a saranchinaite-type structure and unidentified solid phase or phases. The solid solutions having a manganese sulfate as a matrix also yield after complete dehydration two phase systems – solid solutions with an alluaudite-type structure and a solid phase with a vanthoffite-type structure, Na$_6$Mn(SO$_4$)$_4$.

Acknowledgements

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