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New phase obtained at mutual transformations of zinc hydroxy-salts

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The hydroxy-salt minerals are normally stable over a small range of external conditions (such as Eh, pH, T, P, concentration of solutions, etc.). Therefore, they are converted easily into each other through changes in the crystal structure. The investigated initial zinc hydroxy salts are characterized by specific layered structures in which the zinc cations are both octahedrally and tetrahedrally coordinated as the ratio of octahedrally to tetrahedrally-coordinated zinc atoms is 3:2 or 3:1. In the process of detailed examination of the transformations during reaction of Zn-hydroxy nitrates (3:2 ratio) with sulfate solutions, Zn-hydroxy sulfates (3:1 ratio) with nitrate solutions and exchange reactions of Zn-hydroxy sulfate samples with alkali iodides, a stable phase with powder diffraction pattern not described in the ICDD database was obtained. Data of XRD, SEM-EDS, DTA-TG-MS and FTIR were used to characterize the new phase. The obtained new phase is characterized by a greater value of d_{001} = 17.84 Å comparing to that of the initial samples (d_{001} between 9.70–11.10 Å). The chemical data shows the only presence of cations of zinc and sulfur. The new phase chemical formula calculated from the chemical and thermal analyses could be defined as $Zn_4(OH)_6SO_4 \cdot 2–2.25H_2O$. The formation conditions as well as the mechanism of transformation were described and discussed: the new phase is formed at pH = 4.5–8 and the main mechanism of transformation is dissolution and subsequent crystallization.

Keywords: new Zn-hydroxy sulfate phase, characteristic data, transformation mechanism.

INTRODUCTION

Zinc hydroxy-salts are widespread in nature and are of interest in different areas. Primary sulfides of zinc are an important component of sulfide ores. In the oxidation zones, zinc is predominantly represented by hydroxy salts ($Zn_{1+x}(OH)_2A_{x/m}^{m-} \cdot nH_2O$, where A = Cl^-, CO_3^{2-}, SO_4^{2-}), carbonates (smithsonite) and silicates (hemimorphite) [1–2]. Zinc hydroxy-salt minerals have been also described as zinc and brass shifting products as well as zinc-containing slags [3–4]. Podda et al. [5] have established that the precipitation of hydrozincite from mine waters occurs due to photosynthetic microorganisms.

The excellent resistance of zinc and zinc-plated steel under natural conditions is due to the formation of a protective corrosion layer of zinc hydroxy-salts (zinc rust). The mineral composition of this layer highly depends on the exposure environment and its protective action is determined by both the morphology and the arrangement of the layer crystals [6]. Zinc hydroxide salts have been also investigated for other useful properties: ion-exchange and sorption properties [7–11], photo-catalytic properties [12], hydrogen-gas sensing properties [13], and as precursors of nanosized ZnO for various applications [14–15].

The hydroxy salt minerals normally are stable over a small range of external conditions (e.g. Eh, pH, T, P, concentration of solutions, component ratio, impurities, etc.) and are commonly associated with many other minerals of similar compositions in same parageneses. Unlike stable rock-forming minerals, these minerals react to minor environmental changes through changes in the crystal structure [16–17]. The strict limits of the conditions of formation and stability imply complete or partial dissolution and subsequent crystallization as a transformation mechanism of their mutual transformations.

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The investigated zinc hydroxy salts are characterized by specific layered structures in which the zinc cations are both octahedrally and tetrahedrally coordinated. The fundamental building unit of the structures is a sheet of octahedra with vacancies that share upper and lower faces with tetrahedra (Fig. 1). The octahedron is built mainly of OH groups as only in the structures of zinc hydroxysulfates some of the OH groups of the zinc octahedron are substituted by oxygen atoms of the sulfate groups. Zn-tetrahedra consist of three OH-groups of the octahedral layer (of the free octahedron), and the fourth (apical) position is directed to the interlayer and is occupied by a H_2O molecule, chlorine anions or oxygen atoms of the CO_3 group. The ratio of filled to vacant octahedral sites is 3:1 or 6:1 and respectively, the ratio of octahedrally to tetrahedrally-coordinated zinc atoms is 3:2 or 3:1. Thus, the octahedral-tetrahedral layer can be characterized as "interrupted decorated sheet" [18]. The zinc-hydroxide layer has a positive charge, which is compensated by the non-hydroxide anions in the structures. The hydroxide layer in the structure of Zn hydroxy sulfates (gordaite and Ca-gordaite) has a negative charge because of the simultaneous occupation of the two types of non-hydroxide anion sites in the tetrahedra and octahedra. This "excess" charge is compensated by $[Na(H_2O)_6]^+$ or $[Ca(H_2O)_9]^{2+}$ groups introduced into the interlayer. Sodium or calcium cations act as "anionic bond-valence absorbers" while the water molecules as bond-valence transformers in the sense of Schindler & Hawthorne [19]. This variety of different functionalities in the mineral structures of the group is a prerequisite for mutual transformations by different mechanisms: ionic (cationic and anionic) exchange, water-anion exchange; dehydration – rehydration, etc. On the other hand, the field and experimental studies show that the mutual transformations of hydroxy-salt minerals are typical of the weathering zones and are one of the reasons for the varied paragenesis.

Consecutive conversion was also observed in experiments to form zinc rust on galvanized steel under different conditions: in the Cl^-environment the sequence is ZnO-hydrozincite- simonkolleite-gordaite, while in the urban or industrial environment it is ZnO-hydrozincite- namuwite and with the time the ZnO and the hydrozincite gradually disappear [21–22].

The reactions of zinc hydroxy-nitrate with Zn-, Ni- and Co-chloride solutions are the first experimental study of transformations of zinc hydroxy salts [23]. The system has been studied later and pseudomorphic and topotaxic character of the transformations with oriented nucleation and crystal growth has been proposed [24]. Reactions of the

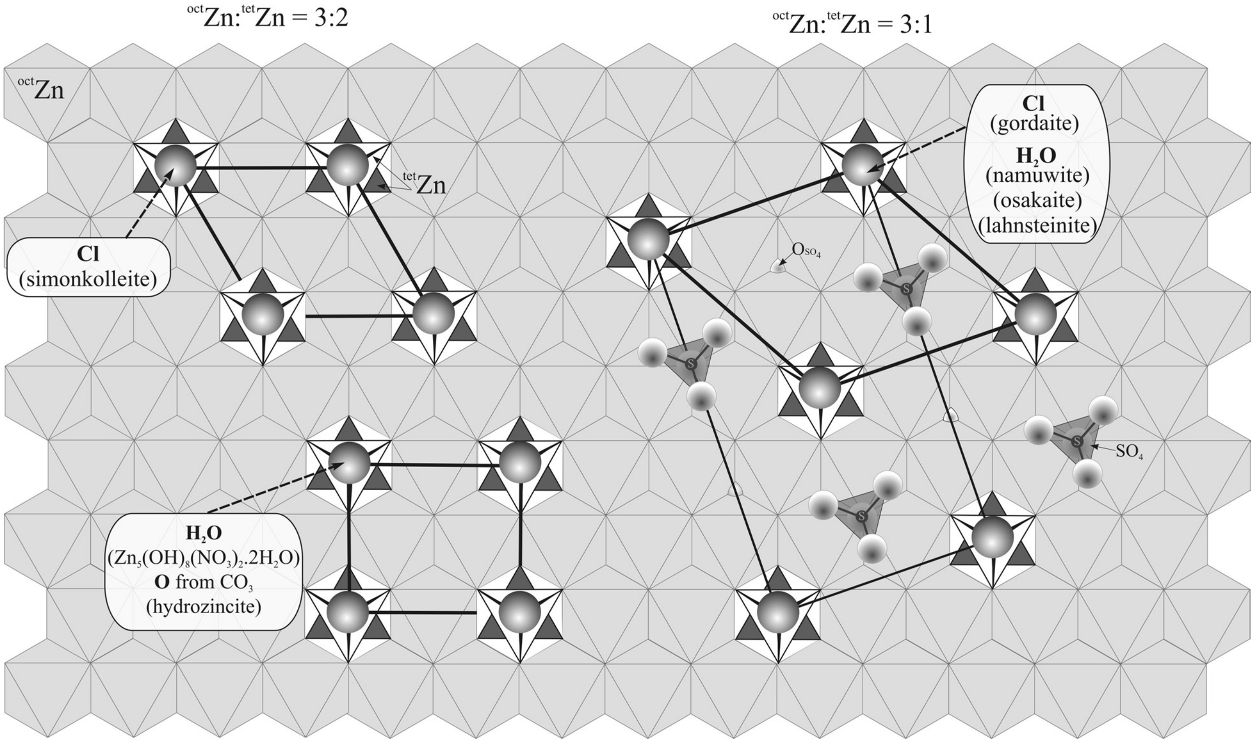

Fig. 1. Unit cells and atom distributions of Zn-hydroxy-salts on projection 001 of Zn hydroxide sheet.

same precursor with terephthalate and benzoate aqueous solutions have been studied allowing an ion exchange mechanism with a change in the arrangement of the vacant octahedra [7].

In the process of a detailed examination of the transformation mechanisms (in both the 3:1 and 3:2 systems) during reaction of Zn-hydroxy nitrates with sulfate solutions and Zn-hydroxy sulfates (namuwite, gordaite) with nitrate solutions and the exchange relationships in the sulfate agents, a stable phase with powder diffraction pattern not described in the ICDD database was obtained.

The aim of this work is to present the characterization data of this new phase (chemical composition, XRD, FTIR, thermal behavior: DTA-TG-MS, SEM: morphology) and to give an idea of the formation conditions and the transformation mechanism.

EXPERIMENT

Initial materials: In the present study synthetic analogues of Zn-hydroxy-salts minerals were used. This is due to the inaccessibility of a sufficient amount of mono-mineral in natural conditions and the fact that the natural samples are always with isomorphic impurities (mainly copper) which would hamper the interpretation of the results. In all experiments analytical grade chemicals were used.

Namuwite ($Zn_4(OH)_6(SO_4)\cdot 4H_2O$) was obtained by mixing of 1g ZnO powder with 30 ml 0.5M solution of $ZnSO_4$ with periodic stirring for 72 hours.

Gordaite ($NaZn_4(OH)_6(SO_4)Cl\cdot 6H_2O$) was obtained by mixing of 1g ZnO powder with 30 ml mixed solution of 0.5M $ZnSO_4$ and 1.5M NaCl in a ratio 1:1 at periodic stirring for 120 hours.

Ca-gordaite ($CaZn_8(OH)_{12}(SO_4)_2Cl_2\cdot 9H_2O$) was obtained through reaction between 1g mixed ZnO-CaO powder in a ratio 5:1 and 30 ml mixed solution of 1M $ZnSO_4$ and 1M $ZnCl_2$ in a ratio 1:1 at periodic stirring for 72 hours.

Nitrate compound ($Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$) was obtained by alkalization of 1M $Zn(NO_3)_2$ solution by titration with 1M NaOH or by urea [$(NH_2)_2CO$)] hydrolysis at 95 °C to pH=7.

After syntheses, the obtained samples were washed in distilled water and dried in air at room temperature.

Obtaining of new phase: *1) During reaction of both Zn-hydroxy nitrates with sulfate solutions and Zn-hydroxy sulfates with nitrate solutions:* The samples of initial $Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$ were treated with sodium or ammonium sulfate at pH 5, 6, 7 and 8 for 24–48 h; The samples of initial namuwite and gordaites were treated with $NaNO_3$ at 25 and 55 °C, $Mg(NO_3)_2$, $Sr(NO_3)_2$.

All experiments were performed at room temperature with periodic stirring. The resulting products were washed with distilled water, filtered and dried in air.

2) During attempts of exchange reaction in sulfate samples with alkali iodides: The initial samples of namuwite, gordaite and Ca-gordaite were dispersed in solutions of NaI or KI. The solid to solution ratio was adjusted to provide at least a tenfold excess of exchangeable ion. The reaction duration was one – three days. The resulting products were washed with distilled water, filtered and dried in air.

All experiments of synthesis, exchange and transformation are repeated at least twice.

Analyses: The initial and treated samples (new phase) were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FTIR) and differential thermal analyses and the thermogravimetry with mass-spectroscopy (DTA-TG-MS).

The powder XRD patterns were recorded on a TuR M62 diffractometer using filtered Co Kα radiation in the 2Θ range 4–80°, step size 0.02°.

The SEM investigations and chemical analysis of some samples were performed by SEM fitted with energy dispersive spectrometer (EDS). Apparatus JEOL – model JSM-6010PLUS/LA, 20kV accelerating voltage and spot size 65 nm.

The infrared spectra were recorded by a Tensor 37 FTIR Bruker spectrometer in the spectral region 400–4000 cm^{-1}. The spectra were collected at room temperature on samples prepared by the standard KBr pallet technique after N_2-purging and with a spectral resolution of 4 cm^{-1} after averaging over 72 scans.

The DTA-TG-MS were carried out on the DTA-TG analyzer SETSYS2400, SETARAM at the following conditions: temperature range from 20 to 1000 °C, in a static air atmosphere, with a heating rate of 10 °C min^{-1}, and 10–15 mg samples weight. Simultaneous analysis of the evolved gases was performed via mass spectrometry using an OmniStar mass spectrometer connected to the TG apparatus. The intensities related to the main m/z value of the following volatiles H_2O (18), O_2 (32) and SO_2 (64) were examined.

RESULTS AND DISCUSSION

Initial samples: The powder X-ray diffraction shows that all obtained products are pure and well crystallized materials (Fig. 2a, c, e). The XRD-patterns correspond to the phases in the ICDD database as follows: $Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$ – PDF card No 24-1460; namuwite – PDF card No 35-0528;

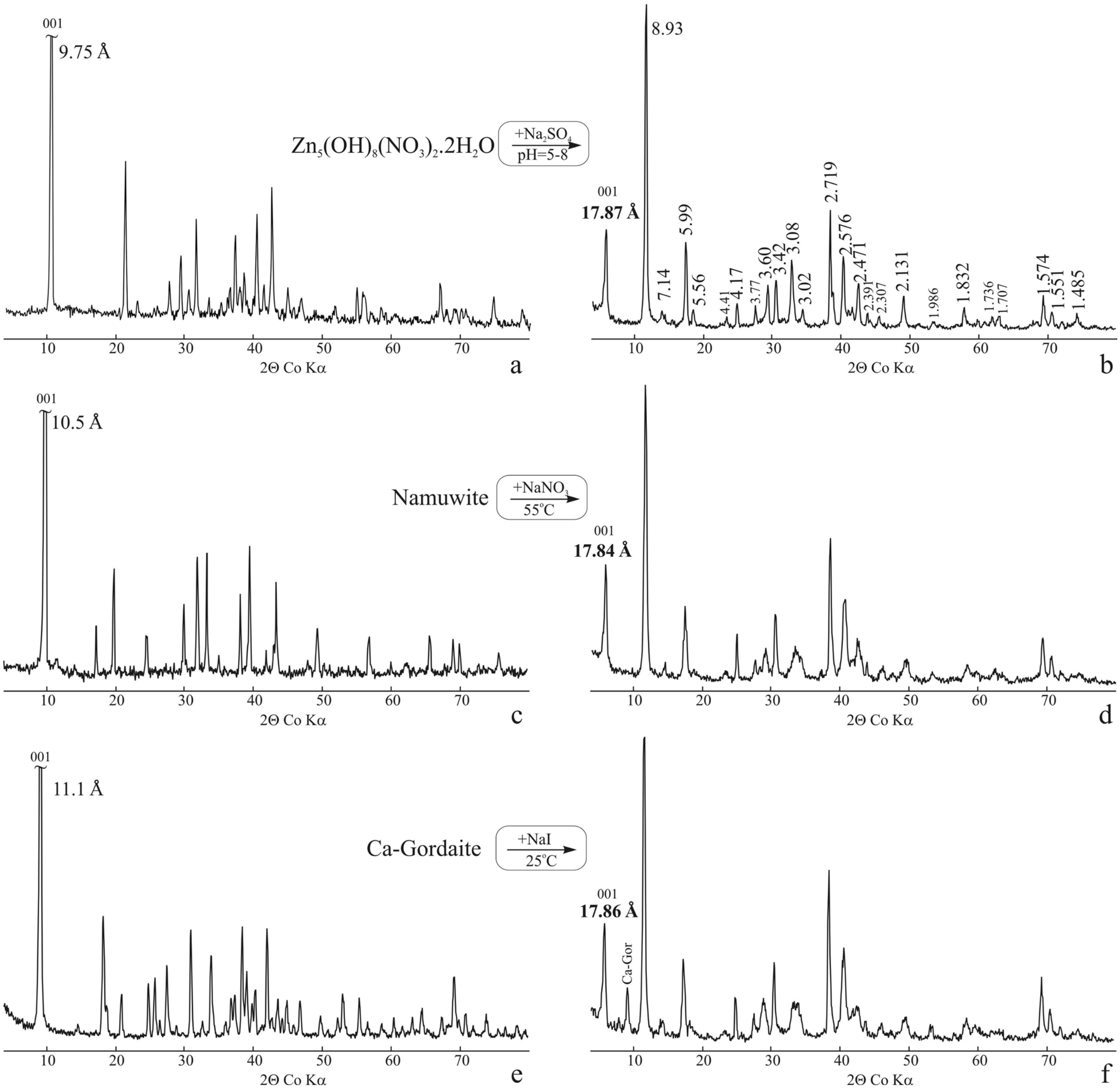

Fig. 2. Powder XRD patterns of: *a–b*) initial and treated with Na_2SO_4 $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$; *c–d*) initial and treated with $NaNO_3$ namuwite; *e–f*) initial and treated with NaI Ca-gordaite.

gordaite – PDF card No 88-1359 and Ca-gordaite – PDF card No 89-0851.

Plated to finely lined crystals with hexagonal or trigonal outlines are observed in SEM in accordance with the hexagonal symmetry of the octahedral layers of the initial samples. The size of the crystals depends on the method of synthesis. The NaOH precipitated crystals have a cross-sectional area of up to 2 μm and a thickness of 0.03–0.1 μm. Crystals obtained by hydrolysis of urea as well as from ZnO are in the order of magnitude larger than previous ones and reach cross-sections of 10–30 μm and thickness of 0.5 to 2 μm (Fig. 3a, c, e). Among the crystals of $Zn_5(OH)_8(NO_3)_2.2H_2O$ phase (Fig. 3a) according to its monoclinic symmetry (SG C2/m, a = 19.48 Å, b = 6.238 Å, c = 5.517 Å [25]), various pinacoid and prism crystal forms are observed as their relative development varies depending on the synthesis method. The gordaite crystals (SG P-3; a = 8.3556 Å, c = 13.0252 Å according to [26]) are scaly specimens with characteristic spiral subdivisions on the basal wall (Fig. 3c). The namuwite mineral (SG P-3; a = 8.33Å, c = 10.54Å according to [27]) is represented by finely flaky to finely

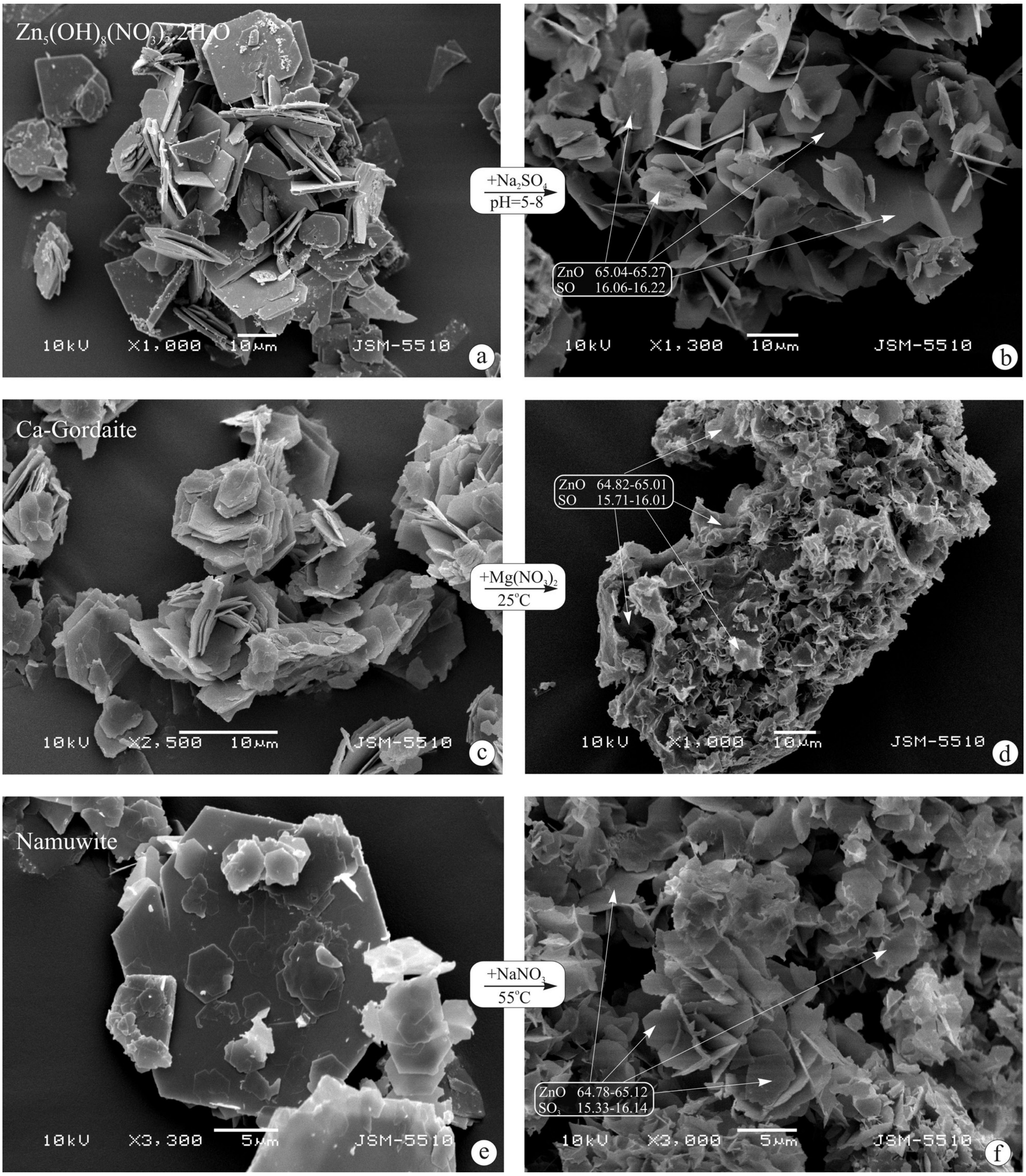

Fig. 3. SEM microphotographs of: *a–b*) initial and treated with Na_2SO_4 $Zn_5(OH)_8(NO_3)_2·2H_2O$; *c–d*) initial and treated with $Mg(OH)_2$ Ca-gordaite; *e–f*) initial and treated with $NaNO_3$ namuwite. Chemical data of new phase obtained by EDS are also presented.

cryptic crystals (sometimes bent), with hexagonal outlines (Fig. 3e).

The new phase: During investigation of the transformation relationships between nitrate hydroxy salts (^{oct}Zn : ^{tet}Zn ratio = 3:2) and sulfate hydroxy salts (3:1 ratio) an unidentified phase in the ICDD database was obtained (Fig. 2b). This phase is a product of two type of reactions: interaction between both the nitrate hydroxy salts with sulfate solutions (Na_2SO_4 and $(NH_4)_2SO_4$; pH = 4.5–8) and the sulfate hydroxy salts with nitrate solutions ($NaNO_3$, $Mg(NO_3)_2$ and $Sr(NO_3)_2$).

As can be seen, the phase is characterized by a greater value of the d-spacing of the first reflection (d_{001} = 17.84 Å), which is in multiple dependence with other reflexes of 8.93 Å and 5.99 Å. The hk0 characteristic lines of the sulfate zinc hydroxy salts (d_{110} = 4.17 Å, d_{210} = 2.719 Å, d_{140} = 1.574 Å) are also registered in the XRD pattern of the new phase (Fig. 2b), which suggests the similarity or proximity of the hydroxide layers. The EDS chemical data of the products obtained from both types of hydroxy sulfate in the presence of various nitrates shows that only cations of zinc and sulfur were found in the phase composition without presence of an alkaline or alkaline earth cations and other non-sulfate anions (Fig. 3 b, d, f). At that way, this phase can be defined as zinc-hydroxy sulfate hydrate. Such kinds of the known minerals are osakaite ($Zn_4(OH)_6SO_4{\cdot}5H_2O$), namuwite ($Zn_4(OH)_6SO_4{\cdot}4H_2O$) and lahnsteinite ($Zn_4(OH)_6SO_4{\cdot}3H_2O$). The thermal study data, however, shows that the water content is less than that of the hydroxy-sulfate salt minerals – namuwite and gordaite (Fig. 4). The new phase chemical formula calculated from the chemical and thermal analyses could be defined as $Zn_4(OH)_6SO_4{\cdot}$ 2–2.25H_2O. Less hydrated zinc hydroxy sulfate compounds are known and investigated in the lit-

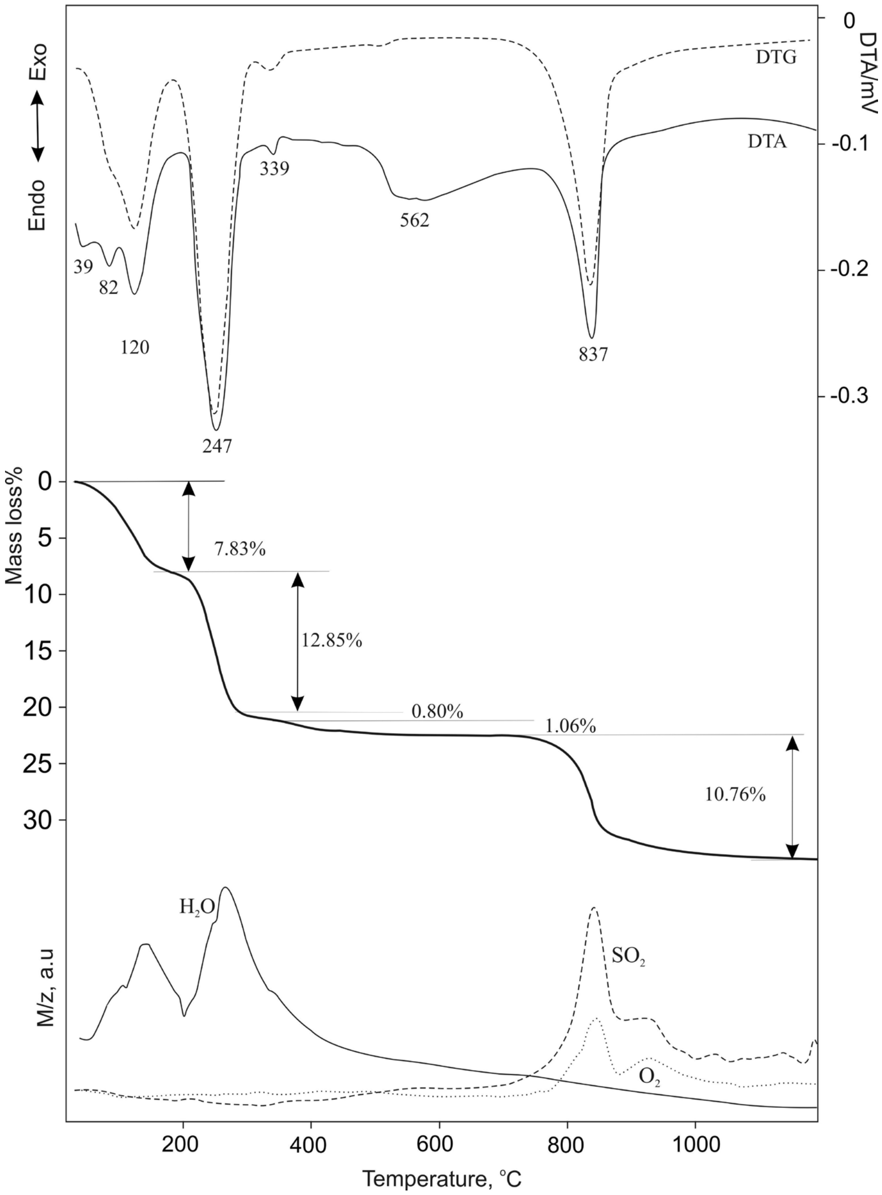

Fig. 4. DTA-TG(DTG)-MS data of the new phase obtained by treatment of $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ with Na_2SO_4.

erature ($Zn_4(OH)_6SO_4 \cdot 2H_2O$; $Zn_4(OH)_6SO_4 \cdot 1H_2O$ and $Zn_4(OH)_6SO_4 \cdot 0.5H_2O$), which however have been characterized by a completely different diffraction pattern [25, 28–30]. The comparison of the FTIR spectra of the new phase with the other sulfate hydroxy salts also shows some differences. Except the SO_4 (600, 1111 и 1060 cm^{-1}) and OH (3344 cm^{-1}) absorption bands, a weak water band (1624 cm^{-1}) and two weak bands at 1391 and 1506 cm^{-1} which very precisely correspond to a bidentate bonded carbonate group [31] are also observed in the infrared spectrum of the phase obtained from $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and Na_2SO_4 (Fig. 5b).

The presence of carbonate may be due to the NaOH used for synthesis of the starting zinc hydroxy nitrate. Since EDS shows no presence of carbonate, it could be assumed that the carbonate is most probably surface adsorbed.

It is interesting to note that a phase with the same powder XRD diffraction pattern has been obtained

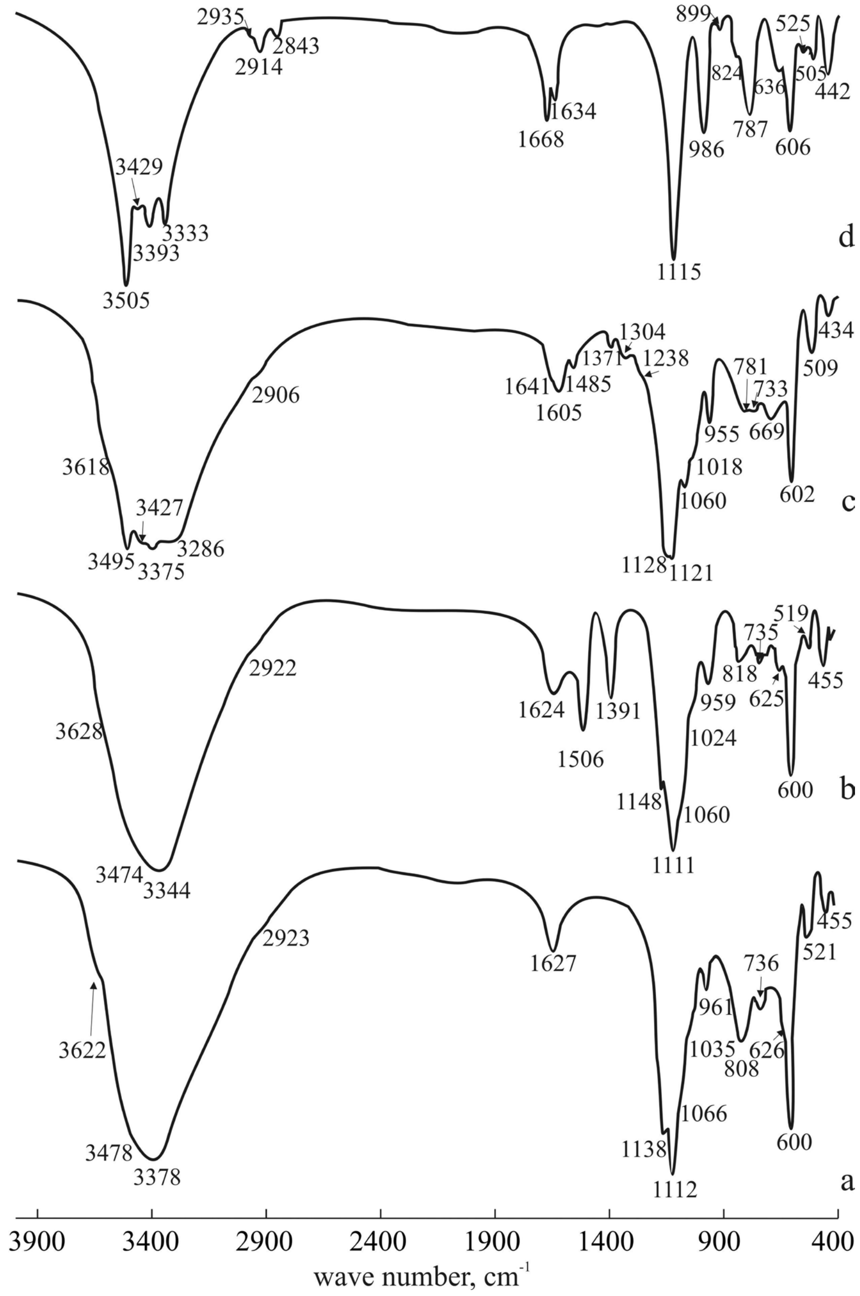

Fig. 5. FTIR spectra of: *a*) the new phase obtained by treatment of namuwite with NaI; *b*) the new phase obtained by treatment of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ with Na_2SO_4; *c*) namuwite; *d*) gordaite.

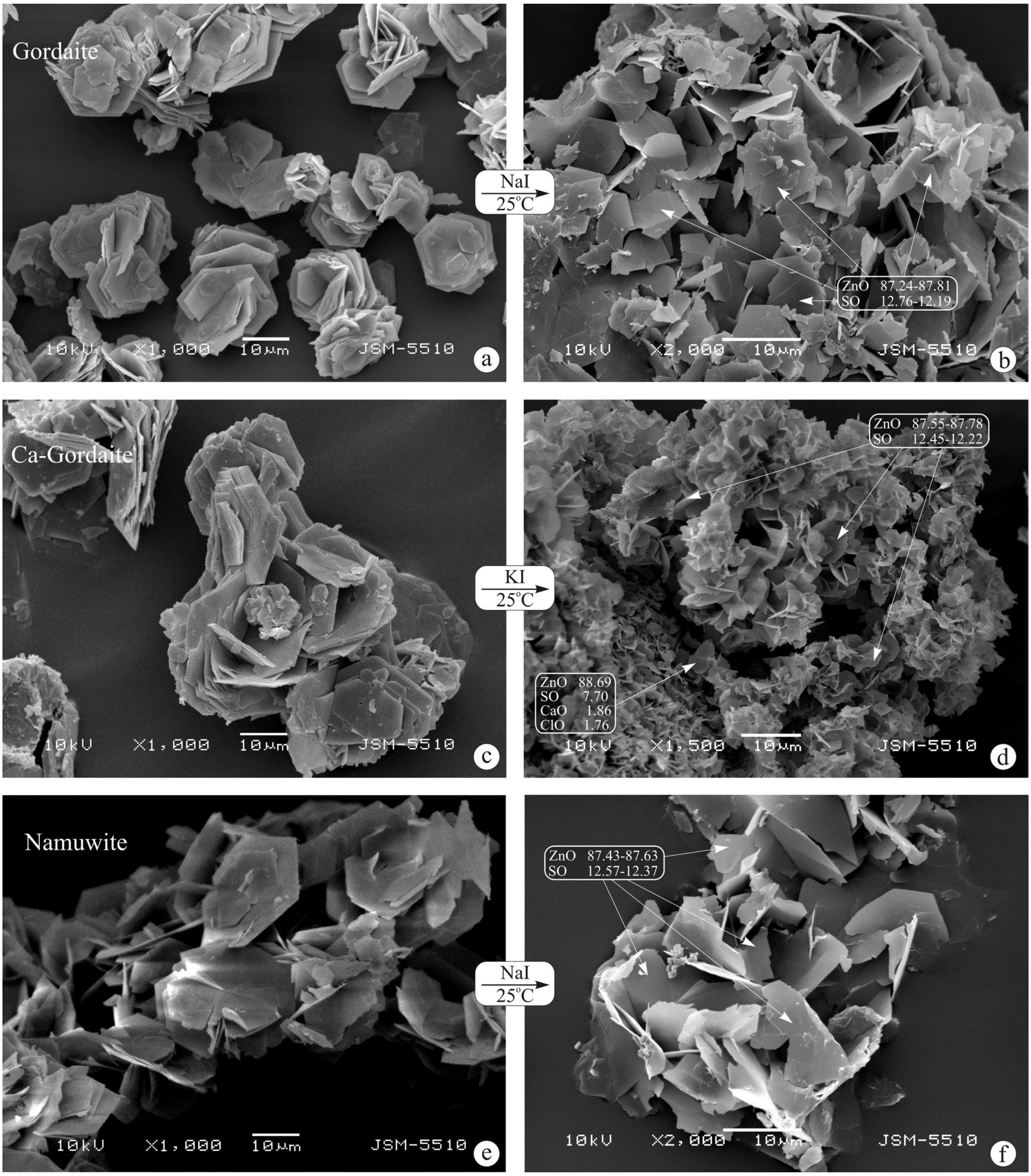

Fig. 6. SEM microphotographs of: *a–b*) initial and treated with NaI gordaite; *c–d*) initial and treated with KI Ca-gordaite; *e–f*) initial and treated with NaI namuwite. Chemical data of new phase obtained by EDS are also presented.

in the cation exchange reactions of the sulfate hydroxy-salt mineral gordaite with solution of $LiNO_3$ and $Ca(NO_3)_2$ [32–33]. The authors of this study claim that their obtained products are gordaites with compensating interlayer cations of Li^+ or Ca^{2+}. The greater value of the d-spacing of the first reflection they attributed to the bigger water content in the interlayer space, caused by the high hydration ability of Li^+ and Ca^{2+}. Unfortunately, chemical data for the presence of the two cations as well as any data for the increased content of interlayer water has not been provided in their study. Most likely, in their case, in an attempt to cation exchange in gordaites with nitrate salts, the same new phase was obtained.

Mechanism of the new phase formation: SEM data shows that the studied phase forms extremely thin, often curved hexagonal crystals with no relation to the orientation of the precursor crystals (Fig. 3b, d, f). This result suggests that the main mechanism of transformation is dissolution and subsequent crystallization.

From a crystal chemical point of view, the formation of pure hydroxy sulfates of the type $Zn_4(OH)_6SO_4 \cdot nH_2O$ in the presence of nitrates could be explained by the peculiarities of the apical position of the Zn tetrahedron from the hydroxide layer. This position is loaded with a half positive charge and can be occupied by water molecules in the minerals osakaite-namuwite-lahnsteinite or by chlorine anions in the structures of the gordaites. Apparently, the position could not be occupied by a large monovalent anion. In support of this, is also the structure peculiarities of the starting zinc hydroxy nitrate $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ in which the apical position of the zinc tetrahedra is occupied by water molecules (Fig. 1), and the NO_3 groups are located freely between the zinc tetrahedra [25].

The results of the experiments show that the pH of the solutions has a controlling role for the formation of one or another representative of zinc hydroxy sulfates by reaction between $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and sulfate solutions. It was found that at pH = 4.5–8, the new phase was formed, while under more acidic conditions (pH from 4.5 to 2.5), namuwite was obtained.

To investigate the effect of the size of the monovalent anion on its ability to occupy the apical position of the zinc tetrahedra, a series of experiments was performed by treating the two major types of zinc hydroxy sulfates (namuwite and gordaite) with solutions of NaI and KI. Sodium and potassium iodide solutions were selected for two reasons: (i) the large iodine size and (ii) the neutral character (pH ≈ 7) of the NaI and KI solutions. As in the case of nitrate anions the I^- anion is very large in order to be able to occupy the apical position, and as a result, the studied new phase was again obtained (Fig. 1c).

The chemical and morphological data (Fig. 6) of the products obtained by treatment with iodide solutions showed that the resulting products are completely identical to the investigated new phase obtained in the presence of nitrate anions. The DTA-TG(DTG)-MS curves showed also identical thermal behavior. Only difference was observed in the FTIR spectrum, where the presence of carbonate was not registered (Fig. 5a), which supports the assumption that in the product obtained by reaction between $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and sodium or ammonium sulfate solutions, the carbonate could be surface adsorbed. However, the ability of the structure to absorb and include a carbonate group should not be completely excluded.

CONCLUSIONS

(i) A new zinc hydroxy sulfate phase with a composition $Zn_4(OH)_6SO_4.2–2.25H_2O$ was obtained. The conditions of three different ways of synthesis were established and described: during transformation reaction of Zn-hydroxy nitrates with sulfate solutions; Zn-hydroxy sulfates with nitrate solutions and exchange reaction of Zn-hydroxy sulfate samples with alkali iodides;

(ii) Data of XRD, SEM-EDS, DTA-TG-MS and FTIR were presented for characterizing the new phase;

(iii) The formation conditions as well as the mechanism of transformation were described and discussed: the new phase is formed at pH = 4.5–8 and the main mechanism of transformation is dissolution and subsequent crystallization. The possible reasons for its formation were discussed as well.

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НОВА ФАЗА, ПОЛУЧЕНА ПРИ ВЗАИМНИ ТРАНСФОРМАЦИИ НА ЦИНКОВИ ХИДРОКСИ-СОЛИ

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(Резюме)

Минералите хидроксисоли обикновено са стабилни в тесен диапазон на външни условия (като Eh, pH, T, P, концентрация на разтвори и др.). Поради тази причина, те се превръщат лесно един в друг чрез промени в кристалната им структура. Изследваните изходни цинкови хидроксисоли се характеризират със специфични слоести структури, в които цинковите катиони са координирани октаедрично и тетраедрично, като отношението на октаедрично- към тетраедрично координираните цинкови атоми е 3:2 или 3:1. В процеса на подробно изследване на трансформациите по време на взаимодействие на Zn-хидрокси нитрати (отношение 3:2) със сулфатни разтвори, Zn-хидрокси сулфати (отношение 3:1) с нитратни разтвори и обменни реакции на Zn-хидроксисулфатни образци с алкални йодиди, е получена стабилна фаза с прахова дифракция, която не бе намерена в базата данни на ICDD. За охарактеризиране на новата фаза са използвани данни от XRD, SEM-EDS, DTA-TG-MS и FTIR. Получената нова фаза се характеризира с по-голяма стойност d_{001} = 17,84 Å в сравнение с тази на изходните образци (d_{001} между 9,70–11,10 Å). Химичните данни показват само наличието на катиони на цинк и сяра. Новата фаза има химична формула $Zn_4(OH)_6SO_4\cdot 2–2,25H_2O$, която е изчислена от химичните и термичните анализи. Описани и дискутирани са условията на образуване, както и механизма на трансформация: новата фаза се образува при pH = 4,5–8 и основният трансформационен механизъм е разтваряне с последваща кристализация.