R E V I E W

on PhD thesis for receiving the educational and scientific degree "Doctor",
professional field: 4.4 Earth Sciences, doctoral program "Mineralogy and crystallography"

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Subject: **„ Crystal chemistry and thermal decomposition of copper and zinc hydroxy-sulfate minerals"**

Reviewer: Prof. Vladislav Vladimirov Kostov, PhD, IMC-BAS, Member of the scientific jury appointed by Order № 424РД-09/28.10.2021

1. Relevance of the problem developed in the dissertation in scientific and/or scientific-applied terms.

Synthetic and natural hydroxy sulphates, whose crystal chemical features and thermal characteristics are the subject of research in the dissertation meet the definition of anionic clays because they have a layered structure, charge of the layer, suggesting ion exchange and intercalation properties. Such compounds, as well as their derived products, are the subject of research due to their various properties such as catalysts, antacids, stabilizers, flame retardants, anion exchangers, heat pumps and others. In particular, the minerals of zinc and copper hydroxyl-salts are part of the evolution of sulphide deposits and due to the narrow limits of their stability, they are informative of the conditions of mineral formation and are indicators of changes in the environment in which this occurs. Their presence in spent mining and chalda indicates that they play an important ecological role in preventing the migration of toxic ions into the environment. These compounds are also the subject of research due to the fact that they are the main components of the corrosion layer of zinc, copper, brass and bronze products. Their study is a challenge, both because of their crystal chemical diversity in terms of cationic and anionic composition, and because of the easy, fast and most often reversible phase transitions that occur among members of this group with even minimal change in some of the parameters of the reaction environment in which they are formed. The doctoral student shows that she is well acquainted with the topicality and complex nature of the problems developed in the dissertation and this finds a synthesized expression in the formulation of goals and objectives, as well as selected synthetic techniques and analytical methods for studying the phases. The presented results fit into the hitherto known facts about the studied objects, but also bring new knowledge about them, both scientifically and scientifically and appliedly.

2. State of the problem and creative evaluation of the literary material

The doctoral student demonstrates a very good ability to successfully handle the scientific literature, selected according to the goals and objectives of the dissertation. 145 sources are cited. The literature review is aptly divided into three parts, which relate generally to: genesis and application, crystal chemical features and classification schemes of the studied compounds. Each of them is analysed creatively in terms of results achieved, as well as to identify opportunities for new

research to resolve controversial issues or lead to new knowledge. This approach subsequently leads to purposeful choices made in the actual experimental part and concerning the staging of the set syntheses, ion exchange reactions and techniques for determining the order of obtaining the different phases, isomorphic substitutions and their quantification and reversibility. Subsequently, the obtained own results are addressed and interpreted in view of their place in relation to the hitherto known knowledge of the studied objects.

3. Research methodology

The objects of study are mainly synthetic layered monocationic Cu^{2+} or Zn^{2+} and two-cationic (Cu-Zn) hydroxy-sulfate phases. Samples of one natural phase - serpierite from the Bulgarian lead-zinc deposit Zvezdel, Eastern Rhodopes were also studied.

One of the emphases of the research is on mastering various synthesis techniques such as: co-precipitation by drip alkalization of sodium sulfate sulfate solutions; co-precipitation of solutions at constant pH; solid-reagent reactions and reactions between hydroxysol and halide, sulphate or nitrate solutions (recrystallization and ion exchange).

The crystal chemical features of the studied compounds - layered nature, water content, and diversity of cationic and anionic composition, possibility of different types of phase transformations that occur under external influences such as heating or ion exchange require the application of a set of modern analytical methods for their study. The main analytical methods used for the purposes of the dissertation are: differential thermal analysis (differential scanning calorimetry) - thermogravimetry-mass spectroscopy (DTA (DSC) -TG-MS) and powder X-ray diffraction (PXRD). From the exposition of chapters 2 and 3 I am left with the impression that they have been sufficiently mastered by the doctoral student. Her knowledge exceeds the operators' skills in handling the equipment and allows her to convincingly interpret the results obtained. Additionally used are: scanning electron microscopy - electron probe microanalysis (SEM-EDS); Fourier transform infrared spectroscopy (FT-IR); single crystal XRD diffractometry (Single Crystal XRD), etc.

4. Analytical characteristics of the representativeness and reliability of the material on which the contributions of the dissertation are built.

The dissertation is written in good professional language, in a concise style. It is technically carefully designed and includes an introduction, literature review, experimental part, results and discussion, conclusion, contributions, cited literature. Contains 132 pages, which include 85 pcs. Figures, 20 pcs. Tables, 12 pages of literature, 17 pages of appendices. The illustrative part and the analytical data of the applications provide an opportunity for the reader to get directly acquainted with the specifics of the results obtained. Impressive are the precision of the speech and the in-depth detail of the results obtained in their interpretation, which is an indication of a very good knowledge of the studied materials and understanding of the processes that occur with them. An example of this are the issues related to the conditions of preparation of the synthetic analogue of the mineral lahnsteinite and the findings of this compound in nature.

In terms of crystal chemistry, the studied objects show the greatest sensitivity to ion exchange reactions affecting both the cationic and anionic part, as well as to the processes occurring with them

during heat treatment such as dehydration, dehydroxylation and separation of different gas phases (H_2O, Br_2, Cl_2, SO_2, and O2). The results of their application are observed as obtaining ion-exchanged forms of the initial products, synthesis of new phases, phase transitions, decomposition, and passing through various intermediates to reach the final ones. A set of mutually complementary methods has been used to adequately record these results. The applied basic analytical techniques - thermal analysis and powder X-ray diffraction, in addition, allow for reflection and quantification of the same phenomena from the observed reactions and processes. An example of this is the comparison of weight losses and accompanying thermal events related to the dehydration processes of the studied objects and the corresponding d-values of their basal reflexes, which mark the change in the size of interplanar distances in response to these events. This is most successfully illustrated for the synthetic analogues of Zn-hydroxy-sulphate minerals with the general formula: $Zn_4(OH)_6(SO_4)\cdot nH_2O$ (n = 5, 4, 3) - osakaite, namuwite, lahnsteinite and their derivatives. Undoubtedly, the joint presentation of the results of these studies strengthens their reliability and contributes to the persuasiveness of their interpretation.

5. Scientific and scientific-applied contributions of the dissertation:

In the course of the presentation the doctoral student presents results, some of which confirm older observations and facts about the objects of research. They are mainly related to the crystal chemical changes that occur for some of the studied phases during heating or exchange reactions. An example of this is the data obtained on the processes of thermal decomposition of namuwite and competently conducted studies to determine the maximum degree of isomorphic substitution of Zn^{2+} by Cu^{2+} in its structure.

However, Zlatka Delcheva has managed to highlight such results, which challenge the opinions currently adopted for these compounds. The results of the analysis of the dehydration of the material encompassing the compounds of the group of osakaite-namuwite-lahnsteinite provoke a new reading of the chemical formula of these minerals in terms of the crystal-structural role of water molecules. From a crystallochemical point of view, they can be said to be tetrahydrate (osakaite), trihydrate (namuwite) and dihydrate (lahnsteinite), respectively. These results are directly relevant to the nomenclature and place of these compounds in the currently accepted classification schemes for these compounds and are a challenge for future research.

Not a small part of the results of the dissertation brings new knowledge about the studied materials. Among the scientific and applied achievements are the results related to the production of bromine-containing amorphous phase in the thermal decomposition of Br-gordaite, as well as nanosized ZnO as a final product of decomposition of most Zn-hydroxy salts with possible application in catalytic industry. Among the scientific achievements, the solution of the crystal structure of a "new Zn-hydroxy-sulfate phase" undoubtedly stands out, confirming a pre-made theoretical model based on characteristic data and analysis of the thermal behavior of this new compound for science. Personal contributions are the preparation of new forms of gordaite: cationic Sr (by ion exchange) and anionic Br form (by direct synthesis and ion exchange). The other contributions are correctly indicated at the end of the dissertation.

6. To what extent are the dissertation and contributions personal work of the candidate?

The acquaintance with the dissertation unquestionably reveals the active participation of the doctoral student in the performance of differential thermal analysis (differential scanning calorimetry) -thermogravimetry-mass spectroscopy (DTA (DSC) -TG-MS) and powder X-ray diffraction experiments, as well as P in the analysis and description of the results obtained. Its participation in the synthesis of the samples and the production of their ion-exchanged forms is also indisputable. I am not as convinced about the degree of learning of single crystal X-ray analysis as a method for deciphering crystal structures. However, I know that Zlatka Delcheva has participated in some of the experiments and I believe that in the future she will upgrade her skills with new knowledge about this important research method, presented at an extremely high hardware and professional level at our institute. I accept that during her doctoral studies the dissertation student has acquired both theoretical knowledge and significant practical experience not only in the specific field of her research.

7. Evaluation of the publications on the dissertation: number, nature of the publications in which they are printed, citations.

There are three publications presented on the topic of the dissertation. The points received from them are 36.67 and they cover and exceed the minimum requirements of the current legal framework for obtaining the educational and scientific degree "Doctor" at IMC-BAS. For the period 2018-2020, the results obtained during the preparation of the dissertation are reflected in two papers with the rank of the journals in which Q4 was published and in one of the journals with rank Q2. So far, a total of four quotes have been noticed. The doctoral student regularly participates and presents her results with poster presentations in appropriate scientific forums such as the symposiums of the Bulgarian Crystallographic Society, the conferences of the Bulgarian Geological Society and others. Information about such participations in 9 forums for the period 2016-2021 is presented and she is the first author everywhere.

8. Critical remarks and motivated recommendations for future use of scientific contributions.

Along with the excellent impressions of the achieved results, which fully cover the goals and objectives of the dissertation, I have some critical remarks, but I will omit as insignificant those that relate to stylistics, punctuation and some of the terms used.

There is a separate part in Chapter 3. Results and Discussion and this is 3.2.2. Serperite. It reports mineralogical characteristics and data on a crystal structure of a representative of the group of devilline from the Bulgarian lead-zinc deposit Zvezdel, Eastern Rhodopes, solved for the first time in Bulgaria. The obtained structural data for this mineral give a new look at the crystal structure of this compound compared to those published so far, which is an indisputable achievement and not only for the Bulgarian mineralogical science. In describing the crystal structure, it is reported that: "there are four sulphate tetrahedra on both sides of the octahedral layers. Two by two they have a common oxygen atom that is part of the layer, inclined in opposite directions to the normal of the layer. Figure 84 shows the layer and the four sulphate tetrahedra depicted in different colours. The

impression is that the doctoral student perceives the simultaneous presence in space of two pairs of sulphate tetrahedra, each of which shares oxygen in a common peak. This is impossible due to the extremely close positioning of sulphur atoms and oxygen atoms located in the interlayer space of any two of these represented as paired polyhedra, and this is clearly understood from the bond lengths between the respective atoms presented in Table 4 of Annex 2.

It seems that the statistical distribution of each of in fact only the two sulphate tetrahedra, located one on each side of the octahedral layer relative to the normal of the same layer, is not well understood. To some extent, the established two alternative orientations for each sulphur polyhedron are implied by the incomplete colour-filled circles depicting the sulphur atoms in Figure 84. This is an indication of partial occupancy in these positions. However, the appendices do not contain information on the occupancy of the atomic positions at all, and the text does not mention anything about the methodology of their specification. Hence, the explanations for the combinations of mutual arrangement of S-tetrahedra in the structure remain unclear. In general, without belittling the achievements in this part of the dissertation, I believe that it is isolated from other studies. Correlation, interpretation of the results and their connection with those obtained for the synthetic representatives of the considered compounds are omitted or not sought. This part of the dissertation stands as an unnecessary ornament to the integrity of the rest of the work and I perceive it more as a request for future intentions of Zlatka Delcheva to develop her knowledge and skills in the direction of single crystal X-ray studies of the studied and other objects.

These comments do not affect the essence of the work in relation to the majority of the main goals and objectives. To the doctoral student Zlatka Delcheva I have the following recommendations for her future research:

- The synthetic and natural water-containing hydroxy salts with layered structure are extremely favourable for the study of phase transformations, accompanied by structural and quantitative changes that occur when heated in the range from room temperature to about 600-700 °C in connection with dehydration and dehydroxylation. Some of these processes are reversible, others are not. In this respect, their study by the Rietveld method applied to powder X-ray data of samples heated in real time (*in situ*) to these temperatures and their re-cooling to room temperature would provide new information about the products (initial, final and intermediate) of these processes, which would correlate much better with the results of thermal analyses. Additionally, this method allows for more accurate quantitative measurements, and from structural refinements important crystal chemical characteristics such as the degree of distortion of some building blocks, such as cationic polyhedra, can be investigated.

- In May 2021, the CNMMN - Commission on New Minerals and Mineral Names of the IMA - International Mineralogical Association published a list of approved by these institutions mineral symbols, which are alphabetical (Latin) abbreviations of their already established names. I recommend their use for the objects of research in the future, when they should be indicated in tables and figures (graphical images, curves of experimental results, microphotographs, etc.).

I also have the following question to the PhD student: Why for the simulated structure of Sr-gordaite the correction for the parameter c was made in accordance with the measured values of d_{006} (Fig. 46, p.69) and not the value d of any harmonic reflex (*00l*) with lower value of the index *l*, for example: *l* = 1, 2, 3, etc., as is done for Na-gordaite, for example (Fig. 39, p. 64)?

9. Does the abstract correctly present the main points and scientific contributions of the dissertation?

The abstract has a very good technical content and design. It is prepared according to the requirements and reflects the main aspects of the dissertation.

Conclusion:

Based on the above analysis of the presented dissertation of Zlatka Delcheva, which meets the requirements of the current legislation, I give my positive assessment and allow myself to recommend to the esteemed scientific jury to vote for the award of the educational and academic degree "Doctor" by professional field 4.4. Earth Sciences, PhD program "Mineralogy and Crystallography" to Zlatka Delcheva.

04.01.2021 г.

Reviewer:

/Prof. Vladislav Kostov, PhD/