

STATEMENT

on a PhD thesis for obtaining an educational and scientific degree "Doctor" in the scientific field: 4.4. Earth Sciences, PhD program: Mineralogy and Crystallography

Author: Zlatka Georgieva Delcheva, full-time doctoral student in the period 10.2016-10.2019, currently a specialist geologist at the Institute of Mineralogy and Crystallography "Acad. Ivan Kostov" - BAS, Acad. Georgi Bonchev Str., Bl. 107, Sofia

Topic of the PhD thesis: "Crystal chemistry and thermal decomposition of copper and zinc hydroxy-sulfate minerals"

By Assoc. Prof. Dr. Nadia Lubomirova Petrova, member of the Scientific Jury, appointed by Order 424RD-09-/28.10.2021 of the Director of the Institute of Mineralogy and Crystallography "Acad. Ivan Kostov"

Relevance of the problem developed in the dissertation

Zinc and copper hydroxy-salt minerals are part of the evolution processes of sulfide deposits and indicators of environmental changes. Therefore, they are an important component in the assessment of the ecological situation in the areas of used mines and tailings ponds. They are also the subject of research due to the fact, that they are the main component of the corrosion layer of zinc, copper, brass and bronze products. Cu-Zn hydroxy-salt compounds exhibit a number of useful properties: ion exchange and sorption, photocatalytic, flame retardation, as drug - carrier hybrid materials. The final product in their thermal decomposition is nanosized oxide with applications in the catalytic and ceramic industries. In the PhD thesis, a complex study of (Cu; Zn) - hydroxy-sulfate minerals and their synthetic analogues is performed in terms of crystal chemical and crystal structural features, order of obtaining, thermal behavior, products of thermal decomposition and stability, giving the necessary scientific prerequisites for proof of properties and discovery of new or modified materials with potential applications for different fields. In this sense, the topic of PhD thesis is relevant and can serve as a basis for future research.

Brief description of the PhD thesis

The volume of the dissertation is 132 pages, which includes 12 pages of literature, 85 figures, 20 tables and 17 pages of applications.

The aim of the proposed PhD thesis is to study the crystal chemical properties and their influence on the thermal characteristics of two groups of hydroxy-sulfate minerals: 1) layered Zn^{2+} hydroxy-sulfate minerals with hydroxide layer with cation vacancies and 2) layered Cu^{2+} hydroxy-sulfate minerals with hydroxide layer with OH "vacancies".

Literature review

The doctoral student knows in detail the state of the scientific topics she is working on. The literature review includes 145 titles and focuses on the topic of the PhD thesis, as the facts known so far about the genesis, distribution and applications, crystal chemical, crystal structural and thermal features of (Cu; Zn) - hydroxy-sulfate minerals, as well as criteria for their

classification affiliation are presented in an appropriate sequence. Since, in the known mineralogical classifications, hydroxy-salts do not have a separate classification position, the doctoral student uses a creative approach to quantitatively link of the (OH) groups with additional anions in the structures of hydroxy-salts.

Analysis of the methodological approaches for achieving the goal of the PhD thesis

In the PhD thesis synthetic analogues of (Cu; Zn) - hydroxy-sulfate minerals and one natural sample are used. Depending on the set goals and objectives, Zlatka Delcheva used different synthesis techniques: co-precipitation, solid-liquid reagent reactions, or ion exchange. The applied combination of methods of analysis (differential thermal analysis, thermogravimetry, mass spectroscopy, powder X-ray diffraction, scanning electron microscopy, electron probe microanalysis, infrared spectroscopy with Fourier transform, atomic adsorption analysis, single crystal X-ray diffraction) is suitable for research purposes. The PowderCell and Vesta programs are also used to analyze the experimental results.

Evaluation of the achieved results and contributions of the PhD thesis

The results obtained from the complex study of Zn and Cu hydroxy-sulfate phases (analogue minerals and natural sample) reveal general and specific features in crystal chemical and crystal structural terms of the two types of hydroxy-sulfate minerals (layer, interlayer space, charge, isomorphism, etc.), thermal decomposition, thermal decomposition products and stability. Based on these studies, various possibilities (or impossibilities) for cation and anion exchange have been proven and shown, as well as possibilities for obtaining a new phase.

The PhD thesis has a scientific and applied contribution to modern research in the field "Mineralogy and Crystallography", as the main contributions and merits of the PhD thesis can be summarized as follows: (i) a new reading of the chemical formula of minerals with the namuwite type hydroxide layer has been proposed in terms of the crystal structural role of water molecules; (ii) new ion exchange forms of gordaite: Sr-cationic and Br-anionic are synthesized and characterized in crystal-chemical and thermal terms; (iii) the obtaining of a "new Zn-hydroxy-sulfate phase" has been established and characterized in structural and thermal terms; (iv) the isomorphic structural positions have been established and the degree of Cu↔Zn isomorphism in the structures of the minerals from the ktenasite group has been assessed; (iv) for the first time morphological, chemical and structural data of a serpierite sample from a Bulgarian deposit have been reported.

Evaluation of the publications on the PhD thesis and the personal participation of the doctoral student

The results of the PhD thesis are published in 3 scientific publications, 1 of which in a journal with Q2 (Journal of Thermal Analysis and Calorimetry) and 2 of them in journals with Q4 (Bulgarian Chemical Communications, Review of the Bulgarian Geological Society). In them the doctoral student is in the first place, which shows her active participation in the conducted research and the design of the publications. Nine reports are presented at international and national scientific forums. Two of the publications have been cited 4 times (Skopus).

During the dissertation process the doctoral student showed impressive growth, initially in terms of mastering synthesis procedures and characteristic methods (mainly thermal and X-ray structural), and later in analyzing and interpreting the results and their graphical design and presentation in writing form. My personal impressions of her work are related to precision and persistence in conducting a huge number of experiments, as well as responsible attitude and competence in the work in the thermal laboratory not only with objects related to her thesis, but also those, related to other projects and scientific topics in the institute.

I have no critical remarks regarding the PhD thesis. The abstract contains 48 pages following the sequence of the PhD thesis and reflects the main results and contributions to it.

In conclusion, I consider that Ph thesis of Zlatka Delcheva completes and develops the knowledge of the crystal chemistry and the thermal behavior of (Cu; Zn) - hydroxy-sulfate minerals and reveals opportunities for their potential applications. The conducted research is at a high experimental level and with using of modern analytical methods. The obtained results are discussed in depth, taking into account the literature data so far. I conclude, that the presented PhD thesis, the abstract and the number of publications fully meet the requirements set out in the Academic Staff Development Act (Art. 2 part 1, 2 and 3, etc.), the Rules for application of the law for the development of the academic staff (Appendix to Art. 1a, part 1, etc.) and the criteria of the Institute of Mineralogy and Crystallography "Acad. Ivan Kostov" - BAS.

Based on the above, I give my positive assessment and propose to the esteemed Scientific Jury to award **Zlatka Georgieva Delcheva** educational and scientific degree "Doctor" in the professional field "4.4. Earth Sciences", doctoral program "Mineralogy and Crystallography".

03.01.2022

Prepared by:

Assoc. Prof. Dr. Nadia Petrova