

## Opinion

On the PhD thesis for receiving the educational and scientific degree "Doctor" in the scientific field  
4.4. Earth Sciences, PhD program "Mineralogy and Crystallography"

Author of the PhD thesis: Zlatka Georgieva Delcheva

PhD Title: Crystal chemistry and thermal decomposition of copper and zinc hydroxy-sulfate minerals

Reviewer: Iovka Koseva, Assoc. Prof., PhD

The presented thesis concerns actual topics, related to the various properties of anionic clays and their products after thermal decomposition. The application of these substances as catalysts, antacids, stabilizers, flame retardants, anion exchangers, heat pumps, etc. makes this research relevant in solving a number of environmental problems such as corrosion of zinc, copper, brass and bronze products, as well as in assessing the environmental situation in the areas of mines and tailings. The ion exchange and sorption properties of these materials play an important ecological role, preventing the migration of toxic ions into the environment. They are also used as composite materials, in the zinc and lead hydrometallurgy, in photoluminescence, in the catalytic industry, for the production of nano-sheets for applications in the solar sensor industry. The preparation of nano-scale products after the thermal decomposition of these compounds is of particular interest to the catalytic and ceramic industries.

The PhD thesis is structured in the following chapters: introduction, goals and tasks, state-of-the-art review, materials and methods, experimental part, obtained results, conclusions, contributions, references and two appendices. The PhD thesis is written on 132 pages, contains 85 figures, 20 tables, 145 literature sources and 17 pages of appendices.

The main goal of the PhD thesis is to investigate 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 cationic vacancies and 2) layered  $Cu^{2+}$  hydroxy-sulfate minerals with layer with OH "vacancies".

The state-of-the-art review is presented on 37 pages and covers 145 references, which deal with the topics discussed in the thesis worldwide. The PhD student correctly analyzes and summarizes the literature data and draws the appropriate conclusions from them. The methods for synthesis and analysis are also presented in details.

The goals and tasks are clearly formulated and the right approaches for their solution are sought. The applied synthesis methods (co-precipitation, solid - liquid reactions, exchange reactions) and methods of analysis (DTA, TG, MS, PXRD, SEM, EDAX, FTIR, Single crystal XRD) are appropriately selected for the purposes of the study. The PowderCell and Vesta programs for the analysis of the experimental results are studied and applied.

The main contributions presented in the PhD thesis are: 1) A new reading of the osakaite, namuit and lanscheinite minerals chemical formulas is made from the view point of the water molecules role in the crystal structure; 2) New ion exchange forms of gordaite with strontium and bromine are synthesized and the obtained phases are characterized crystallochemically and thermally for the first

time; 3) A new Zn-hydroxy-sulfate phase is obtained and characterized structurally and thermally; 4) The isomorphic structural positions are established and the degree of isomorphism between copper and zinc in the structures of the minerals from the group of ktenasita is estimated; 5) Morphological, chemical and structural data of a serpyerite sample from a Bulgarian deposit is reported for the first time. The obtained results have both scientific and practical orientation, in particular in the assessment of the ecological situation in the areas of mines and tailings.

My personal impressions of the PhD student Zlatka Delcheva are that she shows precision in the experiment work, depth in analyzing the results and the ability to summarize them in an appropriate way in her thesis.

The results are published in 3 scientific papers, 1 of which in a journal with Q2 (Journal of Thermal Analysis and Calorimetry) and 2 in journals with Q4 (Bulgarian Chemical Communications, Review of the Bulgarian Geological Society). 9 reports are presented at international and national scientific forums. No citations are noticed.

Notes: Foreign words such as "temperature region" (pp. 52, 74, 76, 78, 90, 93, 111) and "decomposition" (pp. 52, 53, 74, 75, 76, 78, 80, 81, 89, 90, 91, 93, 108, 109, 110, 111, 118, 120, as well as in the title) are used in the thesis and in the abstract.

The abstract correctly covers the main experimental results and contributions of the thesis.

I have the following questions to the PhD student:

1. Why in the presence of urea crystals are better shaped (page 47 of the thesis)?
2. At what pH do you precipitate ZnSO<sub>4</sub> with NaOH (Table 6, page 37 of the thesis)?

Conclusion:

I believe that the relevance, volume of experimental research, scientific contributions and scientific indicators, the presented PhD thesis fully meets the requirements of Law for development of the academic staff in the Republic of Bulgaria and the Regulations of the Institute of Mineralogy and Crystallography for its application. All these give me a reason to recommend strongly to the Members of the Scientific Jury to award Zlatka Georgieva Delcheva the educational and scientific degree "Doctor" in the scientific field 4.4. Earth Sciences, PhD program Mineralogy and Crystallography.

07.12.2021

Prepared by:

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