

Opinion

On the PhD thesis for receiving the educational and scientific PhD degree 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: Tsveta Stanimirova, Assoc. Prof., PhD

The documents and materials presented by the doctoral student meet the requirements of the Law on Higher Education, the regulations for its application and the internal regulations of the Institute of Mineralogy and Crystallography of the Bulgarian Academy of Sciences.

The state-of-the-art review is presented on 132 pages of main text, 85 figures, 20 tables, 145 literature sources. The appendices outside the main text are 2 in number (17 pages). The main text of the presentation is structured in the following chapters: Introduction, Purpose and tasks; Literature review; Materials and methods; Experimental part; Results obtained; Conclusions; Contributions and References.

Objects of study are representatives of layered hydroxy-salt minerals, which in the last few decades have been the subject of intense scientific interest not only as an integral part of the development of sulfide deposits and important factors in assessing the ecological situation in mines and tailings, but also due to the possibilities for their application as catalysts, antacids, stabilizers, flame retardants, anion exchangers, heat pumps, etc.

The main goal of the doctoral thesis - study of the crystal chemical properties of Zn and Cu hydroxy-sulfate minerals with structurally different hydroxide layers (with cationic and OH vacancies for Zn^{2+} and Cu^{2+} , respectively) - was achieved by using an appropriate diverse set of experimental (synthesis, ion-exchange) and analytical (powder and single XRD, SEM-EDS, DTA-TG-MS, AAA, FTIR) methods, with an emphasis on the use of thermal methods both in the evaluation of certain properties such as hydration and ionic volume, and in the determination and characterization of thermal decomposition products.

The obtained results are presented accurately by presenting a complex crystal chemical characteristic of the studied substances. Based on the analysis and interpretation of the results, general features and properties are derived and an explanation of the differences in the crystal chemical relations for the two groups (Zn and Cu) of hydroxy sulfate minerals is presented.

The main contributions presented in the PhD thesis are:

- 1) General regularities and specific features in the crystal chemical behavior of Zn and Cu hydroxy-sulfate minerals with layered structure are derived;
- 2) A new reading of the osakaite, namuinite and lahnsteinite minerals chemical formulas is made from the view point of the water molecules role in the crystal structure;
- 3) New ion exchange forms of gordaite with strontium and bromine are synthesized and the obtained phases are characterized crystal chemically and thermally for the first time;
- 4) A new Zn-hydroxy-sulfate phase was obtained and crystal chemically and thermally characterized. A structure was proposed and refined;

5) The isomorphic structural positions are established and the degree of isomorphism between copper and zinc in the structures of the minerals is estimated;

6) For the first time, data (morphology, composition, association and paragenesis) for a serpierite specimen from a Bulgarian deposit were reported. A new smaller elementary cell has been proposed to describe the structure.

All the obtained results have both scientific and practical orientation for evaluation of the possible useful properties.

The results are presented in 3 scientific papers (1 in a journal Journal of Thermal Analysis and Calorimetry - Q2; 1 in Bulgarian Chemical Communications- Q4 and 1 in Review of the Bulgarian Geological Society –Q4) and 9 reports at international and national scientific forums. Four citations have been noted.

In conclusion, the presented doctoral thesis is a completed scientific research with scientific and scientific-applied contributions, fully meeting the requirements for obtaining the scientific-educational PhD degree.

PhD student Zlatka Delcheva shows in-depth knowledge of the issue, and during the development, she has mastered a number of laboratory and analytical research methods, gained experience and skills to analyze the results and present them in good scientific language.

All this gives me enough reasons to recommend to the members of the Scientific Jury to award Zlatka Georgieva Delcheva the educational and scientific PhD degree in the professional field 04. 04. Earth Sciences, doctoral program Mineralogy and Crystallography.

28.12.2021

Prepared by:

/Tsveta Stanimirova, Assoc. Prof., PhD/