B U L G A R I A N A C A D E M Y O F S C I E N C E S

G E O L O G I C A L I N S T I T U T E "S T R A S H I M I R D I M I T R O V"

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REVIEW

of a Ph.D thesis for obtaining the educational and scientific degree ***"Doctor"***
in the doctoral program ***"Mineralogy and Crystallography"***
Author of the thesis: ***Zlatka Georgieva Delcheva, IMC-BAS***
Thesis topic: ***Crystal chemistry and thermal decomposition of copper and zinc hydroxy-sulfate minerals***
Reviewer: ***Prof. Dr. Thomas Noubar Kerestedjian, GI-BAS***

1. Is the scientific problem developed in the dissertation current?

The topic of the proposed dissertation is undoubtedly current. Copper and zinc hydroxy-sulphates are stable in a narrow range of environmental conditions, which makes them particularly suitable as indicators of these conditions. Being a common component of exogenous alteration of ore deposits, they can contribute to the characterization of both natural exogenous processes and the effect of remediation and conservation measures taken during reclamation of mining sites. These minerals are also a major component of patinas on weather-exposed metal, and their knowledge can be used to select measures for the preservation of cultural and historical heritage. The ion exchange properties, as well as the products of thermal decomposition of these minerals represent a potential for other applications in practice too. More important than the possible practical applications, however, are the scientific contributions of the work, because along with the new data that are offered, new questions are raised, that can trace the route for future research. The structural characteristics of minerals, as well as their behaviour in interaction with the external environment are always current, as they open up opportunities for new practical applications from the widest range.

2. Does the candidate know the state of the problem and creatively evaluate the literary material?

The candidate undoubtedly knows very well the state of the problem, which is evident from the numerous and relevant citations, both in the introductory and in the discussion part. This knowledge is evident in the well-formulated goals and objectives of the study, as well as in the well-chosen research methods.

3. Can the chosen research methodology give an answer to the set goals and tasks of the dissertation?

It can and undoubtedly gives convincing answers to the many set goals and objectives of the dissertation. Here, however, I would like to add that from the powder X-ray diffraction data, the Brag positions and the relative intensities of the reflections were mainly used. Naturally, when studying known structures, especially when it comes to layered ones, where the most significant phenomena are directly reflected in the interplanar distances of the interlayer, this approach is acceptable and often sufficient. However, I believe that if the information from the full profile (Rietveld method) had been used, the results would have been, if not more detailed, then at least more convincing, especially as regards the population of mixed-populated structural positions.

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

The study (with one exception) was performed on synthetic analogues of the mineral phases, which is in favour of the study and brings additional confidence in the quality of the studied material. The methods of synthesis are very well described and the synthesis is carried out precisely and competently. Subsequent studies of the synthetic phases have also been carried out precisely and competently, which is confirmed by the results obtained, which are in line with theoretical expectations. I find the contributions of the dissertation completely reliable.

Here is the place to note that the exception I mentioned above refers to a natural specimen of serpierite from a Bulgarian deposit. This part of the work stands a little off the main line of research. It is valuable in itself, but does not contribute significantly to the value of the dissertation, which is good enough without it. This study is in some sense incomplete because the test specimen differs from the Laurion type specimen in both chemical composition and structure. Although the defined structure can be considered as a sub-structure of the type, it is worth considering the possibility of distinguishing a new mineral species (polymorphic modification).

5. What are the scientific and / or scientific-applied contributions of the dissertation:

- Formulation and substantiation of a new scientific problem (field);
- Formulation and substantiation of a new theory (hypothesis);
- Proving with new means of significant new aspects of existing scientific problems and theories;
- Creation of new classifications, research methods, new constructions, technologies, preparations;
- Obtaining and proving new facts;
- Obtaining confirmatory facts;
- Significance of contributions to science and practice.

The contributions of the dissertation are clearly and correctly listed by the author. They are five and for the first four of them I have no hesitations (for the fifth see the comment in the previous paragraph). Each of these contributions is a valuable scientific achievement.

It is difficult for me to classify them according to the above scheme, because it is obviously made by bureaucrats who have no idea of the principles of functioning of the scientific system, or even of the basic Aristotle's principles of classification.

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

I cannot be sure of the answer to this question, but undoubtedly no part of the work has been plagiarized. In some places in the text, the experienced hand of the supervisors is evident, but this is normal and should be. This is the role of the research supervisor. Some studies have been performed by IMC colleagues, but this is clearly stated and also normal. This is the way to transfer knowledge between generations. The doctoral student has worked in a good cohesive team and this definitely contributes to the quality of work. The role of the doctoral student himself is clearly visible and dominant in the whole work and this makes a very good impression. I am convinced that in the process of research on the dissertation the doctoral student has gained significant experience, which will be an excellent basis for a good scientific career.

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

The doctoral student has two impactful publications, one in a renowned Bulgarian journal and nine papers at conferences in the country and abroad. For the record, I will note that this covers both the requirements of the old law on degrees and titles (in the jurisdiction of which the procedure is under consideration) and the requirements for registration with NACID.

Only impact publications are cited, with two citations each. I find this a very good certificate. In the field of earth sciences, very few publications are cited in the first year after publication. However, if they are noticed and cited in the second (as is the case here), the probability of receiving dozens of citations in the coming years is very high.

8. Whether the results of the dissertation have already been used in scientific practice, or they achieved a direct economic or other effect?

I am not aware if the results reported here have been used in practice or have had an economic effect. However, I must point out that research always has only one addressee, and that is the world scientific community. Practical results and economic effect are expected from the development activity, which every scientist can and should do at a certain moment, but not in his dissertation. This work should only show the doctoral student's ability to carry out research and nothing else should be a criterion for its evaluation.

9. Critical remarks and motivated recommendations for future use of the scientific and / or applied scientific contributions.

I have one and the same remark to both data-tables from the single crystal solution of the two defined phases: "new phase" and serpierite?. The composition of the phase in both cases is incorrectly stated with respect to hydrogen. In the case of serperite it is zero, and in the case of the "new phase" only the hydrogen content of the water molecules is taken into account, and that of the hydroxyl groups is absent. I am aware that "invisible" hydrogen due to low electron density would cause invalid CheckCif and this is a way to circumvent the formal logic of the program, but in the dissertation or publication the composition must be specified correctly and the related parameters -

mass and density, which are also incorrectly presented, recalculated. Otherwise, the reader may be misled.

I also have a more general remark, rather stylistic: Often the author does not make a clear enough distinction between the "raw" fact and what he thinks this fact means. The author's course of thought between the fact and conclusion must always be clearly traceable to the reader. This is often missing from the presentation and I recommend the doctoral student to pay attention in his future publications.

10. Does the abstract correctly reflect the main principles and scientific contributions of the dissertation?

Yes. The abstract is very informative, concise and perfectly shaped. In practice, it is a more compact version of the dissertation and is easy to read, retaining attention from beginning to end.

11. Other matters on which the reviewer considers that he should take a stand.

I think the issue of the serpierite deserves to be brought to a quick conclusion in a good journal. In the dissertation there are other very interesting as yet unpublished data that deserve independent publication in impacting sources too. I advise the doctoral student to start this immediately, because only a few months of dealing with other issues are enough to change priorities, and in the worst case, this data will remain unpublished forever (personal bitter experience).

12. Conclusion with positive or negative assessment for the presented dissertation.

I had the pleasure of reviewing a wonderful dissertation. From all the above, it is obvious that I would recommend without hesitation to award the doctoral student the educational and scientific degree of doctor.

01/01/2022 Reviewer:

Thomas Kerestedjian