C A U Kiel University
Christian-Albrechts-Universität zu Kiel
Faculty of
Mathematics and Natural Sciences

Christian-Albrechts-Universität zu Kiel, 24098 Kiel

Prof. Dr. Astrid Holzheid
Experimental and Theoretical Petrology

Institute of Geosciences
Christian-Albrechts-Universität zu Kiel

Ludewig-Meyn-Straße 10, 24118 Kiel
F. R. of Germany

www.petrologie-mineralogie.ifg.uni-kiel.de/en

-- To whom it may concern --
St. Petersburg State University

Authorized Person
Astrid Holzheid

Mail, Phone, Fax
astrid.holzheid@ifg.uni-kiel.de
phone +49(0)431-880-1451
fax +49(0)431-880-4376

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Examiner's report
of the thesis

"Novel sulfate inorganic materials with transition metals: crystal chemistry and properties"

for the degree of candidate of geological and mineralogical sciences of
St. Petersburg State University
Scientific specialty 1.6.4.
Mineralogy, Crystallography, Geochemistry, Geochemical Methods of Mineral Exploration

It is a pleasure to write this recommendation letter for acceptance of the degree of candidate of geological and mineralogical sciences submitted by Diana Olegovna Nekrasova.

At first, I would like to clarify that I do not know Ms. Nekrasova in person and will thus be able to only judge her written performance.

Ms. Nekrasova's thesis consists of eight main chapters. The first chapter provides an overview about the experimental and analytical methodologies and the following chapters describe in detail the various novel compounds - synthesized by Ms. Nekrasova - and their respective crystal-chemical features, physical properties as well as outlooks to future practical significances. These chapters are bracketed by a detailed introduction chapter and a conclusion chapter.

Six individual publications do exist with Ms. Nekrasova being first author in three out of the six publications. All were published in international well-known peer-reviewed journals. Her Russian scientific supervisor at State University St. Petersburg, Professor Dr. O.I. Siidra, is - beyond others - co-author

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of all articles. Her French scientific supervisors at Université de Lille, Associate Professor Dr. M. Colmont and Professor Dr. O. Mentré, both affiliated to Ecole Nationale Supérieure de Chimie de Lille, are - beyond others - co-authors of five articles.

The introduction chapter (chapter 1) of her written thesis is a well-structured short introduction which highlights the relevance of novel inorganic sulfate minerals, summarizes e.g., envisaged aims, individual tasks, used methods, key results, presentations at conferences and publications, respectively, and concludes with acknowledgements. Ms. Nekrasova refers to her 6 scientific articles in Web of Science indexed journals and 5 abstracts of international conferences. I believe that the added information “Chapters” (including short summaries), “Approbation of the study”, “Publications”, and “Acknowledgments” are requirements by the doctoral degree regulations of State University St. Petersburg and/or Université de Lille, otherwise they would be out of place in the introduction chapter.

The final chapter as conclusion chapter (chapter 10) summarizes the findings regarding the crystal-chemical features and physical properties as well as similarities. The chapter lists consecutively all findings of the synthesized compounds and thus repeats the information of the subchapter “chapters” in the introduction chapter. Unfortunately, some kind of an outlook to future needed work is missing.

As consequential thought, a question for the candidate might be to provide a reflection about important missing information and define urgently needed future work at the Q&A-part of her defense.

In the following, I will individually summarize and comment on each of the eight main chapters, i.e. chapters 2 to 9 in the written thesis.

Chapter 2 (Experimental part and methodology) provides (i) a comprehensive overview of the six used methods and the determination of the chemical composition, (ii) brief but detailed enough information about the calculations, i.e. bond valence calculation, distortion parameter, first-principle calculations, quantum Monte-Carlo simulations, and structural complexity calculations, and (iii) information about the new synthetic compounds, the syntheses techniques, and the investigation of the starting material with the aid of DTA-TG and HTXRD to monitor the crystal formation processes.

As consequential thought, a question for the candidate might be related to more in-depth information regarding the finally used methods and their applicability to natural environments. For example, syntheses in an inert atmosphere or under vacuum might be far from those conditions that prevail at conditions of mineral formation from volcanic gases. The candidate should comment on that.

In chapter 3 the new mineral glykinite, $Zn_3O(SO_4)_2$, found in the vicinity of the exhalative fumaroles of the Tolbachik volcano, Kamchatka, Russia, is described in detail regarding its crystal structure. The content of the chapter seems to be published in one of the six papers (Nazarchuk et al., 2020). At first glance the chapter seems to be a bit out of place, but the information is needed in chapter 5 as chapter 5 - beyond others - deals with synthesis, crystal structure and properties of synthetic analogs of glykinite. In addition, chapter 3 introduces to the formation of $[Zn_3O]^{4+}$ chains based on OZn_4 tetrahedra.

In chapter 5 the candidate mentions impurities of copper in the new mineral glykinite and the possibility of having Na^+ containing glykinite analogues as new possible materials for Na^+-based batteries. However, neither Cu^{2+} (57pm) nor Cu^+ (46pm) have similar ionic radii compared to Na^+ (~100pm). As consequential thought, a question for the candidate might be related to the distortion of the crystal structure when incorporation Na- instead of Cu-cations. Although this comment might not belong to chapter 3, but knowledge about the crystal structure of glykinite is needed to answer the question.

The main scientific novelty of this thesis is the use of slightly modified natural inorganic sulfide minerals - so-called geo-inspired materials - as complex functional materials like electrochemical cells, i.e. batteries. A brief introduction into batteries is given in chapter 4 entitled "Synthesis of an analogue of saranchinaite $Na_2Cu(SO_4)_2$, crystal structure and physicochemical properties". After information about synthesis of $Na_2Cu(SO_4)_2$, including detailed crystal chemical characterization, electrochemical and magnetic properties are discussed in detail and related to the crystal structure. The candidate concludes its introduction of the chapter with the sentence "...we demonstrated the electrochemical behavior of $Na_2Cu(SO_4)_2$ either vs Na or vs Li to understand of principle of battery working." No Li-bearing phases are synthesized. Thus, I do not understand how the candidate was able to demonstrate the above-mentioned behavior.

As consequential thoughts, (i) a question for the candidate might be related to more in-depth information regarding the two types of cells (electrolytic cells and galvanic cells) and examples of geo-inspired materials for both types of cells; and (ii) to explain the deeper meaning of the last sentence of the introduction, especially as no Li-bearing phases were investigated.

In chapter 5 (Synthesis, crystal structure and properties of Zn and Mg analogs of itelmenite and synthetic analog of glykinite) the quaternary Na_2SO_4-$CuSO_4$-$MgSO_4$-($ZnSO_4$) system was used to synthesize various analogues of itelmenite and glykinite. Based on element maps various anhydrous sulfates, including solid solutions, formed. Thus, the question arises about the reproducibility of the synthetic phases. Evaluation of Na^+ ion diffusion in the Na-based sulfates allow statements about the suitability of those phases as sulfate-based cathode materials.

As consequential thoughts, (i) a question for the candidate might be related to the solid solutions and their reproducibility regarding the synthesis; and (ii) how the crystal structure should be tuned to allow an even more pronounced Na^+ ion diffusion.

Chapter 6 is the longest and most comprehensive chapter. At first complex synthetic analogs ($K_2Cu_3O(SO_4)_3$) of puninite (A=Na), euchlorine (A=$Na_{0.5}K_{0.5}$), and fedotovite (A=K) as well as related Rb- and Cs-bearing $Rb_2Cu_{3.07}O_{0.07}(SO_4)_3$ and $Cs_2Cu_{3.5}O_{1.5}(SO_4)_3$ phases were synthesized and their respective crystal chemistry studied, including careful checking of the starting materials. In the following a brief introduction to main magnetic generalities is given and the interaction of the magnetic hexamers [Cu_6O_2] in the structures is described in detail. Lattice relaxation after replacement of Na and K by the bigger ions of Rb and Cs leading to a slight addition of $(CuO)_x$ to the structure is studied in the second part of the chapter and the most likely return to S = 1 magnetic clusters is discussed.

Although not directly linked to chapter 6, but the candidate might be asked to provide simple examples of 0D, 1D, 2D, and 3D units with the studied [O_xCu_y] complexes (i.e. dimers, chains, layers, frameworks).

Chapter 7 builds on the knowledge of the former chapters and expands this knowledge to the polymorphism in solid solutions of $A_2M_3(SO_4)_4$ with A = Rb, Cs and M = Co, Ni. Various new compounds got synthesized by solid-state syntheses and in great detail structurally characterized by single-crystal and powder X-ray diffraction. Prior the final synthesis and to ensure the use of the most suitable synthesis temperature DTA and TG determination were performed on the starting material mixtures.

As also more fundamental questions could be asked, the candidate could explain briefly and in simple words why thermogravimetric determinations (DTA and TG measurements) of the mixtures will provide information on the temperature of crystallization of the synthetic phases.

To recall the entire study was inspired by geological minerals that might be of great value as complex functional materials after slightly tuning the components and crystal structure. Chapter 8 focuses on sulfate analogues of copper and alkali metals (Na, K) bearing sulfates, i.e. of the most known compounds that form in volcanic fumaroles. Although Rb and Cs are rare in fumarolic minerals, former studies of the Russian supervisor reveal existence of four novel Rb-Cu-sulfates ($Rb_2Cu(SO_4)Cl_2$, $Rb_4Cu_4O_2(SO_4)_4(Cu_{0.83}Rb_{0.17}Cl)$, $Rb_2Cu(SO_4)_2$, $Rb_2Cu_5O(SO_4)_5$, $Rb_2Cu_2(SO_4)_3(H_2O)$).
While chapter 8 is devoted to detailed characterization of the crystal structures of those Rb-Cu-bearing sulfates as natural samples are sparse, chapter 9 follows a similar approach as this chapter focusses on morphotropism in fumarolic minerals related to two anhydrous cesium sulfates $Cs_2Cu(SO_4)_2$ and $Cs_2Co_2(SO_4)_3$. Both cesium sulfates were never synthesized before and are absolutely new compounds. They have no structural analogs and, thus, add to the family of anhydrous alkali transition metal sulfates and the determination of the crystal structure of $Cs_2Cu(SO_4)_2$ completes the series of $A_2Cu(SO_4)_2$ (A = Na, K, Rb, Cs) compounds. Chapters 8 and 9 nicely illustrate the importance of synthesis of possible replacement minerals or solid solutions even if natural analogues are not yet found.

Again more fundamental questions that are linked to chapters 8 and 9 asked to the candidate could be (i) to provide some kind of an overview about the most and least common cations in volcanic fumaroles, (ii) to summarize the (geological) region of origin of the least common cations enriched in fumarolic gases, and finally (iii) to provide other examples of morphotropism, i.e. examples about crystals whose similar physical structure are due to the similar chemical composition.

Chapter 10 is the final conclusion chapter, summarizing all other chapters (see above for more details).

Ms. Nekrasova was not only able to synthesize new compounds, but also to fully characterize the crystal structures of all synthesized compounds, including review of natural sulfates, and - if applicable - derive electrochemical, magnetic, thermal and optical properties.

All chapters are reasoned in themselves and also logic flow exists for all consecutive chapters. Frequent typos and creative English grammar slightly diminish the excellent piece of work.

However, it is beyond doubt that the submitted thesis of Ms. Nekrasova is a 'solid piece of work' and the high level of the PhD is out of question.

The thoughts of mine above regarding questions and topics for discussion should not be counted or judged as criticism of Ms. Nekrasova's work and her findings.

Ms. Nekrasova should be granted the award of candidate of geological and mineralogical sciences at St. Petersburg State University - scientific specialty 1.6.4.: Mineralogy, Crystallography, Geochemistry, Geochemical Methods of Mineral Exploration.

With kind regards,

A. Holzheid

Prof. Dr. Astrid Holzheid
Head of Petrology and Mineralogy
Kiel University

Institut für Geowissenschaften
der Universität Kiel
-Petrologie-
Olshausenstr. 40 · D-24098 Kiel