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Examiner's report
of the thesis

"Crystal-chemical features of novel compounds with selenite and tellurite anions"

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 Mishel Markovski.

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

Mr. Markovski's thesis consists of four main chapters. The first chapter provides a literature review and the following chapters describe in detail the various novel compounds - synthesized by Mr. Markovski - and their respective crystal-chemical features. The four chapters are bracketed by a detailed introduction chapter and a conclusion chapter.

Six individual publications do exist with Mr. Markovski being first author in five out of the six publications. All were published in international peer-reviewed journals, mainly in 'Zeitschrift für Kristallographie- Crystalline Materials'. His scientific supervisor Professor Dr. O.I. Siidra, State University St. Petersburg, and associate Professor Dr. D.O. Charkin, Moscow State University, are – beyond others – co-authors of all articles. Dr. Charkin is first author in the publication in which Mr. Markovski is second author.

The introduction chapter of his written thesis is a plain listing of facts. The topic relevance and research goal are not put into any context. The statement "The study of crystal-chemical features and physicochemical properties of Se and Te minerals and synthetic compounds is a field of science that is highly relevant, both from a fundamental and practical point of view" does not help to understand why the study got performed as neither the relevance nor the fundamental and practical point of view are explained in more details. I expect that this information will be given by Mr. Markovski in his oral presentation of the defense. The methods of research are well described and easy to follow. All needed information, including references available in the literature, is provided. Commendable is the part of the introduction entitled "Thesis statements to be defended", but unfortunately Mr. Markovski added already information regarding his findings in this paragraph. This should be part of the conclusion chapter and not the introduction chapter. I believe that the other added information like "Reliability of the results", "Theoretical and practical significance", "Approbation of the study", "Publications", "Contribution of the author", "Scope and structure of the thesis" and "Acknowledgments" are requirements by the doctoral degree regulations of State University St. Petersburg, otherwise they would be out of place in the introduction chapter.

The final chapter as conclusion chapter summarizes the findings regarding the crystal-chemical features of the 18 synthesized novel compounds with Tl^{+}, Se^{4+} and Te^{4+} cations and ends with the sentence "The results obtained are of both fundamental and practical interest for further research in crystal chemistry, mineralogy, and structural chemistry of Se and Te in low oxidation states". Unfortunately, more details about the needed fundamental and practical interest for further research are missing.

As consequential thought, a question for the candidate might be to provide exactly this missing information at the Q&A-part of his defense.

In the following, I will individually summarize and comment on each of the four main chapters.

Chapter 1 (Literature data / 1.1. Mineralogy and geochemistry of Se and Te oxide minerals / 1.2. Crystal-chemical features of Se(IV) and Te(IV) in oxides) provides a comprehensive overview regarding the elements selenium and tellurium as well as similarities in the S-Se-Te series and Se-Te minerals. The importance to gain knowledge about the stability of secondary Se and Te minerals in oxidation zones and their key roles in understanding the geological conditions and formation processes are explained. As the present knowledge is based mainly on profound basic knowledge of the crystal-chemical features of well-known minerals, Mr. Markovski synthesized Se^{4+} and Te^{4+} oxide compounds, some with additional copper and alkali metals in the structures, and carefully studied those to widen the knowledge and to be able to better understand the geological conditions and formation processes.

As consequential thought, a question for the candidate might be related to more in-depth information regarding the mentioned S-Se-Te series and possible geochemical twins of selenium.

Chapters 2 to 4 are dedicated to the various above-mentioned synthesized compounds.
Mr. Markovski conducted an experimental mineralogy, geochemistry and crystallography project and used state-of-the-art experimental and analytical techniques.
All three chapters are structured in similar way: (1) Description of the synthesis, (2) Single-crystal X-ray diffraction experiments, (3) Infrared spectroscopy, if appropriate (i.e., IR spectroscopy of copper

and alkali metals hydrogen selenites and copper-free K, Cs and Ca hydrogen selenites), (4) Magnetic properties, if appropriate (i.e., magnetization measurements of lithium selenite halide), and (5) Derivation of the crystal structure.

Based on the single-crystal X-ray diffraction results, Mr. Markovski was able to derive the crystallographic data and refinement parameters for all 18 novel crystal structures. With the aid of infrared spectroscopy further details about the bonding based on stretching and bending modes were possible to derive for (i) $[CsNO_3]Cu(HSeO_3)_2$, (ii) $[RbNO_3]_2Cu(HSeO_3)_2$, (iii) $[NH_4NO_3]_3Cu(HSeO_3)_2$, and (iv) $Li_2(Se_2O_5)(H_2O)_{1.5}\cdot CuCl_2$. Temperature-dependent susceptibility and field-dependent magnetization information was extracted based on the magnetization measurements of the lithium selenite halide compound $Li_2(Se_2O_5)(H_2O)_{1.5}\cdot CuCl_2$. This information helped to further characterize the compound and its bonds, respectively, as well as compare the newly synthesized compound with layered hydroselenites (literature date).

Mr. Markovski was not only able to synthesize 18 new compounds, but also to fully characterize the crystal structures. In addition, the candidate developed a method for the synthesis of hydrogen selenites of alkali and alkaline earth metals and was also able to derive crystal physical information in one of the compounds ($Li_2(Se_2O_5)(H_2O)_{1.5}\cdot CuCl_2$). Eleven of the new compounds belong to new structural types.

The main findings can be summarized as follows:

(1) Key features of some of the new structural architectures are strongly linked to the host-guest principle, namely the stereochemical active lone electron pairs of Te^{4+} cations and their respective influence on the further structure. Due to this new structural architecture copper cations are incorporated in the structure in two oxidation states in Cu-containing tellurite chlorides.

(2) Mr. Markovski was also able to synthesize for the first time a Cu-Tl-containing tellurite-tellurate without additional cations.

(3) Furthermore, based on the finding of synthesized hydrogen selenites of alkali and alkaline earth metals it is now known that the pH of the environment has a strong influence on the formation of those compounds and the existence of morphotropic series of some compounds could be demonstrated.

(4) In the structurally related chemical families of nitrates and halides with layers of $Cu(HSeO_3)_2$, the substitution of nitrate with halogen anions revealed structural features with alternating layers of neutral $Cu(HSeO_3)_2$ and electrically neutral layers of alkali metal nitrates $[ANO_3]$ ($A = Cs^+, Tl^+$) leading to the formation of homologous series.

(5) The dependence of the radius of alkali metal cations with elongation of various parts of the structures are well defined and might be used in the future to predict the crystal structures of new compounds.

(6) First observations regarding changes of the interlayer interactions in copper-free Ca hydrogen selenites during hydration might bear important information applicable to mineral formation in nature and changes of physico-chemical properties of those secondary minerals.

Mr. Markovski ends his main text of the thesis with the sentence "The results obtained are of both fundamental and practical interest for further research in crystal chemistry, mineralogy, and structural chemistry of Se and Te in low oxidation states".

During the defense Mr. Markovski could provide more information about the natural environment where Se and Te will be present in low oxidation states.

In his oral defense, Mr. Markovski should provide additional information regarding his findings related to expected thermodynamic properties of the novel compounds, their use to shed light to better understand the geological conditions and formation processes of secondary Se and Te minerals in oxidation zones as well as possible (harmful?) bioavailability of the novel compounds. It would have been beneficial to provide those thoughts already in the written thesis as well.

Furthermore, an outlook for future work might be a suitable topic of discussion that is directly linked to naturally occurring Se and Te compounds.

It is beyond doubt that the submitted thesis of Mr. Markovski is a 'solid piece of work'.

The thoughts of mine above regarding questions and topics for discussion should not be counted or judged as criticism of Mr. Markovski work and his findings.

Mr. Markovski should be granted the award of candidate of geological and mineralogical sciences at St. Petersburg State University.

With kind regards,

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