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-- To whom it may concern --
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Review of the member of the dissertation council

for the dissertation of Vasily Yurevich Grishaev

on the topic

**“CRYSTAL CHEMISTRY OF NEW MINERAL RELATED SELENITES WITH
MONO- AND DIVALENT METAL CATIONS”**

submitted

**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 Vasily Yurevich Grishaev.

At first, I would like to clarify that I never scientifically work together with Mr. Grishaev and will thus be able to bias-free judge his written performance.

Mr. Grishaev's thesis consists of four main chapters, an introduction and a paragraph with conclusions at the end of the written thesis.

Seven publications do exist with Mr. Grishaev being first author (1) or co-author (6). The first author of those six publications is either his Russian scientific supervisor at State University St. Petersburg Prof. Siidra or Ass. Prof. Charkin from Moscow State University with his Russian scientific supervisor - beyond others – as co-author of all articles. Mr. Grishaev presented his research also at various international and Russian conferences.

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

The introduction chapter is a well-structured short introduction which highlights the general relevance of the topic as well as mentions the main objectives of the study and executed research methods, respectively. The candidate summarizes - amongst others - his key results, presentations at conferences and links the main scientific results to the seven publications. The candidate defined three thesis statements related (i) to selenites with organic compounds, (ii) to hydrated selenites with added Pb, and (iii) to mineral-like selenite halides.

It seems to me – by also judging from the slightly different wording of the subchapters' titles of chapter 4 – that chapter 4 might be added late as the candidate wrote in the paragraph Scope and structure of the thesis "The work consists of an introduction, three chapters, a conclusion and a list of cited literature.", although his thesis has four chapters.

Unfortunately, the candidate missed to add more words on the mentioned CTP method. Does he mean the Catalyst-Transfer Polycondensation method? The method is neither added in the paragraph "Research methods" of the introduction chapter nor in chapter 4 or at any other page in the main text.

In Chapter 1 (Literature data / Mineralogy and geochemistry of selenium & Crystal chemistry of selenium), the candidate provides a rudimentary overview of - in general - selenium and some of its minerals. The candidate wisely chose those minerals that do have at least some of the cations in common with his synthesized selenites.

The subchapter "Crystal chemistry of selenium" is content-wise appropriate, but - in comparison to the other text - abound with typos. Did the candidate run out of time and was not anymore able to proof-read this subchapter?

Chapter 2 (New acidic selenites of alkali and transition metals) with its subchapters 2.1. (Crystal chemistry of new acid selenites of copper and alkaline metals), 2.2. (Crystal chemistry of new acid selenites of transition metals and organic cations), and 2.3. (Crystal chemistry of new non-centrosymmetric compounds $\text{KNO}_3 \cdot 3\text{H}_2\text{SeO}_3$ and $\text{NaHSeO}_3 \cdot 3\text{H}_2\text{SeO}_3$) is organized by providing information about the synthesis, the SC XRD results and derived crystal chemistry of the synthesized compounds. Infrared spectroscopy was added by the new acid selenites of copper and alkaline metals, while second harmonic generation investigation was conducted on the non-centrosymmetric compounds. All subchapters do have the same structure with (i) information about the synthesis route and optical descriptions of the synthesized selenites, (ii) details regarding the SC XRD measurements and gained crystallographic and structural data, and (iii) description of the derived crystal structure, including detailed illustrations of the coordination environments of the various dominant cations and general projections of the crystal structure. Infrared absorption spectra were obtained for one of the Cu-Na-selenites $[(\text{NaCl})[\text{Cu}(\text{HSeO}_3)_2]\text{-II}]$ and second harmonic generation signals for the non-centrosymmetric compound $\text{KNO}_3 \cdot 3\text{H}_2\text{SeO}_3$ to confirm the various bonds and the non-centrosymmetric character of the crystal structure, respectively.

It is out of doubt that the candidate did a tremendous volume of work, synthesized new selenites and added knowledge to different acidic selenites of alkali and transition metals. However, some thoughts regarding next steps needed to use this knowledge (physico-chemical

parameters – although I am aware of the fact that the selenites' sizes are too small for further investigations) and “applications” of the knowledge are missing.

Chapter 3 (New aqueous lead selenites) with its subchapters 3.1. (Crystal chemistry of $\text{Pb}_2(\text{ReO}_4)_2(\text{SeO}_3)\cdot 2\text{H}_2\text{O}$ and $\text{Pb}_2(\text{ReO}_4)_2(\text{HPO}_3)\cdot 2\text{H}_2\text{O}$) and 3.2. (The new compound $\text{Pb}_4(\text{SeO}_3)_3(\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$) shares similar structure with chapter 2 as at first information about the synthesis is provided followed by SC XRD results and derived crystal structure of the synthesized compounds. Subchapter 3.1 and its respective dedicated compounds were also studied by XRD and IR analysis resulting – based on the IR spectra and detected bands – on precise information of the existing groups, molecules and species (ReO_4^- , H_2O , SeO_3^{2-} and HPO_3^{2-} , respectively).

Again, it is out of doubt that the candidate did a tremendous volume of work, but I am missing thoughts of the broader impact of the findings.

It seems again that the candidate run out of time prior the submission deadline of his thesis as the scientific notation of the new compound (subchapter 3.2) varies.

Chapter 4 (New anhydrous selenites of heavy and transition metals) with its subchapters 4.1. ($\text{Cd}_7\text{Cu}_2(\text{SeO}_3)_8\text{Br}_2$), 4.2. (A new bismuth selenite chloride, $\text{Bi}_5(\text{Se}_2\text{O}_5)(\text{SeO}_3)_5\text{Cl}_3$) and 4.3 (Crystal chemistry of new compounds in Pb-Cu-SeO₃-Cl/Br system) shares again similar structure with chapters 2 and 3 with at first information about the synthesis followed by SC XRD results and derived crystal structure of the synthesized compounds.

Although I repeat myself, the candidate seems to be a glutton for work, doing superb synthesis, careful investigations and interpretations that enable him to derive sophisticated crystal structures, but information about the impact of the findings for future work is missing.

The final chapter of the thesis is the conclusion chapter that briefly lists the findings. 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 and still missing information as well as to define urgently needed future work at the Q&A-part of his defense.

Unfortunately, some flaws in the written part of the thesis linked to sloppiness and careless performance of the English version of the thesis exist (e.g., two individual words are not separated by spaces, words are written twice), as well as typos (e.g., “easy” typos that still allow to recognize the proper word or “severe” typos that make it impossible to guess the proper word). The style of the reference list is also not consistent and in some references the authors are separated by comma, while in other references semicolon is used. This is an indication of sloppiness and is highly unprofessional.

However, still it is beyond doubt that the submitted thesis of Mr. Grishaev is a ‘solid piece of work’ and the high level of the PhD is out of question.

The thoughts of mine above regarding flaw, questions and topics for discussion should not be counted or judged as severe criticism of Mr. Grishaev’s work and his findings.

Mr. Grishaev 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.

The dissertation is a scientific qualification work that resolves a scientific problem important for the development of the relevant field of science or provides new science-based technical, technological or other solutions and developments vital for the national development.

No violations of paragraphs 9 and 11 of the Order No.11181/1 as of November 19, 2021 "On the Procedure for Awarding Academic Degrees at St. Petersburg State University" have been detected.

The dissertation meets the criteria of dissertations for the academic degree of candidate of sciences, established by the specified Order. The dissertation is recommended for the defense at St. Petersburg State University.

Member of the dissertation council
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