

Report on the PhD thesis manuscript “Crystal Chemistry of new oxide compounds of Se⁴⁺ and Se⁶⁺” by Vadim Kovrugin.

The submitted PhD thesis manuscript concerns the synthesis and crystal chemistry of several new phases in various chemical systems containing selenites, selenates and mixed selenite-selenates based frameworks. The chemical flexibility and mineralogical importance of these species justify the importance of this very broad study. The experimental investigations and results cover a broad range of chemical series from, from transition metal selenites, to heavy atoms (Bi, uranyl ...) selenites which gives to Vadim Kovrugin a strong expertise in the topology and crystal-chemistry of complex inorganic compounds. Not only oxides but also mixed anion phases (including halides, phosphites ... etc), hybrid materials, and lonepair cations have been prepared and accurately characterized which reinforce my excellent impression about the ability and talent of the candidate.

The proposed work includes a very important synthetic/chemistry aspect, including powder elaboration and crystal growth. Vadim Kovrugin has used standard high temperature routes, solvothermal routes but also more puzzling so-called “chemical vapour transports” (CVT) methods, focusing on the achievement of well-crystalline phases for further studies. Even though the prepared phases are dominated by selenites SeO₃²⁻ groups very stable in the full pH and redox- diagrams of selenium salts, more or less protonated SeO₄²⁻ selenates have also been isolated and studied after solvothermal precipitations. I also noticed the efforts provided to prepare single phases for further characterizations such as the magnetic ones. At this point, an important skill in inorganic chemistry was necessary.

Besides the discovery of almost 40 novel structures or isomorphs (which is rather impressive I must say), I would like to highlight very positive features which characterize the manuscript and outstanding results such as :

- The general excellent quality of the crystallographic work and detailed analysis with art-quality figures.
- The ability of Vadim to handle either “classical” either “alternative” (i.e. oxo-centered anion polyhedral description) models specifically adapted to particular counter cations and frameworks.
- The use of systematic listings and classifications of antagonist phases in related systems (see p. 37 and concerned paper)
- The systematic search in very complex solvothermal systems, tuning several chemical parameters (see p. 17, 23, 43 and concerned papers)

- The original evidence of the analogy between Se lonepair and P-H bonds, with important future impact (see p.44).
- The very subtle evidence of the analogy between two very closed $Pb_4(V_3O_8)_2(SeO_3)_3(H_2O)$ polymorphs (see p.27).
- ...

The manuscript by itself is very condensed due to editorial constraints and it may suffer from the choice of Vadim to have privileged the structural work – sometimes in a redundant manner, compared to the publications given in the appendix -. However , my remark should be nuanced, taking into account the exceptional volume and versatile amount of provided work and published results.

In details, this work led to nine research papers published in high level international journals and several other ones are planned. They are gather at the end of the manuscript and give a complementary lighting on the manuscript main text. Here one could appreciate how Vadim's work stand at the inorg. chemistry/mineralogy interface, which could not appear in the manuscript. The scientific production, by its own, confirms the very good quality of the proposed work. Here again, it is striking that not only the crystallographic aspect - which appears central in the manuscript – but also a lot of extra spectroscopic, physical and chemical features have been analyzed and are clearly detailed. They will be most certainly discussed at the defense.

In summary given my very favorable impressions, I can conclude that this thesis represents a high-rank research from scientific point of view. Both the scientific production but also the thesis itself undoubtedly confirm the qualification of Vadim Kovrugin of having fulfilled abilities for obtaining his PhD thesis. Therefore I give my unrestricted recommendation to the responsible advisory board to continue and complete the PhD process.

Dr Olivier Mentré

