

Review of the PhD thesis
«Crystal Chemistry of Novel Oxide Compounds of Se⁴⁺ and Se⁶⁺»
submitted by Vadim M. Kovrugin for the degree of Doctor of Philosophy in Geology
at the St.-Petersburg State University, Russia

It is a pleasure for me to be acknowledged with the PhD thesis by Vadim Kovrugin. Even a brief reading of the abstract referred to 39 new compounds synthesized and studied by the author inspires that we deal with the solid experimental work. Further reading of the thesis well corroborates with that first look. The valuable list of references, many of them being published in the top-ranked journals, confirms that the presented thesis is quite complete scientific study.

As a reviewer, however, I would like to make some comments to that thesis. Most of the remarks can be considered as cosmetic ones, but the following thing, albeit related to the representation of the experimental data, looks important to me. The Chapter 2.6, «Crystal chemical studies of uranyl selenates and selenite-selenates» (p. 70) is related to the structural study of 16 selenite and selenate compounds. The cationic part of all of them is represented by the quarternized aliphatic amines. It is well known that those amines, when having two or more carbon atoms per molecule, can not be unambiguously characterized using the so-called **sum formula**. For example, the sum formula [C₂H₈N] can be equally ascribed to both dimethylammonium, [Me₂NH₂]⁺ and ethylammonium, [EtNH₃]⁺ – structurally, the two absolutely different cations. Than what we can see: the author of this PhD thesis expresses the compound c6.16, [C₂H₈N][(H₅O₂)(H₂O)][(UO₂)₂(SeO₄)₃(H₂SeO₃)](H₂O) (p. 59) as 48-letter formula, in which 41(!) letter is devoted to detailed layout of the inorganic part (even distinguishing between the two different water molecules) ...and leaves unattended the above discussed ambiguity, [C₂H₈N]. Why than the author doesn't write the formula in the following way: [C₂H₈N] H₁₁O₂₃Se₄U₂ ? Much shorter. And if somebody wants to know the structural features of uranium and selenium, the reader can simply go through the supplementary materials (or read the footnotes to the one-page tables). But, if all the chemists would represent the organic parts of the formulae in this way, the majority of the papers would be unreadable.

Several minor comments.

p. 9. «already well-known compounds in order to optimize their physical and chemical properties by doping, coating, shaping etc... the so-called “material science”». I think, the author somewhat overrates the value of the so-called “pure science”. It is quite common that the materials science, being multidisciplinary one, includes all aspects of the “pure science” plus a bit more – just listen the journals like the Chemistry of Materials. I believe there is no so-called “material science” or so-called “pure science” – but, of course, one can meet the scientists and the so-called “scientists”.

p. 10 «The field of selenides (Se²⁻) essentially insoluble in water is out of the scope of this work». That is a mistake: there is a lot of water-soluble selenides.

p.10 «Natural selenites notably dominate selenates among known minerals, as probable result of the easy reduction processes of selenates to selenites and elemental selenium in aqueous environments.» That can be a matter of discussion. There can be other reasons for the absence of selenates on the Earth, the first one is a value of Se(IV)/Se(VI) redox potential which can not be realized in the most of the terrestrial environments.

Coming back to the PhD thesis itself: the comments listed above do not compromise the overall high quality of the submitted thesis. It is obvious that the presented work meets the highest international standards, and I am confident with my conclusion that Vadim M. Kovrugin is worthy of the award of the PhD degree in Geology at St.-Petersburg State University.

Sergey N. Britvin, Dr.
Associate Professor, Department of Crystallography
Institute of Geosciences
Saint-Petersburg State University