Review

of the Dissertation of Vadim M. Kovrugin «Crystal Chemistry of Novel Oxide Compounds of Se^{4+} and Se^{6+}» submitted for the degree of Doctor of Philosophy in Geology at the St. Petersburg State University

The dissertation of Vadim Kovrugin contains results of of syntheses, and the detailed crystal chemical study of 39 novel Se oxide compounds in the oxidation states of +4 (selenites) and +6 (selenates) with broad structural diversifications. The bioavailability and mobility of selenium in the environment are controlled by their speciation, i.e. their structural and chemical properties, such as oxidation state, coordination, nature of ligands, complexation, etc. Depending on the conditions, selenium may be present in the form of adsorption complexes, can coexist with other elements in solid solutions, or may form their own phases. In the latter case, the structural stability of these phases plays a crucial role in determining the mobility of this element and its release to the biosphere. So, Vadim Kovrugin's dissertation has the particular interest from both scientific and public points of view.

The dissertation consists of 73 pages, including 8 published articles, six of which is primary authorships for the candidate. In my opinion, this shows convincingly that Vadim Kovrugin is the major contributor to the project, and that he obtained most of the experimental evidence leading to the conclusions made in this dissertation.

To give a brief overview of contents, the dissertation has three Parts: (1) **introduction**, (2) **brief description of results** and (3) **conclusion and perspectives**. Main results obtained by V. Kovrugin are given in Part 2 followed by seven sections that cover the basic results of the crystal chemical studies of selenites and selenates. The ***Section* 2.1** of reviewed dissertation describes the synthesis of certain compounds and their studies by different methods. The ***Section* 2.2** contains results of synthetic and structural studies of eight novel copper oxoselenites inspired by mineralogical discoveries in such unusual geological conditions as volcanic fumaroles.The ***Section* 2.3** is devoted to investigation of the crystal growth in the PbO-NiO-SeO_2 system in hydrothermal conditions. It led to the synthesis of four novel lead nickel/cobalt selenites. In ***Section* 2.4**, V. Kovrugin describe the pathways for synthesis of lead vanadate selenites, report on crystal structures of three novel phases, and discuss the phenomenon of polymorphism in vanadate selenites. ***Section* 2.5** contains a structural characterization of seven new compounds: one manganese selenate, three bismuth selenites, and three manganese bismuth selenites. The last three phases are the first examples of oxide compounds containing both bismuth and manganese cations. The ***Section* 2.6** contains results of synthetic and structural studies sixteen novel uranyl selenates and mixed valence selenite-selenates. Special interest in these uranyl selenates is clear, because the oxidation of high-level waste results in formation of crystalline selenite compounds and their crystal chemical studies are necessary for investigations and modeling the processes accompanying the decay of unstable uranium isotopes and their release into the environment. The analogy between lone electron pairs of selenite groups and H– P bonds of the phosphite anions is discussed in ***Section* 2.7**.

In the last Part 3 (conclusion and perspectives) Vadim Kovrugin writes about perspectives of future studies with special attention to the emulation and modelling of natural crystal growth processes in order to obtain complex functional materials with a potential in terms of specific physical properties.

I have some insignificant remarks.

It should be noted that the conditions of hydrothermal synthesis of the selenites in the experiments of the applicant are quite different from the conditions of formation of these minerals in the oxidized zones of ore deposits where secondary selenites and selenates formed near the surface

with actively participating aqueous solutions and seasonal variations of temperature and atmospheric pressure (~1 bar). Conditions in experiments with autoclaves are different, higher temperature and pressure, as well as inishial materials submitted by the oxides.

Unfortunately, the physico-chemical conditions of formation of selenites under hydrothermal conditions (including the activity of the components in solution, redox conditions, speciation of elements in solutions, etc.) are not discussed in the thesis. However, in the literature one can find a lot of data on the minerals' stability in the systems metal-selenium-water which is quite essential to analyze the conditions under which selenites and selenates replace selenides, and selen-bearing sulfides in the oxidation zones of sulfide ore deposits or upon weathering of technologic waste.

To summarize it should be stated that Vadim Kovrugin has completed a well designed work and obtained interesting and important results, which are accurately described and discussed in his thesis, the most of data are received by Vadim M. Kovrugin himself or with his active participation. The results obtained are valid, most of them have been published in peer-reviewed Russian and international journals.

This leads this reviewer to conclude that Vadim Kovrugin's dissertation «**Crystal Chemistry of Novel Oxide Compounds of Se^{4+} and Se^{6+}**» and its design correspond to international standards and are sufficient to apply for the degree of Doctor of Philosophy in Geology at the Saint-Petersburg State University.

Prof. Dr. Vladimir G. Krivovichev
Department of Mineralogy
Institute of Earth Sciences
Saint-Petersburg State University,
Russia

29/08/2015