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REFEREE REPORT

on the Ph.D. Thesis of Mr. V. Kovrugin

«Crystal chemistry of new oxide compounds of Se⁴⁺ and Se⁶⁺

(Crystallochimie de Nouveaux Composés d'Oxyde du Se⁴⁺ et de Se⁶⁺)»

The PhD Thesis of Mr. Vadim Kovrugin is dedicated to an important and rapidly developing area of mixed-anion inorganic structures. Several outstanding families are concerned, involving i) structures involving lone-pair cations which are of interest due to their magnetic, catalytic, storage, separation and other applications, and ii) uranyl-organo-inorganic frameworks featuring particularly complex and non-trivial frameworks. The oxidized forms of selenium, namely, its various oxo-anions, bridge the two families into a self-consistent scientific contribution. About forty new compounds, acquired via different and elaborated synthetic routes, have been identified and accurately characterized. The major part of these results has been published as regular articles in high-impact international journals. This illustrates the excellent quality and reliability of the presented results. All synthetic protocols and details of structural characterization are documented in detail. A vast collection of new high-quality data is expected to help in further understanding the crystal chemistry of several peculiar inorganic families; they can be recommended to use as illustrative material for lectures and textbooks in inorganic chemistry.

It is a pity that most characterizations do not go beyond accurate determination and detailed description of the structures. Though selenite (and tellurite) halides are notorious for easy preparation of single crystals but not bulk materials, there are now enough examples where not

only structural, but also magnetic, thermal and other data are presented – particularly for copper selenite halides. The compounds manganese are also interesting for possible magnetic phenomena. I could not unfortunately find whether the attempts in preparing bulk samples have been made (they might be not successful, of course!). The same applies to the uranium compounds where are no magnetic ions but other properties, typical for framework structures, might appear.

I also do not exactly agree with the description of crystal growth via transport reactions. The appearance of hydroselenites in the initially anhydrous systems (metal oxide/halide – selenium oxide) suggests absorption of water during processing. In the description of synthetic procedures, I could not find whether very hygroscopic selenium dioxide was handled in a dry chamber or in air; possibly the latter. It looks like the absorbed water together with hydrogen halides, formed upon thermal hydrolysis, are the true transporting agents in these systems. Nonetheless, this combination appeared to be particularly useful in producing many new compounds which is the author's very important finding. From my own experience, the crystals of truly anhydrous selenite halides are sometimes much harder to obtain.

The small and inevitable “roughness” of the Thesis evidently does not anyway mar the work which creates a nice impression. In my opinion, the Thesis fully meets the requirements (amount of data, quality, consistency), and the author, Mr. Vadim Kovrugin, is indeed worthy of the Ph.D. (Candidate of Sciences) degree.

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