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**Report on the PhD thesis manuscript entitled « *Crystal Chemistry of Novel Oxide Compounds of $Se^{4+}$ and $Se^{6+}$* » presented by Mr. Vadim M. Kovrugin (Université de Lille 1, France – Saint-Petersburg State University, Russia)**

I the undersigned, Dr. Olivier Hernandez, associate Professor at University Rennes 1, France, have evaluated the manuscript written by Mr. Vadim M. Kovrugin, candidate for a PhD thesis defense in *Molecules and Condensed Matter* of University of Lille 1, France. His work entitled « *Cristallochimie de Nouveaux Composés d'Oxyde du $Se^{4+}$ et du $Se^{6+}$* » is an international joint supervision PhD thesis in between University of Lille 1, France (Drs. Olivier Mentré & Marie Colmont, UCCS, UMR CNRS #8181) and Saint-Petersburg State University, Russia (Prof. Serguey V. Krivovichev, Department of Crystallography, Institute of Earth Sciences).

The *document* of 228 pages is organized in two parts: (i) first the "*manuscript*" itself over 54 pages, composed by an introduction, a brief description of the results, conclusion and perspectives, references; (ii) second over 174 pages a compilation of nine papers as appendix (including for some of them supplementary information) whose Mr. Kovrugin is co-author since 2012.

The *manuscript* describes mostly the single-crystal synthesis and crystallographic characterization of 39 new oxide compounds containing selenium in the oxidation state of +4 and +6 and exhibiting a broad range of structural topologies, from 0D to 3D frameworks. The synthesized compounds can been divided into six families (constituting the guiding line of the "Brief description of results" section; the number of new discovered compound(s) being indicated at the end of each line):

(1) Copper selenites (×8),
(2) Nickel and cobalt selenites (×4),
(3) Vanadate selenites (×3),
(4) Selenium compounds with manganese and bismuth (×7),
(5) Uranyl selenates and selenite-selenates (×16),
(6) Iron selenite (×1).

From a crude quantitative viewpoint, the number of new transition metal, post-transition metal and uranyl selenite/selenate crystal compounds synthesized, isolated and structurally solved by single-crystal X-ray diffraction, is really amazing and this already constitutes a real *tour de force* that should be stressed. It is even more noteworthy if one considers the non-standard synthesis methods used at the laboratory (chemical vapor transport; hydrothermal

conditions; isothermal evaporation from aqueous solution), original “geo-inspired” approaches that mimic natural mineralogical or geological processes – for instance occurring in magmatic chambers and involving condensation of gases in natural volcanic fumaroles.

Different experimental techniques, besides those above mentioned, are cited in 2.1 “Objects and Methods” subsection (namely IR spectroscopy, SEM/EDS, SQUID, SHG microscopy). Those techniques have indeed been used in the published papers included at the end of the *document*, but Mr. Kovrugin has made the choice for the *manuscript* itself to focus onto the crystal growth and the subsequent systematic structural description of the 39 novel crystal phases. Maybe Mr. Kovrugin has himself mostly applied the chemical synthesis and the XRD characterizations and felt more at ease with the two latter experimental techniques for the writing of his thesis. Nevertheless few comments of the physical properties exhibited by his original compounds could have been added, for instance concerning the magnetic behavior. Anyway it turns out that the structural analyses are exceptionally detailed, accurate and well-written revealing a real mineralogical and crystallographic culture learned by the candidate. Besides the traditional crystalline atomic models, other structural descriptions or analyses (such as the nodal representation and the resulting graph of Krivovichev *et al.*; the calculation of partial charges using the Henry’s method etc.) are occasionally used in order to rationalize the topological and geometrical features of the different compounds belonging to the same chemical family, or to better understand the bond polarization.

The reading of the appendix, the nine included articles, encompassing international journals as renowned as *Chemical Communications*, *Inorganic Chemistry*, *Crystal Growth and Design*, *Journal of Solid State Chemistry*, *Mineralogy and Petrology*, *Zeitschrift für Kristallographie*, *Mineralogical Magazine*, *Structural Chemistry*, *Mendeleev Communications*, apparently chronologically sorted, reveals without doubt the scale, the quality and the impact of the PhD work undertaken by Mr. Kovrugin since 2012. However it is always difficult from such collective articles only to pull out a personal contribution as should be a PhD thesis. The candidate appears as contacting author for article #1, and first author of articles #2, 4, 5, 7, 8, 9, that is objectively extremely laudatory. By contrast, I have the feeling that the hierarchization of the obtained scientific results could have been more considered by the candidate in the *manuscript* itself, instead of making the choice of completeness. For instance one may highlight the following results: flexibility of organically templated uranyl selenite-selenate, SHG active giant structure in a bismuth chloroselenite, pH-controlled pathway for the elaboration of lead nickel selenites, modular mixed valence $Cu^{(I)}$-$Cu^{(II)}$ lead oxoselenite chlorides etc. **Owing to the density, the quality and the originality of his contribution in the field of the crystal chemistry of metal selenites/selenates, I warmly recommend to authorize Mr. Kovrugin to defend verbally his PhD thesis in the presence of the competent jury**.

Dr. Olivier HERNANDEZ