Review of opponent on PhD dissertation "Crystal chemistry of natural and synthetic titanium and molybdenum oxocompounds" by Anna S. Pakhomova

Atomic energy is exclusively important for the human life. On the other hand, activity of nuclear power plants leads to the accumulation of radioactive wastes that endanger the existence of life on our planet. PhD thesis of Anna Pakhomova is part of the tremendous efforts that humanity spends nowadays to answer the question as to whether further development of nuclear power is reasonable; and if yes, then how should processes and technologies of waste repository be arranged. The important direction of these investigations is studies of atomic and molecular structure of radioactive products of nuclear reactions that should be buried as well as materials that are perspective for the safe disposal of radioactive components. The present thesis was done in the light of this problem.

The main results were obtained by the PhD student under the supervision of Professor S.V. Krivovichev by means of X-ray single-crystal structure analysis. Crystal-structure determination of five molybdates and three titanates (including one mineral) were performed on the high level nowadays typical for Crystallography Department of Saint-Petersburg State University. Crystal structures are fully comprehended by the author, well-described, graphically illustrated by pictures and do not evoke questions. Also the synthesis experiments are sufficiently clearly described.

From the viewpoint of further development of the PhD topic, the following questions could be asked as more likely to be considered as advice for the future.

- 1. Author writes: "Octahedral coordination is the most typical for Mo⁶⁺"... Five-fold coordination for Mo⁶⁺ (trigonal bipyramids and square pyramids) is less common... And in four-fold coordination Mo⁶⁺ forms tetrahedra". Moreover, in the PhD thesis the compounds with different oxygen coordination of molybdenum are exemplified. Continuing this analysis, one might ask, in what cases the certain molybdenum-oxygen coordination polyhedron appear, *i.e.*, whether it is possible to predict oxygen (or other) environment molybdenum atom in particular structure.
- 2. In the Discussion part (p.17), the interesting finding is the dependence shown at Fig. 2. Author writes: "There is a tendency for the increasing the Mo-O bond lengths with increasing coordination number of the oxygen atoms". While agreeing with this interpretation of convincing graphic, "as it might be expected" can be added to the formulation of this regularity. After all, the higher coordination number of oxygen atoms means the greater number of chemical bonds it forms with other cations, and the weaker (and longer) the Mo-O bond.
- 3. About the title of the dissertation. The answer to the question of the generality of the research clearly given by the author in the applied aspect: "Crystal chemistry of molybdates and titanates is of special interest due to the appearance of these compounds in the nuclear fuel cycle". But the fundamental aspect is important as well. How would you formulate crystal-chemical generality of studied molybdates and titanates?

The obtained results by the completeness and reliability fully meet the requirements of the PhD thesis, and author of the thesis, Anna Pakhomova, deserves the award of the required degree.

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