REVIEW

of the PhD thesis

"**Crystal chemistry of natural and synthetic titanium and molybdenum oxocompounds**"

by Anna S. Pakhomova

The PhD thesis by Anna Pakhomova devoted to a series of oxocompounds with Mo and Ti is actual in light of different problems related to nuclear power engineering: molybdates with different cations are formed in the nulear fuel cycle whereas murataite- and zirconolite-type oxides are now considered as perspective crystalline materials for the immobilization of dangerous highly radioactive elements, at the first time actinides.

The thesis reviewed is good representative of classic crystal chemical works. The molybdate compounds were synthesized by the author while other samples, both natural and synthetic, were received from colleagues. Crystal structures of all compounds were solved by the author on single crystals using direct XRD methods. One of the most impressive and interesting parts of the work is detailed, with numerous illustrations, discussion of crystal chemistry of studied samples, especially for murataites, and the extended comparative analysis of their structures involving, in particular, the modular approach. For the characterization of the new mineral species laachite, the distribution of cations with different charges and radii in structure positions plays very important role. Complicated chemical composition of this mineral strongly hampered this work but the evidences given by Anna for the proposed structure model (and, correspondingly, the crystal chemical formula) of laachite seem convincing, including the distribution of Mn between different-type sites.

Some not very significant critical comments and questions take place. (1) No explanation found what was a reason to choose too unusual, from the geometry viewpoint (in combination of α, β and γ angles), unit cell for $Cs_2Mo_4O_{13}$. (2) The high *R* value (15.56%) for synthetic murataite-8*C* also needs explanation. (3) Chemical relationship between studied samples of murataite-3*C* and murataite-8*C* remains unclear from the thesis and included papers. Are they chemically identical, *i.e*. represent real polymorphs? But, in this case, why they show different brightness on SEM (BSE) image (Figure 4)? And, in author's opinion, is chemical composition of murataite the essential feature that determines its structure (type of modification) or no?

In any case, these comments and questions do not decrease my high rating of the thesis by Anna Pakhomova. Her work contains much new, interesting and scientifically valuable information. It is well-organized and well-illustrated, with detailed discussion of the data obtained. The results have obvious practical importance for the nuclear fuel industry (including the ecological aspect). In general, the work can be considered as significant contribution to

crystal chemistry of oxocompounds with high-valent metals (Mo, Ti, Nb), both minerals and their synthetic analogues and relatives. Anna Pakhomova seems a highly qualified crystallographer and crystal chemist who undoubtedly deserves the PhD degree of Saint-Petersburg State University.

Prof. Dr. Igor V. Pekov
Dept. of Mineralogy, Faculty of Geology,
Moscow State University, Russia