Università di Torino
Dipartimento di Scienze della Terra
Giovanni Ferraris, professor emeritus
Via Valperga Caluso, 35 - 10125 TORINO - Italy
Tel. +39 011 670 5121 - Fax +39 011 670 5128 – Home 0161 216072 – Mobile 3331099811
E-mail giovanni.ferraris@unito.it
http://www.crystallography.fr/cims/ferraris.htm

Report on the thesis work submitted by the candidate Anna S. Pakhomova

The core of the results presented by the candidate Anna S. Pakhomova in her thesis work (*Crystal chemistry of natural and synthetic titanium and molybdenum oxocompounds*) concerns the structural characterization of five novel synthetic alkali molybdates: β-$Cs_2Mo_4O_{13}$, $Cs_3(Mo_2O_7)Br$, (1-ethyl-3-methylimidazolium)3K(Mo_8O_{26}), (1-ethyl-3-methylimidazolium)3Rb(Mo_8O_{26}) and (1-ethyl-3-methylimidazolium)2Cs_2(Mo_8O_{26}). For all these compounds the results have been published in international journals and the articles are integral part of the submitted written work of thesis.

Further results obtained during her period of doctorate are presented in the thesis; they concern the crystal structures of murataite-3C and -8C, members of the pyrochlore-murataite polysomatic series, and of the recently approved new minerals species laachite, $(Ca,Mn)_2(Zr,Mn)_2Nb_2TiFeO_{14}$. In four out of five published articles the candidate is first author and declares to have written the text herself.

The candidate has acquired international experience as shown by her stage of six months at Bern University, in the laboratory of professor Armbruster, and the presentation of results at international meetings. Altogether, her attendance to national and international meetings is witnessed by a list of fourteen abstracts.

All the studied compounds are related to problems connected with the management of nuclear waste. In fact, molybdates form in the oxidation process of liquid high-level waste (HLW); consequently, their crystal chemical characterization is necessary for modeling the processes accompanying the decay of unstable uranium isotopes and their release into the environment. Titanates with zirconolite-type (like the new mineral laachite) and murataite-type structures are instead technologically important for their capability of immobilizing radioactive isotopes in their structures.

Most of the studied compounds have been synthesized in the laboratory, either hydrothermally or by ionothemal method. The procedures of synthesis are a valuable part of the

results presented in the thesis work; in particular, the ionothermal method is discussed in the article PII. All the crystal structures have been solved and refined by using single-crystal X-ray diffraction data. The structures are carefully analyzed and described with the help of very clear, original and instructive figures.

The results of the thesis work contribute not only to the structural characterization of compounds that may have technological applications in the treatment of nuclear waste – for example, murataite is being tested for radioactive waste immobilization in Dimitrovgrad facility, Russia - , but they also well contribute to fundamental knowledge in the field of the crystal chemistry of inorganic compounds.

Concerning the second type of contribution, very important and interesting are the analyses of the titanate structures in terms of modularity (polysomatic series pyrochlore – murataite) and of anion-centered frameworks, whose connectivity is analyzed by graph theory. The candidate has also established that in the homologous series $A_2Mo_nO_{3n+1}$ the dimensionality of the structure is increasing with the increasing Mo/A ratio (A = K, Rb, Cs). Finally, taking into account that more and more the occurrence of twinning is mentioned only as an accident on the way of solving a crystal structure, I consider remarkable the photographic documentation on the singular twinning that has been discovered in laachite.

Besides different synthesis methods, single-crystal X-ray diffraction, and methods to solve, refine and assess crystal structures, the candidate has used SEM and TEM microscopy with annexed analytical facilities and infrared spectroscopy.

On the whole, the candidate Anna S. Pakhomova shows that, in the field of structural crystallography, she has reached a well documented and remarkable independence in planning and conducting scientific research, as well as in analysing and discussing the experimental results.

Giovanni Ferraris, professor emeritus

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