

Review of the PhD thesis
«Crystal chemistry of natural and synthetic titanium and molybdenum oxocompounds»
submitted by Anna S. Pakhomova for the degree of Doctor of Philosophy in Geology
at St-Petersburg State University, Russia

Storage of a liquid high-level nuclear waste (HLW) is a real present-day problem and no surprise that a large number of scientists world-wide are involved in research in this area. The submitted thesis does not give us a solution for nuclear waste storage, but provides an important information about crystal structure of various synthetic compounds which could be present in HLW or could be used for HLW storage.

The thesis can be divided in two different parts – the first one is about synthesis and crystal structure of new alkali molybdates, and the second one is about crystal structure of a synthetic Ti-bearing oxide called muratoite and a new mineral in zirconolite group – laachite. The thesis also includes reprints of four papers published in international journals and a summary of the paper published in English version of the Russian journal.

The most interesting part of the thesis is a novel concept of a modular structure of synthetic “murataite” due to the presence of pyrochlore and murataite structural blocks (modules). Also, the study of laachite is a rare example of a crystal structure of natural zirconolite-group minerals. Quite often these minerals are metamict due to presence of U and Th.

Unfortunately, the thesis does not contain any analytical data for the studied samples. This is not critical for synthesized molybdates as they have a simple composition, but important for interpretation of crystal structure of compositionally complex “murataite” and laachite. I am sure that the data is available, but why the author has not included it?

Also I have two comments/questions about the used terminology:

1) The author uses the term “titanates” to describe the studied “synthetic analogues of murataite” and “laachite” (a new mineral in zirconolite-group minerals). So why has the term “titanates” been chosen? Simply because the studied synthetic analogues contain TiO_6 octahedrons? I have not found this term in mineralogical publications related to murataite or zirconolite. These minerals are usually described as oxides or complex oxides. And a more general question - when do you regard a Ti-bearing mineral as “a titanate” and when do you regard a Ti-bearing mineral as “not a titanate”?

2) It is known that murataite is a mineral with the formula $(\text{Y,Na})_6(\text{Zn,Fe})_5\text{Ti}_{12}\text{O}_{29}(\text{O,F})_{10}\text{F}_4$. With the exception of Ti and O, all other essential elements of murataite are absent in the studied samples. However, to describe the studied synthetic compounds the author uses such terms as “synthetic murataite”, “synthetic analogue of muratoite”. In my opinion it is an incorrect usage of a term “muratoite” regarding to the studied samples. They should be described as “synthetic compounds with a murataite-type structure” and not as “synthetic murataites”.

I consider the submitted thesis as an important contribution to the field of nuclear waste. It corresponds to high international standards and Anna S. Pakhomova should be awarded with PhD degree in Geology.

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