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Report on the thesis work submitted by the candidate Elena S. Zhitova

The results presented by the candidate Elena S. Zhitova in her thesis work (*Crystal Chemistry of Natural Layered Double Hydroxides*) concern the structural characterization of polytypes of quintinite, $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3)(\text{H}_2\text{O})_3]$, a natural layered double hydroxide (LDH) from the Kovdor alkaline massif (Kola peninsula, Russia) and the Bazhenovo ultramafic massif (middle Urals, Russia).

The results are documented in five articles - in one of which the candidate is first author - mainly published in international journals, and in twelve abstracts of communications that have been presented at various national and international meetings. The candidate is first author in most of these abstracts.

Due to their peculiar crystal structures and related physical properties, LDHs are technologically important materials. Large quantities of some LDHs are synthesized to be used in industry and various applications, including environmental problems.

Practically only natural LDHs are well crystallized and form crystals that can be used to fully characterize their complex polytypic structures by single-crystal X-ray diffraction methods. In fact, X-ray powder diffraction methods hardly allow the detection of important structural aspects, like cation ordering. The aim of the thesis work is mainly directed to this purpose. All the reported 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 and original figures. The chemical composition of the studied samples has been quantitatively determined by electron microprobe analyses; infrared spectra have been useful too.

A main difficulty that had to be overcome in the structural study of the considered samples has been the presence in their diffraction patterns of classes of weak reflections generated by the ordering of the closely scattering Al and Mg. When present, the candidate has been able to overcome the problem thanks to a careful analysis of sections of the three-dimensional diffraction patterns that

in the thesis are documented by several figures. Thus, it has been possible to obtain important information on the structural ordering of the Mg and Al cations. Due the close scattering power of these two cations, they have been successfully discriminated only by evaluating the cation-O bond lengths.

Often the rows of weak reflections are accompanied by streaks that are indicative of some disorder in the stacking of the layers. This aspect has been mentioned too, but it should deserve a deeper discussion.

As a general result, it has been established that all samples studied in the thesis correspond to quintinite and not to hydrotalcite or manasseite, as was thought previously. Precisely, the occurrence of the following four polytypes of quintinite has been determined: *2H-3c*, *1M*, *2H* and *2H-1c*; two of them were unknown before the thesis work. On the basis of the acquired experience in the study of these polytypes a new scheme for their description is proposed; this scheme takes into account the mentioned cation ordering.

The thesis work has also obtained two important results useful for the general understanding of the mineral species belonging to the hydrotalcite supergroup to which quintinites belong. The members with Mg_2Al stoichiometry strongly tend to cation ordering with consequent formation of superstructures, even if Mg,Al-disordered quintinite does exist too. Besides, it has been shown that both polytype formation and cation ordering depend on the crystallization temperature, disorder being favoured by high temperatures.

The candidate Elena S. Zhitova shows a remarkable capability in solving complex crystallographic problems related to polytypism and the consequences on it of cation ordering. On the whole, in the field of structural crystallography she has acquired an appreciable independence in planning and conducting scientific research as well as in analysing the experimental results.

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