Novel 2:1 Layers Formed by Dehydroxylating (Fe⁶⁺, Mg)-Rich Dioctahedral Mica. Toshihiro Kogure a, Victor A. Drits b, "Graduate School of Science, The University of Tokyo, Tokyo, Japan." Russian Academy of Sciences, Moscow, Russia.
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It is known that dioctahedral 2:1 phyllosilicates are topochemically dehydroxylated by heating. This dehydroxylation induces cation migration in the octahedral sheet in several phyllosilicates [1]. For instance, the cis-vacant (cv) illite transforms to a structure with cation distribution close to the trans-vacant (tv) structure. On the other hand, it was reported that superstructures within a 2:1 layer are formed in celadonite, trans-vacant (Fe³⁺, Mg)-rich dioctahedral mica, by dehydroxylation [2]. The present paper reports the origin and detail of these superstructures by using HRTEM [3].

When celadonite was annealed around 650°C, a primitive a-b super-cell formed. HRTEM images indicate that the superstructure is owing to a long-range cation ordering in the octahedral sheet, in agreement with the suggestion by Muller et al. [2]. However, the image simulation using the site occupancy they proposed could not completely reproduce the experimental contrast. A new model to explain the contrast is under consideration.

Celadonite annealed at ~800°C shows extra reflections which correspond to a 3b super-cell in the c-axis: a first module layer (labeled A), with general composition [(Ag,Cu)₄(As,Sb)S₄]₁, and a second module layer (labeled B), with general composition [(Ag,Cu)S₂]⁻¹. In the structure, (As,Sb)S₄ forms isolated (As,Sb)₄ pyramids typically occurring in sulfosalts, copper links two sulfur atoms in a linear coordination, and silver occupies sites with coordination ranging from quasi linear to almost tetrahedral. In the B layer of the disordered forms, the silver cations are found in various sites corresponding to the most pronounced probability density function locations of diffusion paths.

In this talk it will be presented the state of the art of the crystal chemistry of these minerals on the basis of (1) consideration of the pearceite-polybasite minerals as a family of polytypes, (2) new IMA-approved nomenclature rules, (3) differential scanning calorimetric and complex impedance spectroscopic studies on all the members of the group, (4) study of the ionic phase transitions by high- and low-temperature single-crystal X-ray diffraction and (5) electron diffraction studies.

Keywords: layered silicates; HRTEM; micas

Cation–Cation Interaction (CCIs) in Novel Layered And Framework Uranium Compounds. Evgeny V. Alekseev a, Sergey V. Krivovichev b, Wulf Depmeier b.
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In higher oxidation states, actinides possess an unique coordination chemistry, owing to their tendency to form linear actinyl ions. One of the interesting points in their crystal chemistry is cation–cation interaction (CCIs) between actinyl ions. CCIs are well-recognized for the Np(V), Pu(V), and Am(V) chemistry, but are rather rare for U(VI). In the frame of our research in the area of uranium crystal chemistry we prepared 9 new uranyl compounds with CCIs, six uranyl arsenates: Li₃[(UO₂)₉(AsO₄)] (1), Li₂[((UO₂)₉(AsO₄)](As₂O₃) (2), Li₂[((UO₂)₉(AsO₄)]O (3), Ag[(UO₂)₉(AsO₄)] (4), Ba₂[((UO₂)₉(AsO₄)]O (5), Ba₂[(UO₂)₉(AsO₄)]O (6), one uranyl molybdate: Li₃[(UO₂)₉(As₂O₃)(Mo₇O₂₄)] (7), and two uranyl tungstates: Na₂Li₃[(UO₂)₉(WO₄)] (8), Ag₂Na₂Li₃[(UO₂)₉(WO₄)] (9). Compounds 1, 2, 3, 4, 5, 6 and 7 have framework structures, whereas phases 8 and 9 are based on double layers. In all these structures the uranyl groups have different equatorial coordination: in the...