

Natural layered double hydroxides from the Kovdor alkaline massif, Kola Peninsula, Russia: Cation ordering and formation of superstructures

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Layered double hydroxides (LDHs) constitute an important group of inorganic materials with many applications ranging from catalysis and absorption to carriers for drug delivery, DNA intercalation and carbon dioxide sequestration [1]. There are about 40 mineral species that belong to the group of LDHs, and many of them are important from both geochemical and environmental viewpoints.

The structures of double layered hydroxides (LDHs) are based upon double brucite-like hydroxide layers $[M_n^{2+}M_m^{3+}(OH)_{2(m+n)}]^{m+}$, where $M^{2+} = Mg^{2+}$, Fe²⁺, Mn²⁺, Zn²⁺, etc.; M³⁺ = Al³⁺, Fe³⁺, Cr³⁺, Mn³⁺, etc. The positive charge of the layer is compensated by the interlayer species: anions (CO₃²⁻, Cl⁻, SO₄²⁻, etc.) or both anions and cations (Na⁺, Ca²⁺, Sr²⁺, etc.). Due to the layered character of the structure, LDHs display such structural features as cation ordering, formation of superstructures, charge distribution, stacking faults and polytypism [1].

The main factor of chemical diversity of LDH minerals are: i) chemical nature of the cations M^{2+} and M^{3+} ; ii) $M^{2+}:M^{3+}$ ratio (most common 2:1 and 3:1); iii) chemical nature of interlayer anions (or both anions and cations) [2].

It is necessary to say that as a rule only natural LDHs suitable to single-crystal X-ray diffraction analysis, that allowed to identify such crystal chemical features as cation and anion ordering and formation of superstructures.

In the current work we report a review of the above-mentioned structural features of natural LDHs and present some new results. In particular, we describe the cation ordering (Mg-Al) and formation of superstructures of different polytypes of quintinite $Mg_4Al_2(OH)_{12}(CO_3)(H_2O)_3$ – natural carbonate LDH with $M^{2+}:M^{3+}$ ratio 2:1.

In general, it seems that the Mg_2Al (2:1) composition in natural LDHs shows strong tendency to Mg-Al cation ordering and formation of superstructures dependent upon the temperature of crystallization.

References

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