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Order-disorder approach to calcioaravaipaite, [$PbCa_2Al(F,OH)_9$]: The crystal structure of the triclinic MDO polytype

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ABSTRACT

The crystal structure of calcioaravaipaite, $PbCa_2Al(F,OH)_9$, was initially solved by direct methods in the monoclinic space group $A2/m$ (R = 12.4%). Further study demonstrated the OD nature of the structure, and showed that the crystal was twinned. The structure was solved in the triclinic space group $C\bar{1}$, a = 7.722(3), b = 7.516(3), c = 12.206(4) Å, α = 98.86(1), β = 96.91(1), γ = 90.00(1)°, V = 694.8(3) Å^3, Z = 4, yielding R = 5.1% for 1420 reflections with $F_o > 4\sigma(F_o)$.

Calcioaravaipaite belongs to a family of order-disorder (OD) structures formed by equivalent layers of symmetry $C2/m$. Two maximum-degree-of-order (MDO) polytypes are possible. MDO1 results from a regular alternation of stacking operators $2_{1/2}$ and $2_{-1/2}$ and yields a monoclinic structure with $C2/c$, a = 7.72, b = 7.52, c = 24.12 Å, β = 96.99°. MDO2 results from the sequence $2_{1/2}$ / $2_{1/2}$ / $2_{1/2}$ /… and yields a triclinic structure with a = 7.72, b = 7.52, c = 12.21 Å, α = 98.86, β = 96.91, γ = 90.00°.

The structure of calcioaravaipaite is comprised of two kinds of alternating polyhedral slabs parallel to (001). Slab 1 consists of a fluorite-like double layer of edge-sharing (CaF_8) distorted cubes and slab 2 is a composite of face- and edge-sharing (PbF_{12}) polyhedra and outlying (AlF_6) octahedra, the latter sharing faces and edges with the (PbF_{12}) polyhedra, but no elements with one another. Aravaipaite and calcioaravaipaite share a common fluorite-type layer; however, in aravaipaite the presence of Pb^{2+} rather than Ca^{2+} in this layer results in slabs of strikingly different polyhedral configuration.