Order-disorder approach to calcioaravaipaite, [PbCa$_2$Al(F$_3$OH)$_9$]: The crystal structure of the triclinic MDO polytype

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ABSTRACT

The crystal structure of calcioaravaipaite, PbCa$_2$Al(F$_3$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 $C1$, $a = 7.722(3)$, $b = 7.516(3)$, $c = 12.206(4)$ Å, $\alpha = 98.86(1)$, $\beta = 96.91(1)$, $\gamma = 90.00(1)^\circ$, $V = 694.8(3)$ Å$^3$, $Z = 4$, yielding $R = 5.1\%$ for 1420 reflections with $F_0 > 4\sigma(F_0)$.

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, $\beta = 96.99^\circ$. 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, $\alpha = 98.86$, $\beta = 96.91$, $\gamma = 90.00^\circ$.

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.

INTRODUCTION

Calcioaravaipaite is one of six recently described lead-fluoride minerals from the Grand Reef mine in the Aravaipa mining district of Graham County, Arizona (Kampf et al. 1989; Kampf and Foord 1995, 1996). The mineral was named for its apparent close relationship to aravaipaite. In the original description of calcioaravaipaite, Kampf and Foord (1996) provided the ideal formula PbCa$_2$Al(F$_3$OH)$_9$, which is comparable to that reported by Kampf et al. (1989) for aravaipaite, Pb$_3$Al(F$_3$OH)$_9$. Kampf (2001) determined the crystal structure of aravaipaite and provided the revised ideal formula Pb$_3$AlF$_5$·H$_2$O and the symmetry and unit cell: $P2_1/n$, $a = 25.048(4)$, $b = 5.8459(8)$, $c = 5.6805(7)$ Å, $\beta = 94.013(3)^\circ$. The original X-ray diffraction study of calcioaravaipaite (Kampf and Foord 1996) yielded an A-centered monoclinic cell with $a = 23.906$, $b = 7.516$, $c = 7.699$ Å, $\beta = 92.25^\circ$, which for comparison with aravaipaite was also reported as the alternate primitive triclinic cell: $a = 5.380$, $b = 23.906$, $c = 5.380$ Å, $\alpha = 91.62$, $\beta = 91.38$, $\gamma = 88.38^\circ$ (transformation matrix $0 -1/2 -1/2$ $1/2$ $0$ $0$ $0$ $1/2$ $1/2$).

We derived a promising structural model by using diffraction data collected with reference to the above mentioned A-centered cell and refined it to an acceptable $R$-value (12.4%). However some oddities in the structural results were observed:

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For a full understanding of the subsequent steps it seems proper to introduce first the order-disorder (OD) description of calcioaravaipaite, and then to discuss the solution and refinement of the structure. For an appraisal of the OD theory and its relevance in the structural characterization of minerals, the reader is referred to Đurović (1997, and references therein) and Merlino (1997).

OD DESCRIPTION OF CALCIOARAIPAITE

For a better understanding of the OD features of calcioaravaipaite, reference will be made in this section to a monoclinic cell with $a = 7.72$, $b = 7.52$, $c = 23.96$ Å, $\beta = 92.21^\circ$, obtained from the cell of the original X-ray diffraction study...