

## The crystal structures and Raman spectra of aravaipaite and calcioaravaipaite

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### ABSTRACT

The original structure determination for aravaipaite,  $\text{Pb}_3\text{AlF}_9(\text{H}_2\text{O})$ , indicated it to be monoclinic,  $P2_1/n$ , with  $a = 25.048(4)$ ,  $b = 5.8459(8)$ ,  $c = 5.6505(7)$  Å,  $\beta = 94.013(3)^\circ$ ,  $V = 829.7(2)$  Å<sup>3</sup>, and  $Z = 4$ . Examination of additional crystal fragments from the same specimen revealed that some have a triclinic cell,  $P\bar{1}$ , with  $a = 5.6637(1)$ ,  $b = 5.8659(1)$ ,  $c = 12.7041(9)$  Å,  $\alpha = 98.725(7)^\circ$ ,  $\beta = 94.020(7)^\circ$ ,  $\gamma = 90.683(6)^\circ$ ,  $V = 416.04(3)$  Å<sup>3</sup>, and  $Z = 2$ . The topology of the structure is the same as that reported previously, but the structure refinement is significantly improved, with  $R_1 = 0.0263$  for 1695 observed reflections [ $F_o > 4\sigma F$ ] and 0.0306 for all 1903 reflections, and with the H atoms located. Twinning may be responsible for the original monoclinic cell or the two structures could be order-disorder (OD) polytypes.

New X-ray diffraction data collected on a crystal of calcioaravaipaite,  $\text{PbCa}_2\text{Al}(\text{F},\text{OH})_9$ , showed it to be triclinic,  $P1$ , with  $a = 5.3815(3)$ ,  $b = 5.3846(3)$ ,  $c = 12.2034(6)$  Å,  $\alpha = 91.364(2)^\circ$ ,  $\beta = 101.110(3)^\circ$ ,  $\gamma = 91.525(3)^\circ$ ,  $V = 346.72(3)$  Å<sup>3</sup>, and  $Z = 2$ . This cell is essentially identical to the reduced cell reported in conjunction with an earlier structure solution on a twinned crystal using the OD approach. Our study confirms the findings of the earlier study and significantly improves upon the earlier structure refinement, yielding  $R_1 = 0.0195$  for 2257 observed reflections [ $F_o > 4\sigma F$ ] and 0.0227 for all 2427 reflections.

The structures of aravaipaite and calcioaravaipaite are based upon square-packed layers of F atoms on either side of which are bonded Pb atoms (in aravaipaite) or Ca atoms (in calcioaravaipaite) in fluorite-type configurations. These layers parallel to (001) serve as templates to which on both sides are attached  $\text{AlF}_6$  octahedra and  $\text{PbF}_6(\text{H}_2\text{O})_2$  polyhedra (in aravaipaite) or  $\text{PbF}_{12}$  polyhedra (in calcioaravaipaite). The  $\text{Pb}^{2+}$  cations in these structures have stereoactive  $6s^2$  lone-electron-pairs, manifest in off-center coordinations. The very different sizes of the  $\text{Pb}^{2+}$  and  $\text{Ca}^{2+}$  cations yield fluorite-type layers with very different metrics, reflected in the  $a$  and  $b$  cell dimensions of the two structures; but more significantly, the lone-pair effect results in a very irregular template of F atoms peripheral to the fluorite-type layer in aravaipaite, while the F atoms peripheral to the fluorite-type layer in calcioaravaipaite are in a more regular, nearly planar array. As a result, the interlayer  $\text{AlF}_6$  octahedra and  $\text{PbF}_6(\text{H}_2\text{O})_2$  polyhedra in aravaipaite form a relatively open configuration, while the  $\text{AlF}_6$  octahedra and  $\text{PbF}_{12}$  polyhedra in calcioaravaipaite form a more tightly packed configuration containing no  $\text{H}_2\text{O}$  molecules.

The Raman spectra of aravaipaite and calcioaravaipaite are consistent with the results of the structure studies, except that the spectrum of calcioaravaipaite exhibits the strong bands typically associated with OH stretching vibrations, while the structure refinement is most consistent with full occupancy of all anion sites by only F.

**Keywords:** Aravaipaite, calcioaravaipaite, crystal structure,  $\text{Pb}^{2+}$   $6s^2$  lone-electron-pair, fluorite-type layer structure, order-disorder structure, Raman spectroscopy, Grand Reef mine, Arizona