The crystal structures and Raman spectra of aravaipaite and calcioaravaipaite

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ABSTRACT

The original structure determination for aravaipaite, PbAlF3(H2O), indicated it to be monoclinic, P21/n, with a = 25.048(4), b = 5.8459(8), c = 5.6505(7) Å, β = 94.013(3)°, V = 829.7(2) Å3, and Z = 4. Examination of additional crystal fragments from the same specimen revealed that some have a triclinic cell, PT, with a = 5.6637(1), b = 5.8659(1), c = 12.7041(9) Å, α = 98.725(7)°, β = 94.020(7)°, γ = 90.683(6)°, V = 416.04(3) Å3, and Z = 2. The topology of the structure is the same as that reported previously, but the structure refinement is significantly improved, with R1 = 0.0263 for 1695 observed reflections [Fo > 4σFo] 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, PbCa2Al(F,OH)6, showed it to be triclinic, P1, with a = 5.3815(3), b = 5.3846(3), c = 12.2034(6) Å, α = 91.364(2)°, β = 101.110(3)°, γ = 91.525(3)°, V = 346.72(3) Å3, 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 R1 = 0.0195 for 2257 observed reflections [Fo > 4σFo] 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 bonded AlF6 octahedra and PbF6(H2O)3 polyhedra (in aravaipaite) or PbF6 polyhedra (in calcioaravaipaite). The Pb5+ cations in these structures have stereotypical 6s2 lone-electron-pairs, manifest in off-center coordinations. The very different sizes of the Pb5+ and Ca2+ 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 AlF6 octahedra and PbF6(H2O)3 polyhedra in aravaipaite form a relatively open configuration, while the AlF6 octahedra and PbF6 polyhedra in calcioaravaipaite form a more tightly packed configuration containing no H2O 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, Pb5+ 6s2 lone-electron-pair, fluorite-type layer structure, order-disorder structure, Raman spectroscopy, Grand Reef mine, Arizona

INTRODUCTION

Aravaipaite was originally described by Kampf et al. (1989) from the Grand Reef mine in the Aravaipa mining district of southeastern Arizona. A triclinic cell was reported with a = 5.842(2), b = 25.20(5), c = 5.652(2) Å, α = 93.84(4), β = 90.14(4), γ = 85.28(4)°, V = 827(2) Å3, and Z = 4; however, polysynthetic twinning on (010) made single-crystal studies difficult and frustrated initial efforts to obtain structure data.

A specimen with larger, superior-quality crystals was later provided for study by one of the authors (W.W.P.). Although these crystals exhibited the same pervasive polysynthetic twinning, a small crystal fragment that appeared to be untwinned provided data that allowed the solution of the crystal structure. The cell derived was monoclinic, P21/n, with a = 25.048(4), b = 5.8459(8), c = 5.6505(7) Å, β = 94.013(3)°, V = 829.7(2) Å3, and Z = 4 (Kampf 2001).

Recently, examination of crystals from this same specimen in conjunction with the RRUFF Project (Downs 2006) by one of the authors (H.Y.) determined the long cell dimension to be