Crystal structure determination of anandite-2*M* mica

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Abstract

Anandite, a trioctahedral mica, has an ideal chemical formula of $Ba(FeMg)_3(SiFe^{3+})O_{10}(OH)S$ and a microprobe-derived formula of $(Ba_{0.96}K_{0.03}Na_{0.01})_{\Sigma=1.00}(Fe^{2+}_{2.01}Mg_{0.46}Fe^{3+}_{0.28}Al_{0.10}Mn^{3+}_{0.04}Mn^{2+}_{0.04}Ti_{0.01})_{\Sigma=2.93}(Si_{2.60}Fe^{3+}_{1.40})_{\Sigma=4.00}O_{10}[(OH)_{0.96}S_{0.84}Cl_{0.16}F_{0.04}]_{\Sigma=2.00}$, where S^{2-} primarily substitutes for $(OH)^-$. A single-crystal, X-ray structure determination of anandite-2*M* was refined to $R_1 = 0.0443$ and w$R_2 = 0.1232$ on F^2 in space group *Am*. Cell parameters are: $a = 5.4431(3)$, $b = 9.4719(6)$, $c = 20.042(1)$ Å, and $\beta = 95.046(1)°$. Layer stacking is analogous to a 1*M* stacking pattern (parallel unidirectional $a/3$ shifts within layers and octahedral set I only occupied), however cation order and (S,OH) positional disorder produce a two-layer repeat with β equaling ~95°. Subgroup symmetry of *Am* results from tetrahedral sheets within layers that are non-centrosymmetric with unequal compositions ($Si_{0.61}Fe^{3+}_{0.39}$ vs. $Si_{0.79}Fe^{3+}_{0.21}$) and thicknesses (difference of 0.209 Å), and there is positional and site-occupancy disorder (four sites with S of 0, 30, 52, and 58%) of (S,OH). Characteristics of anandite-2*M*, which are similar to those of anandite-2*O*, include (1) alternation of smaller tetrahedral rings containing four Si-rich tetrahedra (T1a: 1.643 Å, T2b: 1.657 Å) and two Fe^{3+}-rich tetrahedra (T2a: 1.733 Å, T1b: 1.760 Å) and larger rings containing four Fe^{3+}-rich tetrahedra and two Si-rich tetrahedra within each layer; (2) nearly in-phase wave forms of basal O atoms across the interlayer ($\Delta z = -0.110$ and 0.011 Å and across the interlayer $\Delta z = -0.121$ and 0.007 Å); and (3) attraction that results in Ba being shifted toward S (0.070 Å) and S being shifted toward Ba (0.117 Å average) along the *c* axis, relative to the ideal. Bond-valence calculations show that Ba is shifted toward the undersaturated, bridging-basal O atoms of the Fe^{3+}-rich tetrahedra and toward S-rich sites to achieve charge balance. Comparison of anandite-2*M* and anandite-2*O* shows that they possess unit cells (2*M* setting) that have nearly equal *a* axes, unequal *b* and *c* axes, and β (anandite-2*M* is smaller by 0.0371 Å, larger by 0.08 Å, and smaller by 0.089°, respectively). Moreover, anandite-2*O* exhibits larger Fe^{3+}-rich tetrahedral rings than anandite-2*M*, which allow for a greater shift in Ba (difference of 0.03 Å). The ordering and consequent absence of a twofold axis in anandite-2*M* allows the in-phase wave structure of basal O atoms, which was previously thought only possible in the orthorhombic *P* cell.

Keywords: Anandite mica, single-crystal X-ray diffraction, two-layer monoclinic mica polytypes, phyllosilicate, Ba-rich mica, S-rich mica, Fe-rich mica