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The crystal chemical role of Zn in alunite-type minerals: Structure refinements for kintoreite and zincian kintoreite

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Abstract

Kintoreite, $PbFe_3H_{0.94}[(PO_4)_{0.97}(SO_4)_{0.03}]_2(OH)_6$, and zincian kintoreite, $PbZn_{0.3}Fe_3H_{0.24}[(PO_4)_{0.54}(SO_4)_{0.08}(AsO_4)_{0.38}]_2(OH)_6$, have rhombohedral symmetry, space group $R\bar{3}m$, with hexagonal cell parameters $a = 7.2963(5)$ Å, $c = 16.8491(5)$ Å, and $a = 7.3789(3)$ Å, $c = 16.8552(7)$ Å, respectively. The structures have been refined using single-crystal X-ray data to $R_1 = 0.030$ for 374 observed reflections and $R_1 = 0.035$ for 399 observed reflections, respectively. The structures of both minerals comprise rhombohedral stacking of (001) composite layers of corner-shared octahedra and tetrahedra with Pb atoms occupying icosahedral sites between the layers, as in the alunite-type structure. The corner-connected octahedra form three-membered and six-membered rings as in hexagonal tungsten bronzes. The structure of zincian kintoreite differs from other alunite-type structures in having partial occupation, by Zn, of new sites within the six-membered rings in the octahedral layers. The Zn is displaced to an off-center position in the hexagonal ring, where it assumes fivefold trigonal-bipyramidal coordination, to three of the hydroxyl anions forming the ring, and to the apical O anions of the XO_4 tetrahedra on opposite sides of the ring. The different structural modes of Zn incorporation into SO_4-dominant and $(P,As)O_4$-dominant members of $A^{2+}B_3^{3+}(XO_4)_2(OH)_6$ alunite-type minerals are discussed in terms of the different charge-compensation mechanisms involved.

Keywords: Zincian kintoreite, crystal structure, alunite-type structure, single-crystal study