Structure refinement of legrandite and paradamite: crystal chemistry and hydrogen bonds

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Legrandite, Zn₂AsO₄(OH)H₂O and paradamite, Zn₂AsO₄(OH), are zinc arsenate minerals and have a color between pale yellow and yellowish brown. Related minerals of legrandite and paradamite are adamite, Zn₂AsO₄(OH), and so on with different structures. We performed the structure refinement of legrandite and paradamite Oujela Mine, Mapimi, Durango, Mexico, by (RAPID) RIGAKU single-crystal structure analysis system. We determined the hydrogen position by difference Fourier method. We revealed the detail hydrogen bond using bond valence calculation and hydrogen positions and compared crystal structures of these. The structure of legrandite is constituted by two AsO₄ tetrahedrons, ZnO₆ octahedron and three ZnO₅ trigonal dipyramids that have large unique distortion. AsO₄ tetrahedron, ZnO₅ trigonal dipyramid and ZnO₆ octahedron constitutes the unique framework. The structure of paradamite is constituted by AsO₄ tetrahedron and two ZnO₅ trigonal dipyramid that have large unique distortion. In legrandite, 5 coordination of trigonal dipyramids have a distance to be expected from ionic radii but interatomic distance of Zn(3)-O(1) has extraordinary distance. Two OH groups bond to Zn1 and Zn2, Zn3 and Zn4 make the ZnO₅(H₂O)₂ trigonal dipyramid that is bonded to two H₂O group in legrandite. In paradamite, Zn1 and Zn2 make ZnO₅(OH)₂ and ZnO₅(OH) trigonal dipyramid. Hydrogen atoms make a lot of hydrogen bonding in legrandite and paradamite. Crystal structure of legrandite has a tunnel structure continuous that is only parallel to c axis and similar structure is observed in paradamite only parallel to a axis. There are path of proton-conduction in these direction and we conjecture that these proton-conductivity have large anisotropy of one dimension.

Keywords: structure refinement, legrandite, paradamite, crystal chemistry, hydrogen bonds