Crystal Structure and Chemistry of, RIPS-4 $(H_3NCH_2CH_2NH_3)In_3P_3O_{12}(OH)_2$

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Introduction

An indium phosphate was synthesized using a structure directing ethylenediammine as a structure directing agent. Different chemical and structural properties can be expected for open framework indium phosphates than for the more common microporous materials containing Al and Ga phosphates. The increase in atomic radii from Al to Ga and In tends to favor octahedral coordination for In, whereas most tetrahedrally bonded cations share only oxygen atoms at a vertex, as in conventional zeolite molecular sieves, octahedral cations (including Al) may share pairs of oxygen atoms at an edge, or even three oxygen atoms at a face. This variety of linkages is likely to produce many new materials with new and unique topological and chemical properties.

Methods and Materials

RIPS-4 was synthesized from gel composition 2.37 ethylenediamine: $InCl_3$: H_3PO_4: SiO_2: 125 H_2O. Crystals have rod-like morphologies commonly clustered into fan-shaped aggregates. After optical study of many crystals, a 12 x 12 x 42 μm^3 crystal was selected and mounted on the tip of a glass fiber tapered to 1 mm.

Results

Data were collected using bending magnet x-radiation monochromatized [Si (311) crystal] to a wavelength of 0.82657 Å and focused using horizontal and vertical Rh-coated float glass Kirpatrick-Baez mirrors to produce a 50 x 50 μm^2 beam. Data were collected using a Bruker 2K SMART CCD (charge-coupled device) detector mounted at fixed angle 35° 2θ and scanning φ in 0.5° steps with 30 seconds counting per frame. The goniometer was a single-axis Klinger rotation stage, with the axis of rotation perpendicular to the plane of the synchrotron orbit. A total of 507 frames were collected. Unit-cell dimensions were refined by least squares using 2250 reflections. Data were integrated and corrected for Lorentz, polarization, and background effects using Bruker software SAINT.[1] Systematic errors, such as beam decay and absorption, were corrected with the program SADABS[2] on the basis of the intensities of equivalent reflections. A total of 3279 reflections was obtained from 3 to 71° 2θ; of the 1590 unique reflections (R_{INT} = 5.2%), 1413 were classed as observed ($|F_o| \geq 4\sigma_F$).

Discussion

The structure consists of a complex edge- and vertex-shared framework of InO_6 octahedra and PO_4 tetrahedra sharing O atoms and forming cavities occupied by ethylenediamine species (see Fig. 1). One set of octahedra share opposing edges to form chains along the *b* axis matching the structural unit in rutile (Fig. 2). This rutile edge-shared chain has its projecting oxygen atoms shared with the vertexes of either a P tetrahedron or a second type of In octahedron. One O atom is 3-connected to In atoms, and the other O-atoms are 2-connected to In and/or P atoms. A key to this complex crystal structure is the encapsulation of the ethylenediammine inside the open framework, which results in the complex geometry of edge- and vertex-shared metal-oxygen octahedral and tetrahedral polyhedra.

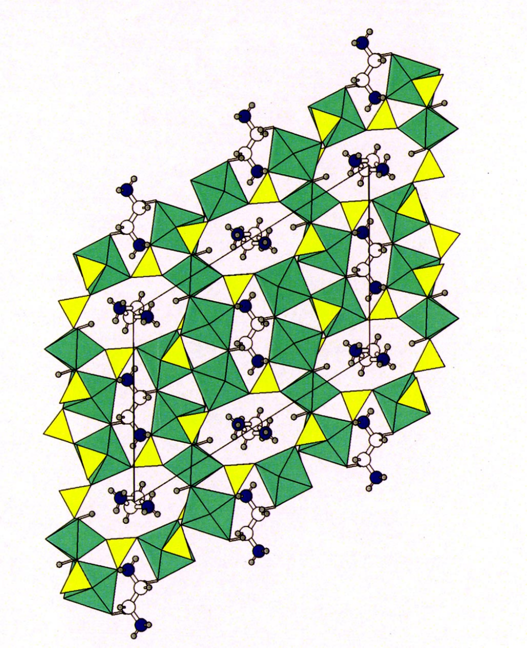

FIG. 1. RIPS-4 structure looking down b. In octahedra are shown as rectangles and P tetrahedra as triangles. Note the 2-D channel system is filled with ethylenediammonium ions (N blue, C white, and H gray spheres).

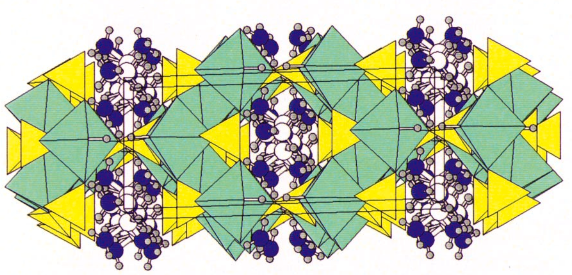

FIG. 2. RIPS-4 structure looking down c, b vertical. Chains are formed by In octahedra sharing edges and by the alternation of In octahedra and P tetrahdra.

The formula determined from all atoms found in the structure, (ethylenediamine)$In_3P_3O_{14}$, has a residual -4 charge. Valence bond calculations indicate there is a proton on each of the two oxygen atoms that only bond to, and bridge between, indium atoms. Two additional positive charges are accounted for by presuming the ethylenediamine is doubly protonated and is really present as an ethylenediammonium ion. The final structural formula for RIPS-4 is therefore $(H_3NCH_2CH_2NH_3)In_3P_3O_{12}(OH)_2$.

The inferred hydrogen positions on framework oxygen atoms and on template molecules have geometries consistent with the formation of hydrogen bonds.

Acknowledgments

This work was performed at GeoSoilEnviro CARS (GSECARS), Sector 13, Advanced Photon Source at Argonne National Laboratory. GSECARS is supported by the National Science Foundation-Earth Sciences, Department of Energy - Geosciences, W.M. Keck Foundation and the United States Department of Agriculture. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

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