

Bjarebyite, $\text{Ba}(\text{Mn,Fe})^{2+}_2\text{Al}_2(\text{OH})_3[\text{PO}_4]_3$: Its Atomic Arrangement

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Abstract

Bjarebyite, $(\text{Ba}_{0.9}, \text{Sr}_{0.1})(\text{Mn}_{0.9}, \text{Fe}_{0.9}, \text{Mg}_{0.2})^{2+}\text{Al}_2(\text{OH})_3[\text{PO}_4]_3$, a 8.930(14) Å, b 12.073(24), c 4.917(9), β 100.15(0.13)°, $P2_1/m$, possesses a new kind of Al-O octahedral arrangement. It is an octahedral chain of composition $[\text{Al}_2\text{O}_6(\text{OH})_3]$ which runs parallel to the b axis and consists of pairs of edge-sharing octahedra, each such edge-sharing pair in turn sharing a corner with another such pair. Similar chains occur in carminite and palermoite. Pairs of (Mn, Fe)-O octahedra share edges with each other as well as with the octahedra constituting the Al-O chains. The Ba^{2+} cations, which reside in large holes, possess an irregular 11-fold coordination with oxygen.

$R(hkl) = 0.062$ for 2313 reflections. Interatomic averages are Ba-O 2.87 Å, (Mn, Fe)-O 2.16, Al-O 1.91, P(1)-O 1.52, and P(2)-O 1.53.

Introduction

Bjarebyite, $(\text{Ba}_{0.9}, \text{Sr}_{0.1})(\text{Mn}_{0.9}, \text{Fe}_{0.9}, \text{Mg}_{0.2})^{2+}\text{Al}_2(\text{OH})_3[\text{PO}_4]_3$, a new species from the Palermo No. 1 pegmatite, North Groton, New Hampshire, was recently described by Moore, Lund and Keester (1973). Its unusual formula indicated that a new type of Al-O octahedral cluster might reside in the structure and, with its simple crystal cell, prompted a thorough structure analysis. We have been much interested in the systematics of polyhedral clustering of first transition series oxysalt crystals, especially of Mn^{2+} , Mn^{3+} , Fe^{2+} , and Fe^{3+} . The behavior of Al^{3+} in crystals formed at moderate to low temperature is so similar to Fe^{3+} that this cation has attracted our attention as well.

Here we would like to interject a sobering observation with which crystallographers who study mineral structures often find themselves confronted. As more and more structures are revealed, it becomes more apparent that Nature is delightfully combinatorial in what She finds the most satisfactory arrangements, and we are forced to wrest what secrets we can in a dogged, systematic way. Thus, the ultimate aim of the student of crystal structures is not to distinguish what is abundant from what is rare, but what exists and what is absent among the myriad hypothetical combinatorial structures which can geometrically and topologically potentially exist. The attempts at systematics of inorganic structure today appear to rest at a stage similar to the systematology of the Periodic Table of chemical elements one century ago.

Experimental

The cell data for bjarebyite, $(\text{Ba}_{0.9}\text{Sr}_{0.1})(\text{Mn}_{0.9}\text{Fe}_{0.9}\text{Mg}_{0.2})^{2+}\text{Al}_2(\text{OH})_3[\text{PO}_4]_3$ (Moore, Lund, and Keester, 1973), are: a 8.930(14), b 12.073(24), c 4.917(9) Å; β 100.15(13)°; V 521.8 Å³; $Z = 2$; space group $P2_1/m$; calculated density (gm cm^{-3}) 4.02 from cell data and 3.86 by a Gladstone-Dale calculation. Specific gravity was determined as 3.95 with a Berman torsion balance.

A small nearly equant single crystal measuring about 0.12 mm in mean dimension was selected from the type specimen and rotated about b on a PAILRED automated diffractometer utilizing a graphite monochromator and $\text{MoK}\alpha$ radiation. Reciprocal lattice layers from $k = 0$ to 18 were collected to a maximum $2\theta = 65^\circ$. Scans about ω showed absorption anisotropy to be less than 4 percent of the mean value at low angles and absorption correction was thus disregarded. Background counts for 20 seconds were taken on opposite sides of each peak. The scan rate was 2.5°/minute and a low, mosaic spread permitted a half-scan interval of 1.8°. Symmetry equivalent reflections were averaged and the data were processed by conventional procedures to obtain $|F(\text{obs})|$.

Solution and Refinement

A three-dimensional Patterson synthesis, $P(uvw)$, showed prominent images parallel to the uw -plane and the probable existence of a mirror plane, this latter being substantiated by the holosymmetric morphology of the crystals investigated. The very prominent Ba-Ba' vectors led to rapid determination

of the structure via the β - and γ' -syntheses of Ramachandran and Srinivasan (1970). All non-hydrogen atoms were located unambiguously.

Least squares refinement required four cycles for convergence and led to

$$R(hkl) = \frac{\sum ||F(\text{obs})| - |F(\text{calc})||}{\sum |F(\text{obs})|} = 0.062$$

for all 2313 reflections. This provided a ratio of data to variable parameters of 40:1 and the low, estimated standard error for the oxygen coordinates ($\pm 0.005 \text{ \AA}$) attests to a well-refined structure.

As scattering curves, we selected the data of Cromer and Mann (1968) for Ba^{2+} , Mn^{2+} , Al^{2+} , P^{3+} , and O^{1-} . The full-matrix least-squares refinement proceeded from a modified version (for IBM 360 computer) of the familiar ORFLS program of Busing, Martin and Levy (1962).

Table 1 provides the atomic coordinate and isotropic thermal vibration parameters and Table 2 lists the structure factor data.

Discussion of the Structure

a. Topology and Geometry of the Polyhedra

The manner of polymerization of $[\text{AlO}_6]$ octahedra in bjarebyite should determine how the Al^{3+} cation coordinates to the isolated $[\text{PO}_4]^{3-}$ tetrahedra and $(\text{OH})^-$ groups as well as how the more weakly bonded Mn^{2+} and Ba^{2+} cations are coordinated. In the bjarebyite structure (Fig. 1) the Al^{3+} cation coordinates to O(3), O(5), and O(6) from the $[\text{PO}_4]^{3-}$ tetrahedra and to the hydroxyls, O(8) and O(9). These hydroxyls are points of polymerization for the octahedra, with O(8) comprising a shared corner and a pair of O(9) ligands a shared edge. The resultant infinite chain (stippled, Fig. 1) runs parallel to the

TABLE 1. Bjarebyite. Site Multiplicities, Atomic Coordinates, and Isotropic Thermal Vibration Parameters*

		x	y	z	B (\AA^2)
X(1) = (Ba, Sr) ²⁺	2	0.5476 (1)	0.7500	0.7420 (1)	0.69 (1)
M(1) = (Mn, Fe) ²⁺	4	.2963 (1)	-.1089 (1)	.2048 (2)	.66 (2)
M(2) = Al ³⁺	4	.0899 (2)	.4003 (1)	.1275 (3)	.61 (2)
P(1)	2	.1563 (2)	.7500	.6853 (4)	.61 (3)
P(2)	4	.3312 (1)	.4409 (1)	.7034 (3)	.63 (2)
O(1)	2	.2804 (7)	.7500	.9422 (12)	.89 (7)
O(2)	2	.2290 (6)	.7500	.4298 (12)	.75 (7)
O(3)	4	.0602 (5)	.6454 (3)	.6888 (8)	.91 (5)
O(4)	4	.3694 (5)	.5557 (3)	.6153 (9)	.97 (5)
O(5)	4	.2561 (5)	.4495 (3)	.9652 (9)	.92 (5)
O(6)	4	.2251 (5)	.3822 (3)	.4657 (9)	.99 (6)
O(7)	4	.4705 (5)	.3688 (3)	.7859 (8)	.92 (5)
O(8) = (OH) ⁻	2	.1220 (6)	.2500	.0066 (12)	.81 (7)
O(9) = (OH) ⁻	4	.0572 (4)	.5567 (3)	.1905 (8)	.77 (5)

*Estimated standard errors in parentheses refer to the last digit.

b axis and has composition $[\text{Al}_2\text{O}_6(\text{OH})_3]$. A similar chain, of composition $[\text{Fe}_2\text{O}_7(\text{OH})_2]$, occurs in the structure of carminite, $\text{PbFe}^{3+}_2(\text{OH})_2[\text{AsO}_4]_2$, as determined by Finney (1963). The distribution of hydroxyls within each two edge-sharing octahedra which are components of these chains imparts to the octahedral pair the point group symmetry m for carminite (Fig. 2a) but $\bar{1}$ for bjarebyite (Fig. 2b). The similarity of the cell parameters and contents of palermoite, $\text{SrLi}_2\text{Al}_4(\text{OH})_4[\text{PO}_4]_4$, to those of carminite suggest a close structural relationship between the two. Since palermoite and bjarebyite occur together, the AlO_6 (and FeO_6) chains involving edge- plus corner-sharing is evidently stable in a particular temperature regime. We are presently investigating the crystal structure of palermoite.

The manner in which the $\text{P}(1)\text{O}_4$ tetrahedron bridges to the octahedral chain is also worthy of note. The corners of adjacent octahedra across the mirror plane are joined by a common tetrahedral edge. This configuration (Fig. 2c) is very common among the "7 \AA chain structures" of which many examples are known to science. Moore (1970a) has reviewed these structures of which abundant representatives are known in low temperature hydrothermal assemblages in pegmatites, occurring later than the bjarebyite and palermoite. The isomorphism of Al^{3+} and Fe^{3+} in such assemblages is characteristic and for these cations it would appear that, with increasing temperature, isolated octahedra form first (strengite, phosphosiderite, variscite); followed by the "7 \AA " corner-sharing chain structures (laueite, paravauxite, etc); followed by an increase in edge-sharing as in palermoite, carminite, and bjarebyite; and finally edge-sharing octahedral chains and sheets.

Of the remaining more weakly held coordination polyhedra, the MnO_6 octahedra (shaded in Fig. 1) are highly distorted and share an edge, O(2)-O(1). These in turn bond, by edge sharing along O(5)-O(9), to the Al-O octahedral chain. The Ba^{2+} cations occur at X(1) large holes within the structure and coordinate irregularly to eleven oxygen atoms, excluding two long contacts with O(5) atoms at 3.17 \AA .

b. Interatomic Distances

Table 3 lists the individual and average polyhedral interatomic distances for bjarebyite. These averages are consistent with the interpretation of the chemical analysis. Thus, M(1) has Mn^{2+} extensively substituted by Fe^{2+} since Mn^{2+} -O averages in structures with octahedral coordination are 2.20 \AA . The M(2)-O

mirror plane, does not appear to form a hydrogen bond since the distance O(8)-O(1) 3.65 Å is too long. However, O(9) = (OH)⁻ apparently forms a bond with the O(5) atom at the next level above (along the z-direction) since O(9)-O(5) is 2.60 Å, an acceptable distance. This would mean that O(5) becomes substantially oversaturated by cations ($\Sigma = 2.08 + 0.16 = 2.24$). Indeed, the M(1)-O(5) and P(2)-O(5) distances are the longest for their polyhedra.

The only remaining cation which deviates considerably from neutrality is O(9) with $\Sigma = 1.33$. Including the hydrogen bond, $\Delta\Sigma = 2/6 - 1/6 = 1/6$. This, too, is reflected in the long M(1)-O(9) and M(2)-O(9) distances. The arrangement $2M^{3+} + M^{2+}$ coordinated to OH⁻ is rather unusual, but it has been recognized in the crystal structure of basic ferrous-ferric phosphates, dufrenite, rockbridgeite, beraunite, etc (Moore, 1970b).

Acknowledgments

Support for this study was provided by the NSF GA 10932-A1 grant and a Materials Research grant (NSF) awarded to The University of Chicago.

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Manuscript received, November 5, 1973; accepted for publication, December 19, 1973.