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The Structure of $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$ and Its Relationship to the Garnet and Other *Ia3d*-Derived Structures

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The hydrated sodium zinc arsenate, $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$, has cubic symmetry, space group $P2_13$, $a = 12.243(3)$ Å, $Z = 4$. The structure was refined to $wR(F^2) = 0.028$ using 548 independent reflections from a microtwinned crystal. Both zinc and arsenic atoms are tetrahedrally coordinated. The ZnO_4 tetrahedra share all vertices with the basal vertices of the AsO_4 tetrahedra to give a 3-D framework that is closely related to the $[B_7O_{12}]^{3-}$ framework of corner-linked BO_4 and BO_3 in boracite. The sodium atoms (CN = 6) and water molecules occupy [110] channels in the framework. The structural relationships with the garnet structure and related *Ia3d*-derived structures are discussed. © 1989 Academic Press, Inc.

Introduction

We have recently commenced a general study of the chemistry of arsenic-containing zinc solutions, with potential application in the hydrometallurgical processing of arsenic-bearing zinc ores. New sodium zinc arsenates have been isolated, including two compounds with cubic unit cells and with X-ray powder diffraction patterns similar to those for the minerals sodalite and garnet.

The latter phase, with composition $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$, was obtained in the form of crystals suitable for a single-crystal X-ray diffraction study. We report here the structure determination and refinement for this compound, and its structural relationship to that of garnet and a number of other related compounds.

Experimental

Preparations were carried out at 250°C in a stainless-steel autoclave, using mixtures of reagent grade ZnO and $Na_2HAsO_4 \cdot 7H_2O$ as starting materials. The title compound formed colorless, multifaceted crystals, typically 0.1 to 0.5 mm, which were easily separated from the other reaction products, ZnO and $NaZnAsO_4$.

Precession camera studies showed cubic symmetry with a cell parameter of 12.2 Å. All the medium and strong reflections could be indexed using a body-centered cell, with extinctions corresponding to the space group $I\bar{4}3d$. However, a number of weak reflections were present that violated the *I* centering and required a reduction in space group symmetry to $P2_13$.

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For the intensity data collection a tetrahedron, 0.19 mm on edge, was mounted along $[1\bar{1}1]^*$ on a Siemens AED single-crystal diffractometer. Operating conditions were Mo$K\alpha$ radiation, θ–2θ scan, θ range 3–25°, scan speed 0.03° (2θ) sec^{-1}. A total of 6986 reflections was measured for h, k, and l ranging from −14 to 14. A standard reflection measured every 3 hr showed less than 1.5% intensity variation. The data were corrected for absorption, minimum and maximum transmission factors 0.24 and 0.32, and reduced to 1102 unique structure amplitudes, for which R_{int} was 0.04.

Refinement of the average structure in $I\bar{4}3d$ was made using SHELX76 (*1*). Refinement of the full structure in $P2_13$, allowing for microtwinning, was made using the programs MXD (*2*) and POWDER (*3*). All values for X-ray scattering factors and anomalous dispersion coefficients were taken from "International Tables for X-ray Crystallography" (*4*). Polyhedral structure diagrams were generated with STRUPLO (*5*).

Structure Determination and Refinement

Average Structure in $I\bar{4}3d$

Because the intensities of the reflections with $h + k + l = 2n + 1$ were typically only 5–10% of those for the I-centered reflections, the average structure in $I\bar{4}3d$ was determined first.

A three-dimensional Patterson map using only the reflections with $h + k + l = 2n$ yielded the positions of the two heavy atoms, arsenic and zinc, at special sites 16(c), 3,(x, x, x; x = 0.23) and 12(a), $\bar{4}$,($\frac{3}{8}$, 0, $\frac{1}{4}$), respectively. The positions of the sodium and oxygen atoms were located in Fourier and difference Fourier maps. In addition to those oxygens coordinated to arsenic and zinc, O(1) and O(2), an atom corresponding to oxygen in scattering power was located in the special site 12(b) ($\frac{7}{8}$, 0, $\frac{1}{4}$). This atom, O_w, was assigned to a water molecule; the calculated weight loss based on loss of this water, 5.7% is in reasonable agreement with the measured value of 5.1% from DTA runs.

Refinement of all positional and isotropic thermal parameters gave an R factor of 0.05 for the I-centered reflections. The thermal parameters were normal for all atoms except O(2), for which U was 0.05. A difference Fourier map showed that the main residual peaks were located around O(2) and As, at a separation from these atoms of about 0.5 and 0.15 Å, respectively.

The $I\bar{4}3d$ refinement showed that the average structure comprised a three-dimensional framework of corner-linked AsO_4 and ZnO_4 tetrahedra with sodium atoms and water molecules occupying cavities in the framework.

Structure Refinement in $P2_13$

By taking account of the weak reflections with $h + k + l = 2n + 1$ the complete structural model can be established in space group $P2_13$, which is the only primitive cubic subgroup of $I\bar{4}3d$. The reduction in space group symmetry is accompanied by a splitting of the As 16(c) site into four independent sites, with associated splitting of the coordinating O(1) and O(2) sites. This allows for independent rotation of each of the AsO_4 tetrahedra about the threefold axes.

An examination of the intensities of the P reflections showed that within experimental error, $I(hkl) = I(khl)$, in conflict with the intensity relationships for point group 23. A plausible explanation is that the $I\bar{4}3d$ average structure is stable at the temperature of preparation and that on cooling through a transition temperature, twinned microdomains of the $P2_13$ structure are formed. The twin laws will be determined by those symmetry elements that are lost in the transformation to the low-temperature phase. Specifically, [110] diad axes (or mirror planes) as twin elements would give rise to the observed equivalence of (hkl) and (khl) intensities if there were equal volume fractions of the twin domains. On the basis of this interpretation a successful refinement of the $P2_13$ structure was achieved by refining on F^2 and combining (hkl) and (khl) pairs as single observations (group reflections).

A number of trial models were established using different combinations of displaced O(2) positions, based on the residual peaks around O(2) in the F map from the $I\bar{4}3d$ refinement. The correct sense of the displacements for the four independent O(21)–O(24) atoms was established by refinement of the trial models. Displacements of the other atoms were introduced one at a time into the refinement. As the refinement converged it became evident that the intensity data were affected by extinction. Four of the strongest low-angle I reflections which were most affected were excluded from subsequent refinements.

The refinement of the atomic displacements, especially those of O(21)–O(24), was unstable when the full intensity data set was used. It was necessary to alternate refinements using all reflections with refinements using only the P reflections. This resulted in satisfactory convergence to a final $wR(F^2)$ value of 0.028 for all 548 reflections. The $wR(F^2)$ value for the 270 P reflections was 0.044. The weighting scheme used was $w = 1/(F_o^2 + F_{min}^2)$, and the quantity minimized is $\Sigma_w(F_o^2 - F_c^2)^2$. In the final refinement a scale factor, six thermal parameters (one for each atom type), and 32 atomic coordinates were varied. The largest Δ/σ was 0.01. Final coordinates and thermal parameters are given in Table I, and bond lengths and angles are listed in Table II. The table of observed and calculated F^2 can be obtained from the authors.

TABLE I

STRUCTURAL PARAMETERS FOR $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$

Atom	x	y	z	U
Zn	0.3757(5)	0.9963(3)	0.2585(2)	0.64(2)
As(1)	0.2181(2)	0.2181	0.2181	0.49(2)
As(2)	0.4715(3)	0.4715	0.4715	
As(3)	0.7329(2)	0.7329	0.7329	
As(4)	0.9803(3)	0.9803	0.9803	
Na(1)	0.0826(10)	0.0076(7)	0.2570(8)	1.54(7)
Na(2)	0.3233(12)	0.4956(9)	0.2512(8)	
O(11)	0.0591(15)	0.0591	0.0591	1.2(1)
O(12)	0.2994(14)	0.2994	0.2994	
O(13)	0.5498(15)	0.5498	0.5498	
O(14)	0.8105(15)	0.8105	0.8105	
O(21)	0.2071(10)	0.2576(10)	0.0861(10)	0.76(9)
O(22)	0.4399(10)	0.3480(10)	0.5255(10)	
O(23)	0.6702(11)	0.8080(11)	0.6365(11)	
O(24)	0.9261(11)	0.8741(11)	0.0509(11)	
O_w	0.8705(30)	0.9981(15)	0.2422(16)	2.5(2)

Discussion

Structure Description

The structure of $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$ is based on a three-dimensional framework of corner-linked ZnO_4 and AsO_4 tetrahedra, with sodium atoms and water molecules occupying framework cavities. The framework is composed of eight-member rings of alternating ZnO_4 and AsO_4 tetrahedra. Each AsO_4 tetrahedron participates in 15 such rings and the ZnO_4 tetrahedra each contribute to 20 rings, giving a total of 60 rings per unit cell. Twelve of these involve one AsO_4 from each of the four threefold axes. These rings are centered on $\bar{4}$ symmetry elements as shown in Fig. 1, with a water molecule at the center of each ring. The remaining 48 rings involve pairs of AsO_4 tetrahedra from one threefold axis plus two AsO_4 tetrahedra from other threefold axes. All vertices of the ZnO_4 tetrahedra are involved in bridging to AsO_4 whereas only three vertices of the AsO_4 tetrahedra are corner-linked to ZnO_4. The fourth vertex of each AsO_4, which is collinear with As on the threefold axes, is nonbridging.

If we consider only those oxygen atoms involved in the connectivity of the frame-

TABLE II

INTERATOMIC DISTANCES AND ANGLES FOR $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$

				O–*M*–O
Zn–O(21)	1.92(1)	O(21)–O(22)	3.27(2)	117.4(6)
–O(22)	1.91(1)	–O(23)	3.17(2)	107.0(7)
–O(23)	2.02(2)	–O(24)	3.11(2)	108.0(6)
–O(24)	1.93(2)	O(22)–O(23)	3.12(2)	105.3(2)
		–O(24)	3.19(2)	112.6(7)
		O(23)–O(24)	3.15(2)	105.7(7)
As(1)–O(12)	1.72(2)	O(12)–O(21) ×3	2.89(2)	115.6(7)
–O(21) ×3	1.69(1)	O(21)–O(21) ×3	2.64(2)	102.7(6)
As(2)–O(13)	1.66(2)	O(13)–O(22) ×3	2.83(2)	114.9(8)
–O(22) ×3	1.69(1)	O(22)–O(22) ×3	2.66(2)	103.5(6)
As(3)–O(14)	1.65(2)	O(14)–O(23) ×3	2.74(2)	110.7(8)
–O(23) ×3	1.68(2)	O(23)–O(23) ×3	2.72(2)	108.2(6)
As(4)–O(11)	1.67(2)	O(11)–O(24) ×3	2.79(2)	112.0(8)
–O(24) ×3	1.70(2)	O(24)–O(24) ×3	2.72(2)	106.9(6)
Na(1)–O(11)	2.52(2)	O(11)–O(21)	3.05(2)	76.1(6)
–O(13)	2.50(2)	–O(21)	3.05(2)	75.8(6)
–O(21)	2.43(2)	–O(23)	3.38(2)	86.5(6)
–O(21)	2.44(2)	O(13)–O(21)	3.96(2)	106.3(6)
–O(23)	2.41(2)	–O(21)	>4.0	119.4(7)
–O_w	2.61(2)	–O(23)	3.65(2)	95.9(7)
		–O_w	3.41(2)	83.9(6)
		O(21)–O(21)	2.64(2)	65.7(7)
		–O(23)	3.48(2)	91.9(6)
		–O_w	3.68(2)	93.6(6)
		O(23)–O_w	3.90(2)	102.1(6)
		O(11)–O_w	3.30(2)	80.2(6)
Na(2)–O(12)	2.49(2)	O(12)–O(22)	3.31(2)	76.8(6)
–O(14)	2.50(2)	–O(22)	3.31(2)	86.1(6)
–O(22)	2.36(2)	–O(24)	3.44(2)	90.9(7)
–O(22)	2.83(2)	–O_w	3.24(2)	83.5(7)
–O(24)	2.33(2)	O(14)–O(22)	3.69(2)	99.0(7)
–O_w	2.37(2)	–O(22)	>4.0	114.3(7)
		–O(24)	3.36(2)	88.1(7)
		–O_w	3.33(2)	86.3(7)
		O(22)–O(22)	2.66(2)	61.0(7)
		–O(24)	3.83(2)	95.6(7)
		–O_w	3.50(2)	95.3(6)
		O(24)–O_w	3.79(2)	107.6(7)

work, then the framework composition is $3ZnO_4 \cdot 4AsO_3 = (Zn_3As_4O_{12})^{2+}$. An analog is the $(B_3B_4O_{12})^{3-}$ framework in boracite, $Mg_3(B_7O_{12})OCl$ (*6*). This compound has a related system of eight-member rings of alternating, corner-linked BO_4 tetrahedra and BO_3 trigonal pyramids. The three-dimensional disposition of rings in boracite gives rise to square-sectioned channels running parallel to the axes of the *F*-centered cubic cell. The magnesium with chlorine atoms reside in the channels. For the *I*-centered cell of sodium zinc arsenate, the corresponding channels in the $(Zn_3As_4O_{12})^{2+}$ framework are parallel to ⟨110⟩ as illustrated in Fig. 2. Whereas in boracite, only half of the rings contribute to the large square channels, in $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$, 48 of the 60 rings per unit cell are involved and the channels are of correspondingly smaller cross-section. As seen from Fig. 2 the sodium atoms all reside in the channels. The water molecules are located in the interchannel regions, at the centers of the 12 rings of the type shown in Fig. 1.

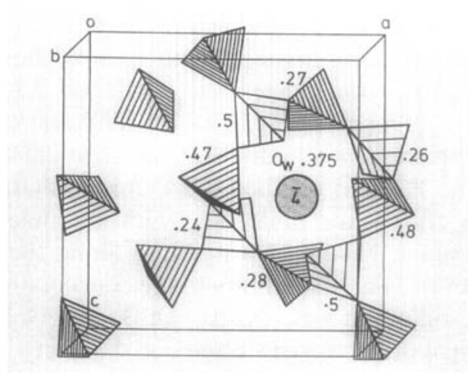

FIG. 1. A (010) slice through the structure of $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$, centered at $y = \frac{3}{8}$, showing an eight-membered ring of alternating ZnO_4 (light shading) and AsO_4 (heavy shading) tetrahedra. A water molecule is at the center of the ring at $\frac{3}{4}, \frac{3}{8}, \frac{1}{2}$. The *y* coordinates are given for the metal atoms at the centers of each tetrahedron in the ring.

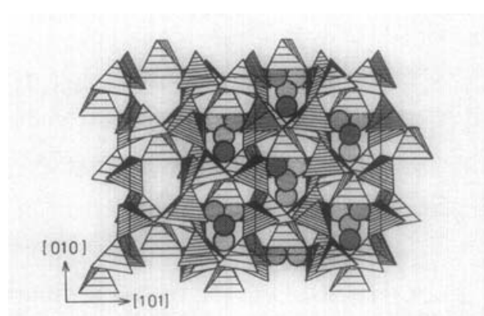

FIG. 2. Polyhedral representation of the structure of $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$, viewed in projection down [101]. ZnO_4 and AsO_4 tetrahedra have nine-line and three-line shading, respectively. Sodium atoms occupying [101] channels are shown by the stippled circles. The [101] channels are shown empty on the LHS of the diagram. The unit cell outline is shown.

The sodium atoms, Na(1) and Na(2), are both six-coordinated, with Na–O bond lengths in the ranges 2.41–2.61 and 2.33–2.83 Å, respectively. The coordination approximates octahedral for both sodium atoms. Pairs of octahedra are corner-shared via the water molecule, with the linear grouping Na–O_w–Na oriented along the $\bar{4}$ axes of $I\bar{4}3d$. In addition to the coordination to sodium atoms, O_w has O(23) and O(24) neighboring oxygen atoms at distances of 2.75 and 2.87 Å, indicative of hydrogen bonding.

The major structural modification associated with the reduction in space group symmetry from $I\bar{4}3d$ to $P2_13$ is rotation of the four independent AsO_4 tetrahedra around the threefold axes. This is shown in Fig. 3, where the $I\bar{4}3d$ and $P2_13$ structures are both viewed along [111]. In $I\bar{4}3d$, alternate triangles of O(2) oxygens along the threefold axes are fully rotated (60°), whereas in $P2_13$ successive triangles are progressively rotated in spiral fashion. Both arsenic and zinc atoms are coordinated to O(2) and the rotations of the AsO_4 and ZnO_4 tetrahedra in the $P2_13$ structure result in a reduction of the sodium coordination number, from seven (5 + 2) to six. In the $I\bar{4}3d$ average structure the sodium atom has five oxygen neighbors at 2.35–2.47 Å plus two at the longer distance of 2.98 Å. In $P2_13$ the sodium 24(d) site splits into two general 12-fold sites. The pair of Na–O(2) bonds at 2.98 Å are replaced by a longer and a shorter bond; at 2.44 and 3.39 Å for Na(1) and at 2.83 and 3.32 Å for Na(2). The O(2) displacements also result in significant changes in the environment of the water molecule. In $I\bar{4}3d$ the nearest-neighbor oxygens to O_w are 3.25 Å away, whereas in $P2_13$, O_w has two oxygen neighbors at less than 2.9 Å as described above.

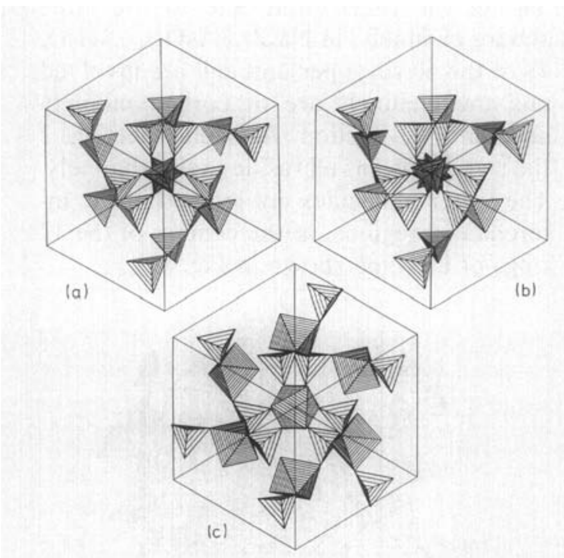

FIG. 3. [111] Projections of (a) the average structure of sodium zinc arsenate in $I\bar{4}3d$, (b) the ordered structure of the sodium zinc arsenate in $P2_13$, and (c) the garnet structure. Only the tetrahedra (and the octahedra in garnet) are shown. Tetrahedra on three axes have heavier shading. In (c) half of the $\bar{4}$ tetrahedra have been omitted to emphasize the close structural relationship to the tetrahedral framework structures shown in (a) and (b). The cell outlines are shown.

Related Structures

The average structure of $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$ in $I\bar{4}3d$ has a direct analogy with the structure of $11CaO \cdot 7Al_2O_3 \cdot CaF_2$ (*7*). This is made clearer if we rewrite the formula of the latter as $Ca_6Al_3(AlO_4)_4 \cdot F$. This compound is cubic, $I\bar{4}3d$, with a = 11.970 Å and with atomic coordinates similar to those of arsenate. Aluminum occupies both the 12(a) and 16(c) tetrahedral sites. The structure is disordered, with one-third occupancy of the 12(b) site by fluorine and with the calcium distributed over two sites separated by 0.5 Å. A closely related compound is $12CaO \cdot 7Al_2O_3$ (*8*), which is a component of cement clinkers. In this compound the 12(b) site of $I\bar{4}3d$ is only one-sixth occupied by oxygen. The calcium atoms are not disordered as in the oxyfluoride. Relative to the position of sodium in the arsenate compound the calcium atom is displaced along the $\bar{4}$ axis by about 0.4 Å. This results in it having seven oxygen neighbors (if the partially occupied

12(*b*) site is included) in the range 2.36–2.52 Å. A recent study showed high oxide ion conductivity in this compound, with bulk conductivities only 8–10 times less than that of yttria-stabilized zirconia (*9*).

The structures of the above compounds are closely related to that of garnet, with general composition $A_3B_2C_3O_{12}$ and space group *Ia*3*d*. The unit cell compositions and atomic positions for the different compounds are compared in Table III. The articulations of polyhedra in the different structures are shown in projection down [111] in Fig. 3.

The garnet structure is difficult to depict because of its dense isometric nature. O'Keeffe and Andersson (*10*) have shown how the representation can be simplified by emphasizing the atomic arrangements along the nonintersecting ⟨111⟩ trigonal axes. The garnet and other structures in cubic subgroups of *Ia*3*d* can then be described in terms of bcc rod packings. The ⟨111⟩ rods in garnet consist of alternating octahedra and trigonal prisms. The octahedra are occupied by the *B* atoms in the special site 16(*a*) (0, 0, 0). The oxygen atoms at the corners of the octahedra occupy the general position 96(*h*) and their packing creates tetrahedral sites, $\bar{4}$ symmetry, at positions 24(*d*) ($\frac{3}{8}$, 0, $\frac{1}{4}$). These sites are occupied by the *C* atoms, while the larger *A* atoms occupy distorted cubic sites, 24(*c*) ($\frac{1}{8}$, 0, $\frac{1}{4}$), between the rods. The grouping of atoms along a ⟨111⟩ rod in $Ca_3Al_2Si_3O_{12}$ is illustrated in Fig. 4.

Removal of the inversion center in going from *Ia*3*d* to *I*$\bar{4}$3*d* results in a splitting of the 96(*h*) site occupied by oxygen into two 48(*e*) sites. The triangular groupings of oxy-

TABLE III

GARNET AND OTHER *Ia*3*d*-DERIVED STRUCTURES WITH 12-Å CUBIC CELLS

Compound	Unit cell composition 1	2	3	4	5	6
Garnet, $Ca_3Al_2Si_3O_{12}$ *Ia*3*d*	Ca_{24}	$^{VI}Al_{16}$	$^{IV}Si_{12}$	$^{IV}Si_{12}$	O_{96}	—
$12CaO \cdot 7Al_2O_3$ *I*$\bar{4}$3*d*	Ca_{24}	$^{IV}Al_{16}$	$^{IV}Al_{12}$	O_2	O_{48}	O_{16}
$11CaO \cdot 7Al_2O_3 \cdot CaF_2$ *I*$\bar{4}$3*d*	Ca_{24}	$^{IV}Al_{16}$	$^{IV}Al_{12}$	F_4	O_{48}	O_{16}
$Cs_6Zn_5(MoO_4)_4$ *I*$\bar{4}$3*d*	—	$^{IV}Mo_{16}$	$^{IV}Zn_{10}$	Cs_{12}	O_{48}	O_{16}
$Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$ *P*2$_1$3	Na_{24}	$^{IV}As_{16}$	$^{IV}Zn_{12}$	$(H_2O)_{12}$	O_{48}	O_{16}
Eulytite, $Bi_4(SiO_4)_3$ *I*$\bar{4}$3*d*, *a* = 10.2 Å	—	—	$^{IV}Si_{12}$	—	O_{48}	Bi_{16}

	*Ia*3*d*	*I*$\bar{4}$3*d*	*P*2$_1$3
1. $\frac{1}{8}$ 0 $\frac{1}{4}$	222 (24)	2.. (24)	1 (12) ×2
2. 0 0 0	.3. (16)	.3. (16)	.3. (4) ×4
3. $\frac{3}{8}$ 0 $\frac{1}{4}$	4.. (24)	4.. (12)	1 (12)
4. $\frac{7}{8}$ 0 $\frac{1}{4}$		4.. (12)	1 (12)
5. 0.04 −0.06 −0.15	1 (96)	1 (48)	1 (12) ×4
6. 0.06 0.06 0.06	.3. (16)	.3. (16)	.3. (4) ×4

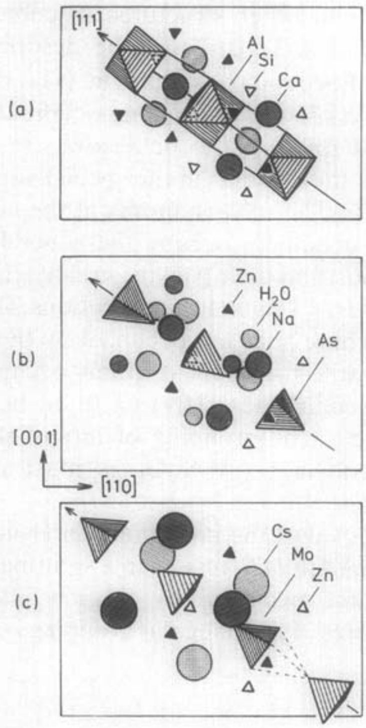

FIG. 4. Representation of the atomic arrangements along the [111] rods in (a) garnet, $Ca_3Al_2Si_3O_{12}$, (b) $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$, and (c) $Cs_6Zn_5(MoO_4)_8$.

gen atoms forming the faces of the octahedra along the three axes thus become independent in $I\bar{4}3d$. The structure of $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$ is derived from the garnet structure by replacing one set of O_3 triangular groups by a set of individual oxygen atoms situated on the three axes in $16(c)$, (x, x, x). The rod structure is thereby changed from alternating filled octahedra and empty trigonal prisms, to alternating filled and empty tetrahedra as shown in Fig. 4b. As a result of the change in the oxygen atom arrangement, half of the tetrahedral sites of the garnet structure are retained and large cavities are opened up at the other $\bar{4}$ sites. These latter sites are occupied by water molecules in the arsenate compound. The special site $24(c)$, $(\frac{1}{8}, 0\ \frac{1}{4})$, occupied by the A atoms in garnet retains its site multiplicity in $I\bar{4}3d$ as $24(d)$, $(x, 0, \frac{1}{4})$. The coordination of the A cation is reduced from 8 to 6.

The 24 oxygen atoms that are retained in the transformation of the garnet to the $I\bar{4}3d$ tetrahedral framework structure show little positional deviation from the ideal coordinates required for regular octahedra in garnet, 0.041, −0.056, −0.153 (*10*). For $12CaO \cdot 7Al_2O_3$ and $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$ (average structure in $I\bar{4}3d$) the values are 0.037, −0.057, −0.151 and 0.036, −0.064, −0.145, respectively. For comparison the oxygen coordinates in the arsenate garnet, berzeliite, are 0.039, −0.052, −0.157 (*11*). In the ordered $P2_13$ structure of sodium zinc arsenate there is considerable deviation from these values due to rotations of the independent O_3 groups about the three axes.

An interesting variation of the $I\bar{4}3d$ tetrahedral framework structures is displayed by the compound $Cs_6Zn_5(MoO_4)_8$ (*12, 13*) (see Table III and Fig. 4c). The oxygen framework and the location of the zinc atoms in the $\bar{4}$ sites are the same as those in the sodium zinc arsenate. However, the molybdenum atoms occupy the alternative set of tetrahedral sites along the three axes, as shown in Fig. 4. The corresponding $Ia3d$ structure would have the trigonal prismatic sites filled and the octahedral sites empty. Such a modification to the garnet structure without other accompanying changes cannot occur because it would create very short bonds between the B atoms in the trigonal prisms and the surrounding A atoms.

The location of the molybdenum atoms in the alternative set of tetrahedral sites along ⟨111⟩ opens up large distorted cuboctahedral cavities at the $12(b)$ $\bar{4}$ sites which are occupied by cesium atoms. These cavities encompass the $24(d)$ sites that are occupied by sodium atoms in the sodium zinc arsenate and so the $24(d)$ sites are empty in the molybdate. The ⟨110⟩ channels that are present in $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$ are effectively blocked off by the reverse orientation of the MoO_4 tetrahedra in the molybdate.

An analogy with the oxygen arrangement in the $I\bar{4}3d$ tetrahedral framework structures is provided by the mineral eulytite, $Bi_4(SiO_4)_3$ (*14*) with space group $I\bar{4}3d$. In this compound the bismuth atoms occupy approximately the same positions as the 16(*c*) oxygens in the tetrahedral structures ($x = 0.087$; cf. $x = 0.069$ in $Cs_6Zn_5(MoO_4)_8$). The two sets of BiO_3 tetrahedra have Bi–O distances of 2.15 and 2.62 Å. The larger set of tetrahedra are "occupied" by the bismuth lone pair of electrons. The SiO_4 tetrahedra in the 12(*A*) sites are rotated about the $\bar{4}$ axes by about 20° relative to the corresponding tetrahedra in $Na_6Zn_3(AsO_4)_4 \cdot 3H_2O$. This allows the structure to collapse down around the other set of $\bar{4}$ sites which are empty in eulytite. The cell dimension is correspondingly reduced from 12 to 10 Å.

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