

Refinement of the Crystal Structure of Berzeliite

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Abstract. Berzeliite $[\text{NaCa}_2(\text{Mg}_{0.85}\text{Mn}_{0.15})_2\text{As}_3\text{O}_{12}, \text{Ia}3d; Z=8, D_c=4.068 \text{ g cm}^{-3}; \text{cell constant at } 20^\circ\text{C}, a=12.355(2) \text{ \AA}; \lambda(\text{Mo } K\alpha)=0.71069 \text{ \AA}]$ has the garnet structure. In the garnet structures, the tetrahedral rotation, α , is positively correlated with the ionic radii of the octahedral and tetrahedral cations and negatively correlated with the ionic radius of the dodecahedral cation.

Introduction. The crystals used were from Langban, Sweden. Partial chemical analysis of the small amount of material available gave the following values: CaO 19.45, Na₂O 5.23, MgO 11.9, MnO 3.80 wt%. Calculation of the formula unit based on a total of five {X} and {Y} sites gave the composition $\{\text{NaCa}_2\}[\text{Mg}_{1.70}\text{Mn}_{0.30}](\text{As}_3)\text{O}_{12}$. Precession photographs exhibited cubic symmetry with systematic absences $h+k+l=2n+1$ (hkl), $2h+l=4n+1$ (hhl) \bar{C} , $k=2n$ ($0kl$) \bar{C} , consistent with the space group $\text{Ia}3d$ observed by Bubeck & Machatschki (1935). A full set of intensity data was collected over one octant out to a 2θ of 65° from an irregular equidimensional crystal of radius 0.12 mm according to the experimental procedure of Hawthorne & Ferguson (1975). A total of 1780 reflexions was collected, and standard data reduction procedures (spherical absorption correction, $\mu R=1.54$) resulted in 292 unique reflexions, of which 233 were considered as observed (3σ). Structure refinement was carried out on an IBM 370/158 computer using the program *RFINE* (Finger, 1969). Scattering factors for neutral atoms were taken from Cromer & Mann (1968) with anomalous dispersion corrections from Cromer & Liberman (1970). The parameters for andradite given by Novak & Gibbs (1971) were used as input to the least-squares routine. Several cycles of full-matrix least-squares refinement resulted in convergence (for isotropic temperature factors) at a conventional R of 4.1% (observed reflexions). Conversion to anisotropic temperature factors of the form $\exp(-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij})$ and addition of variable isotropic extinction correction resulted in convergence at an R of 3.7% and R_w (unit weights) of 4.8%. The final parameters are given in

Table 1. Interatomic distances and angles and the magnitudes and orientations of the principal axes of the thermal ellipsoids were calculated using the program *ERRORS* (L. W. Finger, personal communication) and are given in Tables 2 and 3 respectively.*

Discussion. The garnet structure is described by Gibbs & Smith (1965) and Geller (1967); the atom nomenclature used here, $\{\text{X}_3\}[\text{Y}_2](\text{Z}_3)\text{O}_{12}$, is that of Geller (1967). As the cation positions are fixed by symmetry, variation in cation size is accommodated by rotation of the polyhedra. To represent the rotation of the tetrahedron, Born & Zemann (1964) defined a positional angle, α , to represent the amount of rotation of the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31657 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Interatomic distances (\AA) and angles ($^\circ$) in berzeliite

X(1)-O(4)	2.420 (5) $\times 4$	Y—O	2.098 (4) $\times 6$
X(2)-O(4)	2.521 (5) $\times 4$	As—O	1.694 (4) $\times 4$
Mean	2.471		
As tetrahedron			
O(1)-O(2)	2.641 (9) $\times 2$	O(1)-As-O(2)	102.4 (3) $\times 2$
O(1)-O(3)	2.827 (8) $\times 4$	O(1)-As-O(3)	113.1 (2) $\times 4$
Mean	2.765	Mean	109.5
Y octahedron			
O(1)-O(4)	2.967 (8) $\times 6$	O(1)-Y-O(3)	90.0 (2) $\times 6$
O(1)-O(5)	2.968 (8) $\times 6$	O(1)-Y-O(5)	90.0 (2) $\times 6$
Mean	2.968	Mean	90.0
X triangular dodecahedron			
O(1)-O(2)	2.641 (9) $\times 2$	O(1)-X-O(2)	66.1 (2) $\times 2$
O(1)-O(4)	2.967 (8) $\times 4$	O(1)-X-O(4)	73.8 (2) $\times 4$
O(1)-O(7)	3.558 (3) $\times 4$	O(1)-X-O(7)	92.1 (2) $\times 4$
O(4)-O(6)	2.929 (9) $\times 4$	O(4)-X-O(6)	72.7 (2) $\times 4$
O(4)-O(7)	2.881 (9) $\times 2$	O(4)-X-O(7)	69.7 (2) $\times 2$
O(7)-O(8)	4.177 (8) $\times 2$	O(7)-X-O(8)	113.3 (2) $\times 2$
Mean	3.179	Mean	80.7
Cation-cation distances across shared edges			
X—As	3.089 (1) $\times 2$	X(1)-X(2)	3.783 (1) $\times 4$
X—Y	3.453 (1) $\times 4$		

Table 1. Atomic parameters for berzeliite ($\beta_{ij} \times 10^5$)

	x	y	z	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
X	$\frac{1}{8}$	0	$\frac{1}{2}$	0.55 (4)	44 (14)	114 (9)	β_{22}	0	0	45 (15)
Y	0	0	0	0.55 (5)	90 (8)	β_{11}	β_{11}	-9 (12)	β_{12}	β_{12}
(As)	$\frac{3}{8}$	0	$\frac{1}{2}$	0.20 (3)	31 (6)	32 (5)	β_{22}	0	0	0
O	0.0391 (3)	0.0522 (3)	0.6568 (3)	0.49 (6)	83 (25)	99 (25)	62 (22)	20 (19)	-28 (19)	-4 (19)

Table 3. *Magnitudes and orientations of the principal axes of the thermal ellipsoids in berzeliite*

	R.m.s. displacement (\AA^2)	Angle to <i>a</i> axis ($^\circ$)	Angle to <i>b</i> axis ($^\circ$)	Angle to <i>c</i> axis ($^\circ$)
X	0.059 (9)	0	90	90
	0.073 (9)	90	135	45
	0.111 (6)	90	45	45
	0.075 (13)	55	55	55
Y	0.087 (7)	(i)	(i)	(i)
	0.087 (6)	(i)	(i)	(i)
As	0.049 (5)	0	90	90
	0.050 (4)	90	0	90
	0.050 (3)	90	90	0
O	0.057 (15)	53 (19)	99 (22)	39 (23)
	0.079 (12)	61 (27)	135 (29)	121 (27)
	0.096 (10)	50 (22)	47 (29)	111 (19)

(i) Indeterminate.

tetrahedron about the $\bar{4}$ axis that passes through its centre. α is the smaller of the two angles between the tetrahedral O—O edge normal to the $\bar{4}$ axis and the two crystallographic axes orthogonal to the $\bar{4}$ axis. Inspection of the structure shows that a positive α rotation decreases the size of the dodecahedron relative to the octahedron and tetrahedron. In agreement with this, Meagher (1975) has shown that α exhibits a negative correlation with $r\{X\}$, the ionic radius of the dodecahedral cation, in the aluminum silicate garnets. If tetrahedral rotation is the principal mechanism of cation accommodation in the garnets, α should in general show a negative correlation with $r\{X\}$ and positive correlations with $r\{Y\}$ and $r\{Z\}$. This is shown to be the case in Fig. 1 which shows the variation in α with cation radius for a variety of refined garnet structures. It is $r\{Y\}$ rather than $r\{Z\}$ that has the greater effect on α for constant $r\{X\}$, despite the fact that tetrahedral edge lengths increase at a greater rate than octahedral edge lengths with increasing cation radius (Drits, 1971). This presumably results from the fact that the triangular dodecahedron shares four edges with adjacent octahedra but only two with adjacent tetrahedra. The dominating effect of $r\{Y\}$ for constant $r\{X\}$ is also indicated by the rare-earth garnets $\{\text{R.E.}\}\text{M}_3^3\text{O}_{12}$ (see Fig. 2), where the rate of increase of α with the weighted octahedral-tetrahedral cation radius is similar to that exhibited by those series where only $r\{Y\}$ varies.

Berzeliite has a much larger α angle (29.8°) than other garnets with comparable $r\{X\}$ values; it is apparent from Fig. 1 that this is due to the large $r\{Y\}$ value of berzeliite and not to any change in $r\{Z\}$. Similarly, large α values are to be expected for other garnets containing tetrahedral pentavalent cations as these garnets contain octahedral divalent cations which give much larger $r\{Y\}$ values than those generally encountered in garnets with tri- and tetravalent tetrahedral cations.

Intensity data were collected at the Materials Research Institute, McMaster University, Hamilton. Financial assistance was provided by the National Research Council of Canada and the University of Manitoba.

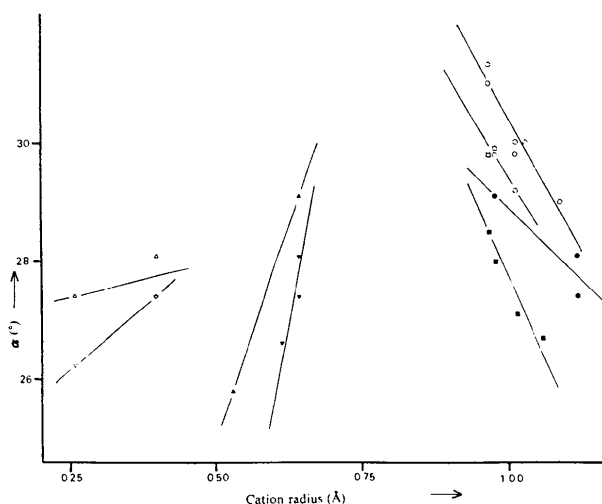


Fig. 1. Variation in tetrahedral rotation angle α versus cation radius for garnet systems with cation substitution on one site only. \circ $\text{M}_3^3 + \text{Fe}_3\text{O}_{12}$, \square $\text{M}_3^3 + \text{Ga}_3\text{O}_{12}$, \bullet $\text{M}_3^3 + \text{Fe}_2\text{Ge}_3\text{O}_{12}$, \blacksquare $\text{M}_3^3 + \text{Al}_3\text{O}_{12}$, \blacktriangle $\text{Mn}_3\text{M}_3^3 + \text{Ge}_3\text{O}_{12}$, \blacktriangledown $\text{Ca}_3\text{M}_3^3 + \text{Ge}_3\text{O}_{12}$, \triangle $\text{Ca}_3\text{Fe}_2\text{M}_3^4 + \text{O}_{12}$, ∇ $\text{Ca}_3\text{Cr}_2\text{M}_3^3 + \text{O}_{12}$.

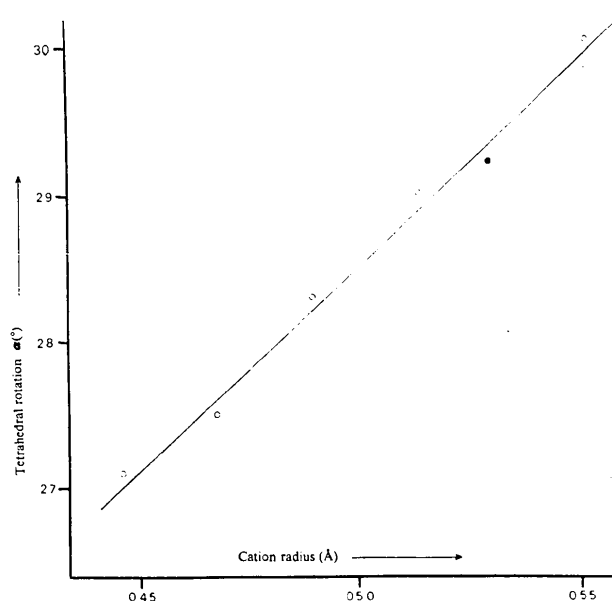


Fig. 2. Variation in tetrahedral rotation angle α versus the weighted mean cation radius for yttrium garnets with cation substitution on both octahedral and tetrahedral sites. \circ $\text{Y}_3\text{Fe}_{5-c}\text{Al}_c\text{O}_{12}$, \bullet $\text{Y}_3\text{Ga}_5\text{O}_{12}$.

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Thioxanthone 10-Oxide

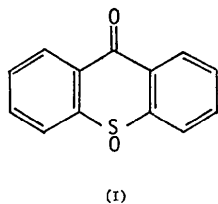
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Abstract. $C_{13}H_8O_2S$; orthorhombic, $Pca2_1$, $Z=4$; M.W. 228.27, $a=21.087$ (3), $b=4.753$ (1), $c=10.227$ (2) Å; $D_x=1.479$, $D_m=1.47$ g cm $^{-3}$ (by flotation); $\lambda(Cu K\alpha)=1.5418$ Å, $\mu(Cu K\alpha)=25.56$ cm $^{-1}$. Final residual $R=0.040$.

Introduction. Single crystals of thioxanthone 10-oxide (I) were obtained in the form of transparent prisms through the courtesy of Dr Andrew L. Ternay of the Chemistry Department of the University of Texas at Arlington.



The unit-cell parameters were obtained by measuring '+' and '-' 2θ values of 15 reflections. The space group, $Pca2_1$ or $Pcam$, was deduced from systematic absences ($h0l$ absent with h odd and $0kl$ absent with l odd). The intensity data were collected on a Syntex $P\bar{1}$ automatic diffractometer at 3°C with a crystal approximately $0.10 \times 0.20 \times 0.35$ mm. A $\theta/2\theta$ scanning mode with graphite-monochromated $Cu K\alpha$ radiation was used to measure 746 independent reflections with 2θ values below 116° , of which 721 were considered as observed by the criterion $I > 2.0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors; no absorption corrections were applied.

The structure was determined by the heavy-atom method, and the correct space group was proved to be $Pca2_1$, as also shown by the noncentrosymmetric distribution of normalized structure factors. The ratios be-

Table 1. Fractional atomic coordinates ($\times 10^4$, except $\times 10^3$ for hydrogens) and thermal parameters

The estimated standard deviations are given in parentheses and refer to the last positions of respective values. The expression for the temperature factor exponent consistent with B values in Å 2 is:

$$-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23}).$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	1356 (0)	1774 (2)	5000 (0)	2.78 (3)	3.01 (3)	2.91 (3)	0.07 (2)	-0.29 (3)	0.72 (4)
O(1)	1342 (1)	-1321 (6)	4720 (4)	3.76 (12)	2.73 (10)	5.73 (23)	-0.11 (9)	-0.23 (12)	-2.13 (14)
O(2)	1664 (1)	7932 (6)	8085 (4)	4.77 (14)	4.19 (14)	5.15 (17)	0.07 (12)	-0.35 (15)	-2.62 (13)
C(1)	516 (2)	5013 (8)	8258 (5)	4.05 (19)	3.22 (17)	3.45 (18)	0.32 (14)	0.50 (16)	-0.09 (16)
C(2)	-59 (2)	3630 (10)	8236 (5)	3.46 (17)	3.85 (19)	4.50 (24)	1.07 (16)	0.93 (18)	0.73 (19)
C(3)	-190 (2)	1648 (9)	7279 (6)	2.75 (17)	3.46 (19)	5.77 (28)	0.06 (14)	0.60 (18)	1.05 (20)
C(4)	254 (2)	1059 (9)	6325 (5)	3.24 (17)	3.34 (17)	4.40 (22)	-0.22 (15)	0.05 (17)	-0.23 (19)
C(5)	2621 (2)	1378 (7)	5166 (5)	2.72 (16)	3.49 (14)	3.84 (20)	-0.26 (13)	0.04 (16)	-1.15 (18)
C(6)	3221 (2)	2103 (9)	5615 (5)	2.89 (16)	4.00 (19)	4.67 (22)	0.34 (14)	0.44 (17)	-0.45 (20)
C(7)	3290 (2)	3981 (10)	6615 (5)	2.87 (16)	3.94 (18)	4.43 (22)	-0.69 (15)	-0.72 (18)	-0.04 (18)
C(8)	2769 (2)	5236 (8)	7181 (5)	3.41 (17)	3.08 (16)	3.59 (20)	-0.89 (13)	-0.52 (15)	-0.63 (16)
C(9)	1602 (2)	5819 (9)	7414 (4)	3.56 (17)	3.09 (15)	2.74 (17)	0.56 (15)	-0.29 (16)	-0.33 (15)
C(11)	982 (2)	4385 (7)	7318 (4)	2.87 (16)	2.24 (13)	2.95 (18)	0.64 (12)	-0.03 (15)	-0.02 (14)
C(12)	843 (2)	2429 (7)	6355 (4)	2.82 (14)	2.43 (14)	2.91 (16)	0.60 (13)	0.20 (13)	-0.11 (16)
C(13)	2099 (2)	2606 (8)	5755 (4)	2.50 (14)	2.31 (13)	2.32 (15)	-0.23 (12)	-0.14 (12)	-0.02 (15)
C(14)	2159 (2)	4544 (7)	6747 (4)	2.98 (14)	2.05 (14)	2.92 (17)	-0.05 (12)	-0.06 (14)	0.20 (14)