

Table 2. Selected geometric parameters (Å, °)

ZrO ₆ polyhedron				
Zr—O(3 ^{i,ii,iii})			2.092 (4)	(× 3)
O(3 ^{i,ii})—O(3 ^{ii,iii})			3.003 (6)	(× 3)
O(3 ^{i,ii,iii})—O(4 ^{iii,i,ii})			2.868 (7)	(× 3)
Zr—O(4 ^{ii,iii})			2.051 (4)	(× 3)
O(4 ^{i,ii})—O(4 ^{ii,iii})			2.921 (6)	(× 3)
O(3 ^{i,ii,iii})—O(4 ^{ii,iii,i})			2.928 (7)	(× 3)
O(3 ^{i,ii})—Zr—O(3 ^{ii,iii})			91.72 (2)	(× 3)
O(3 ^{i,ii,iii})—Zr—O(4 ^{iii,i,ii})			87.57 (2)	(× 3)
O(4 ^{i,ii})—Zr—O(4 ^{ii,iii})			90.80 (2)	(× 3)
O(3 ^{i,ii,iii})—Zr—O(4 ^{ii,iii,i})			89.92 (2)	(× 3)
WO ₄ polyhedra				
W(1)	O(1)	O(3)	O(3 ^{iv})	O(3 ^v)
O(1)	1.736 (4)	2.871 (6)	2.871 (6)	2.871 (7)
O(3)	109.22 (1)	1.785 (3)	2.920 (6)	2.920 (6)
O(3 ^{iv})	109.22 (1)	109.72 (1)	1.785 (3)	2.920 (6)
O(3 ^v)	109.22 (2)	109.72 (1)	109.72 (2)	1.785 (4)
W(2)	O(2 ⁱⁱ)	O(4 ^{vii})	O(4 ^{viii})	O(4 ^{ix})
O(2 ⁱⁱ)	1.713 (3)	2.724 (5)	2.724 (6)	2.724 (5)
O(4 ^{vii})	101.71 (2)	1.799 (3)	3.051 (6)	3.051 (6)
O(4 ^{viii})	101.71 (2)	115.99 (3)	1.799 (4)	3.051 (6)
O(4 ^{ix})	101.71 (2)	115.99 (3)	115.99 (3)	1.799 (4)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $\frac{1}{2} + y, \frac{3}{2} - z, 1 - x$; (iii) $\frac{3}{2} - z, 1 - x, \frac{1}{2} + y$; (iv) z, x, y ; (v) y, z, x ; (vi) $x - 1, y - 1, z - 1$; (vii) $x, y, z - 1$; (viii) $z - 1, x, y$; (ix) $y, z - 1, x$.

Table 3. Lengths and valences of M—O bonds for Zr(XO₄)₂ compounds

	β -Zr(MoO ₄) ₂ ^a		Σ_s	Zr(WO ₄) ₂ ^b		Σ_s
X—O (Å)	1.69	1.76 (× 3)		1.72	1.79 (× 3)	
s ^c	1.80	1.47 (× 3)	6.21	1.70	1.42 (× 3)	5.96
Zr—O (Å)	2.08 (× 3)	2.09 (× 3)		2.05 (× 3)	2.09 (× 3)	
s ^c	0.68 (× 3)	0.66 (× 3)	4.02	0.73 (× 3)	0.66 (× 3)	4.17

References: (a) Auray, Quarton & Tarte (1986); (b) this work; (c) Brese & O'Keeffe (1991).

A list of 177 neutron diffraction reflections has been deposited with the IUCr (Reference: DU1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Low-Pressure Polymorph of Co₃Al₂Si₃O₁₂

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Abstract

The structure of cobalt aluminium silicate garnet, Co₃Al₂Si₃O₁₂, has been redetermined from diffractometer data. Comparison of the present refinement with the published refinements for the M₃²⁺Al₂Si₃O₁₂ garnets suggests that two isostructural phases exist for the Co₃Al₂Si₃O₁₂ garnet which are dependent on the pressure.

Comment

The title compound [hereafter Co(β) garnet] is isostructural with Co₃Al₂Si₃O₁₂ [hereafter Co(α) garnet: $a = 11.455(2) \text{ \AA}$, $x = 0.03421(16)$, $y = 0.05138(15)$, $z = 0.65367(16)$ (Ohashi, Fujita & Osawa, 1981)]. Their mean Co—O distances are similar, but the ratios of the octahedral–dodecahedral shared edge (O[·]·O^v) distance to the dodecahedral–dodecahedral shared edge (O^v·O^{ix}) distance are different. Table 3 summarizes the ratios (O[·]·O^v)/(O^v·O^{ix}) and the tetrahedral position angles (Born & Zemann, 1964) in the M₃²⁺Al₂Si₃O₁₂ garnets. As shown in Fig. 2, the tetrahedral position angle is linearly dependent on the ratio (O[·]·O^v)/(O^v·O^{ix}).

From the Si—O distances [1.627(2) Å in Co(α) garnet and 1.634(1) Å in Co(β) garnet] the electronegativities of the dodecahedral (double tetrahedral) Co(α) and Co(β) atoms are estimated to be 1.8 and 1.6, respectively, on Pauling's scale (Ohashi, Fujita & Osawa, 1981).

Structures for Co-åkermanite, Ca₂CoSi₂O₇, in which the Co atom is tetrahedrally coordinated by O atoms, were reported by Kimata (1983) and Hagiya, Ohmasa & Iishi (1993). Kimata (1983) obtained smaller unit-cell dimensions [$a = 7.8258(4)$, $c = 5.0148(5) \text{ \AA}$, $V = 307.13(4) \text{ \AA}^3$] than those obtained by Hagiya *et al.* (1993) [$a = 7.8417(6)$, $c = 5.0249(3) \text{ \AA}$, $V = 308.99 \text{ \AA}^3$]. The mean Si—O distances in the two Co-åkermanites were found to be 1.608 (Kimata, 1983) and 1.618 (3) Å (Hagiya *et al.*, 1993). These Si—O distances suggest that the electronegativities of the tetrahedral Co atoms are 1.8 and 1.6, respectively, on Pauling's scale (Ohashi, 1984).

The variation of the electronegativities of the tetrahedral Co atoms in garnet and åkermanite suggest that

there are two different electronic states for the tetrahedral Co²⁺ ion [e.g. $(e)^4(t_2)^3$ for Co(α) and $(e)^{4-x}(t_2)^{3+x}$ for Co(β)]. In the tetrahedral site, the shielding constant increases with an increase of the (t_2) electrons and the (t_2) electrons increase with a decrease of the crystal-field strength.

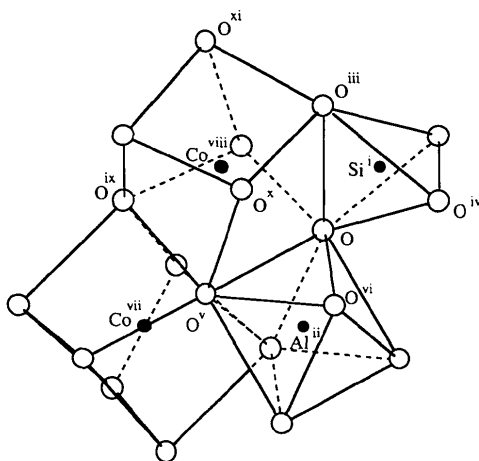


Fig. 1. A portion of the garnet structure.

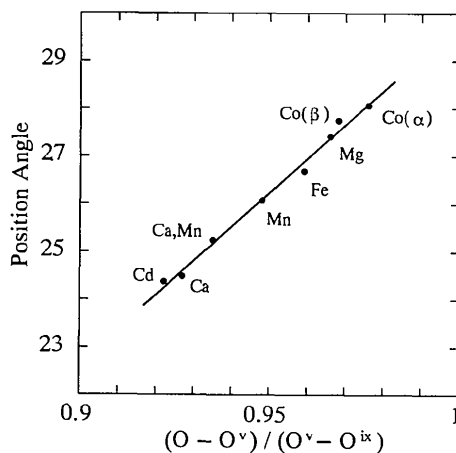


Fig. 2. The variation of the tetrahedral position angle ($^{\circ}$) with the ratio $(O \cdots O^v)/(O^v \cdots O^{ix})$ for the $M_3^{3+}Al_2Si_3O_{12}$ garnets.

Experimental

The samples were synthesized by the hydrothermal method at 5 GPa and 1173 K for 3 h and left at 1 atm at room temperature for 10 y.

Crystal data

Co₃Al₂Si₃O₁₂

$M_r = 507.01$

Cubic

$1a\bar{3}d$

$a = 11.4603(2) \text{ \AA}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 22 reflections

$\theta = 28.9\text{--}29.7^{\circ}$

$V = 1505.18(3) \text{ \AA}^3$

$Z = 8$

$D_x = 4.48 \text{ Mg m}^{-3}$

$\mu = 7.32 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Sphere

0.055 mm (radius)

Pink

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction: spherical
 $T_{\min} = 0.556$, $T_{\max} = 0.565$

936 measured reflections
283 independent reflections
237 observed reflections [$F > 2\sigma(F)$]

$R_{\text{int}} = 0.017$

$\theta_{\max} = 35^{\circ}$

$h = 0 \rightarrow 18$

$k = 0 \rightarrow 18$

$l = -18 \rightarrow 18$

3 standard reflections

monitored every 100 reflections for orientation and every 240 min for intensity
intensity decay: 0.5%

Refinement

Refinement on F

$R = 0.021$

$wR = 0.030$

$S = 1.014$

237 reflections

18 parameters

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} < 0.005$

$\Delta\rho_{\max} = 0.621 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.576 \text{ e \AA}^{-3}$

Extinction correction:

isotropic secondary

Extinction coefficient:

9.201×10^{-8}

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Co	1/8	0	1/4	0.00904 (5)
Al	0	0	0	0.00309 (5)
Si	3/8	0	1/4	0.00384 (9)
O	0.03368 (9)	0.05100 (9)	0.65307 (9)	0.0056 (2)

Table 2. Selected geometric parameters (\AA , $^{\circ}$)

Si ⁱ —O	$\times 4$	1.634 (1)	Al ⁱⁱ —O	$\times 6$	1.889 (1)
O \cdots O ⁱⁱⁱ	$\times 2$	2.511 (1)	O \cdots O ^v	$\times 6$	2.625 (1)
O \cdots O ^{iv}	$\times 4$	2.745 (1)	O \cdots O ^{vi}	$\times 6$	2.717 (1)
Mean O \cdots O		2.667	Mean O \cdots O		2.671
O—Si ⁱ —O ⁱⁱⁱ	$\times 2$	100.36 (5)	O—Al ⁱⁱ —O ^v	$\times 6$	88.03 (4)
O—Si ⁱ —O ^{iv}	$\times 4$	114.21 (5)	O—Al ⁱⁱ —O ^{vi}	$\times 6$	91.97 (4)
Co ^{vii} —O ^v	$\times 4$	2.210 (1)			
Co ^{viii} —O ^v	$\times 4$	2.335 (1)			
Mean Co—O		2.273			
O \cdots O ⁱⁱⁱ	$\times 2$	2.511 (1)	O—Co ^{viii} —O ⁱⁱⁱ	$\times 2$	69.23 (4)
O \cdots O ^v	$\times 4$	2.625 (1)	O—Co ^{viii} —O ^v	$\times 4$	70.49 (4)
O ^v \cdots O ^{ix}	$\times 4$	2.713 (1)	O ^v —Co ^{viii} —O ^{ix}	$\times 4$	73.23 (4)
O \cdots O ^x	$\times 4$	3.313 (2)	O—Co ^{viii} —O ^x	$\times 4$	93.55 (4)
O ^v \cdots O ^x	$\times 2$	2.756 (1)	O ^v —Co ^{viii} —O ^x	$\times 2$	72.31 (3)
O ^x \cdots O ^{xi}	$\times 2$	3.826 (1)	O ^x —Co ^{viii} —O ^{xi}	$\times 2$	109.98 (3)
Mean O \cdots O		2.933			

Symmetry codes: (i) $x - \frac{1}{4}, y, \frac{1}{2} + z$; (ii) $x, y, \frac{1}{2} + z$; (iii) $x, -y, \frac{3}{4} - z$; (iv) $\frac{1}{4} - x, z - \frac{3}{4}, \frac{3}{4} - y$; (v) $\frac{1}{2} - z, -x, \frac{1}{2} + y$; (vi) $y, \frac{1}{2} - z, x + \frac{1}{2}$; (vii) $-z, x, \frac{1}{2} + y$; (viii) $-x, y, \frac{1}{2} + z$; (ix) $-\frac{1}{4} - x, \frac{3}{4} - z, \frac{3}{4} - y$; (x) $z - \frac{3}{4}, y - \frac{1}{4}, \frac{3}{4} - x$; (xi) $\frac{1}{2} - z, x, 1 - y$.

Table 3. Tetrahedral position angles, γ , and the ratios of octahedral–dodecahedral shared edge (O \cdots O v) to dodecahedral–dodecahedral shared edge (O $^v\cdots$ O ix) distances (Å) in $M_3^{2+}Al_2Si_3O_{12}$ garnets

	γ^*	(O \cdots O v)/(O $^v\cdots$ O ix)	Ratio	Reference
Co(α)	28.07	2.639 (3)/2.705 (4)	0.976	Ohashi <i>et al.</i> (1981)
Co(β)	27.75	2.625 (1)/2.713 (1)	0.968	Present study
Mg	27.42	2.617 (3)/2.709 (3)	0.966	Novak & Gibbs (1971)
Fe	26.69	2.655 (2)/2.768 (3)	0.959	Novak & Gibbs (1971)
Mn	26.08	2.678 (2)/2.824 (3)	0.948	Novak & Gibbs (1971)
Ca, Mn	25.25	2.692 (2)†/2.879 (2)†	0.935	Novak & Gibbs (1971)
Ca	24.50	2.756 (2)/2.973 (2)	0.927	Novak & Gibbs (1971)
Cd	24.38	2.739 (8)/2.970 (10)	0.922	Ohashi <i>et al.</i> (1985)

* Born & Zemann (1964).

† Calculated by present authors.

The SDP program system (B. A. Frenz & Associates Inc., 1982) was employed.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of Sodium Cerium(III) Sulfate Monohydrate, NaCe(SO $_4$) $_2$ ·H $_2$ O

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Abstract

The structure of sodium cerium sulfate monohydrate, NaCe^{III}(SO $_4$) $_2$ ·H $_2$ O, comprises distorted NaO $_6$ octahedra, CeO $_9$ polyhedra in the form of distorted tricapped trigonal prisms, and slightly irregular tetrahedral sulfate ions. This structure is isomorphic with that of NaLa^{III}(SO $_4$) $_2$ ·H $_2$ O. All bonds fall within normal lim-

its. The sulfate ion manifested rigid-body behavior but neither of the cation complexes did. As in the previous structural analysis of the La analog [Blackburn & Gerkin (1994). *Acta Cryst.* **C50**, 835–838], the water molecule is modelled as having O-atom disorder but with an ordered H atom. Hydrogen bonds involve only sulfate O atoms as acceptors. The anisotropic atomic displacement parameters are found to be in good agreement with the corresponding parameters determined for the La analog, but in poor agreement with those previously reported for the title salt by Lindgren [*Acta Chem. Scand. Ser. A*, (1977), **31**, 591–594]. Taken together, the data establish that the lack of correction for absorption in the previous study of the Ce salt, rather than some intrinsic property of the Ce salt, is responsible for the displacement parameter discrepancies. The absolute structure has been determined.

Comment

This study of NaCe^{III}(SO $_4$) $_2$ ·H $_2$ O was performed, following our study of the La^{III} analog (Blackburn & Gerkin, 1994), to allow direct comparisons with earlier results for the title salt (Lindgren, 1977). Of particular interest was the characterization of the anisotropic atomic displacement parameters since the corresponding values found in our study of the La analog differed notably from those reported for the Ce salt by Lindgren (1977). Moreover, the structural characterization of the water molecule was also of particular interest since in the La analog the water O atom was best modelled as disordered equally over two sites, but Lindgren's analysis did not ascribe such disorder to the Ce salt.

The experimental crystal belonged to the enantiomeric space group $P3_221$ (see *Experimental*), whereas our experimental crystal of the La analog and Lindgren's Ce crystal belonged to $P3_121$.

This salt is isomorphic with the La analog except for its handedness. The atom numbering corresponds with that chosen for the La analog, and structural descriptions given for the La analog (Blackburn & Gerkin, 1994) apply here with only minor changes.

In the distorted octahedral NaO $_6$ complex, the Na—O distances range from 2.447 (4) to 2.538 (3) Å [average 2.49 (4) Å] and the O—Na—O angles range from 71.7 (1) to 154.2 (2) $^\circ$ (Table 2). The next nearest atoms to Na, at distances of 2.849 (3) Å, are a symmetry-related pair of O(4) atoms. In the CeO $_9$ complex, the Ce—O distances range from 2.477 (3) to 2.582 (3) Å [average 2.53 (3) Å] while the O—Ce—O angles range from 54.4 (1) to 145.7 (1) $^\circ$ (Table 2). These values are in good agreement with our previous values for the La analog and also with those of Lindgren.

The sulfate ion is subject to no symmetry constraints and forms a slightly irregular tetrahedron. The observed S—O distances range from 1.465 (3) to 1.481 (3) Å [average 1.473 (6) Å] and the O—S—O angles range