Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *LATCON* (Lundgren, 1983). Data reduction: *STOEDATRED*, *ABSSTOE* (Lundgren, 1983). Program(s) used to refine structure: *DUPALS* (Lundgren, 1983). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71628 (90 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1083]

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Structures of $LuFeO_3(ZnO)_m$ ($m = 1$, 4, 5 and 6)

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Abstract

The structures of the title compounds, iron lutetium zinc oxides, can be described as a close packing of O atoms, with Lu atoms in octahedral voids and Fe and Zn atoms in tetrahedral voids. Blocks constituting $m + 1$ layers of Fe and/or Zn atoms along the c axis are alternately stacked with single layers of Lu along the c axis.

Comment

In the process of establishing the phase diagrams of the R_2O_3–A_2O_3–MO (R = Sc, Y, In, Ho, Er, Tm, Yb, Lu; A = Al, Fe, Ga; M = Mg, Mn, Fe, Co, Cu, Zn, Cd) system, Kimizuka, Mohri, Matsui & Siratori (1988) and Kimizuka & Mohri (1989) identified several new homologous compounds of $RAO_3(MO)_m$ (m = integer), and estimated that these compounds have $InFeO_3(ZnO)_m$-type structures through both X-ray powder diffraction and electron-diffraction analysis. However, the compounds, including $LuFeO_3(ZnO)_m$, have not been studied by the single-crystal X-ray method and structural details were not known. We have, therefore, determined the structure of the title compounds by the single-crystal method to understand the crystal chemistry of the $LuFeO_3$–ZnO system. The crystals were grown through the solid-state reaction between Lu_2O_3, Fe_2O_3 and ZnO powder in platinum tubes at 1823 K for three days.

$LuFeO_3(ZnO)$ (Kimizuka & Takayama, 1981) is isostructural with the compounds In_2ZnS_4 (Lappe, Niggli, Nitsche & White, 1962) and $YbFe_2O_4$ (Kato, Kawada, Kimizuka & Katsura, 1975; Malaman *et al.*, 1975). As for these compounds, the structures of $LuFeO_3(ZnO)_m$ (Fig. 1) can be described as a close packing of O atoms, with Lu atoms in the octahedral voids of the cubic close-packed layers and Fe and Zn atoms (denoted M) in the tetrahedral voids of hexagonal close-packed layers. Commonly with these compounds, the basic structure consists of LuO_2^- and $(FeZn_m)O_{m+1}^+$ layers alternately stacked along the c axis. Bond lengths and angles in each coordination polyhedron (Fig. 2) are listed in Table 2. LuO_6 octahedra share edges forming a continuous layer on the c plane; O—Lu—O bond angles deviate by 10° from the ideal values of 90°. The M [excluding $M(1)$ for m = even] atoms shift from the centre of gravity of the coordination tetrahedra along the c axis in the opposite direction to the apical O atom to form trigonal bipyramids, resulting in long bonds to the apical O atoms [M—O^{ii} 2.215 (8)–2.990 (15) Å; Table 2]. For m = even, the $M(1)$ atom is on the centre of the equatorial triangle by the requirements of symmetry. The O—M—O angles are between 120 and 113°; these angles approach the ideal angle of 109.47° [110.8 (3)° in ZnO (Abrahams & Bernstein, 1969)] when their Zn content increases.

For the compound with $m = 1$, the displacement parameters U_{33} of Lu and O(1) were abnormally large; therefore, the X-ray photographs were exam-

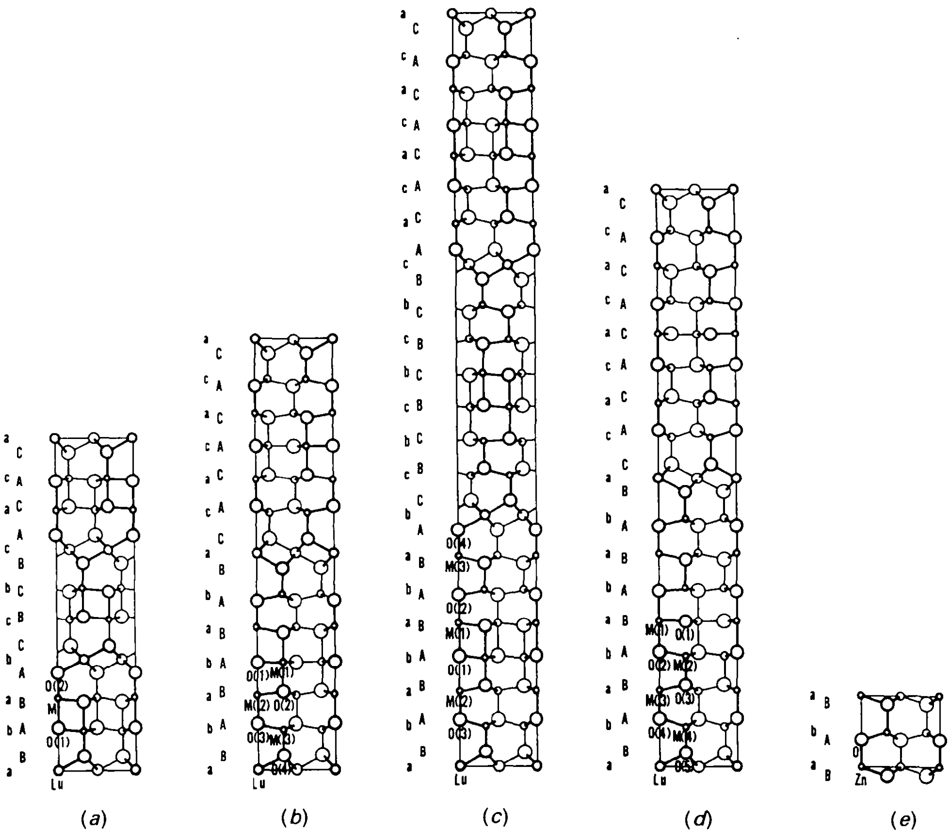

Fig. 1. Projection on $(\bar{1}10)$ of $LuFeO_3(ZnO)_m$: (*a*) $m = 1$, (*b*) $m = 4$, (*c*) $m = 5$, (*d*) $m = 6$ and (*e*) ZnO. (See footnote to Table 2.)

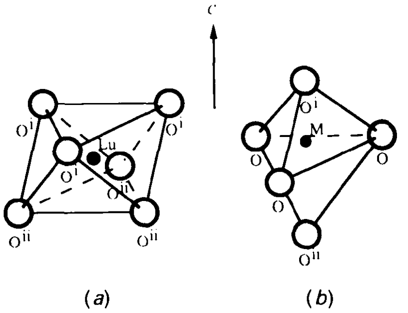

Fig. 2. Environment of (*a*) the LuO_6 octahedron and (*b*) the MO_5 bipyramid. (See footnote to Table 2.)

ined carefully to check for the presence of any reflections due to superlattice structure. However, no superlattice reflections were detected. As a check for possible slight deviation to lower symmetry, a trial structure refinement was attempted, splitting the Lu-atom site along the *c* axis. The *R* factor decreased significantly from 0.036 to 0.025 and shifted the positions by ± 0.14 Å. Because these deviations were uncertain, we have listed the average structures of the title compounds in Table 1. For compounds with $m = 4$, 5 and 6 the X-ray photographs, with enough exposure time, clearly indicate that there is no diffuse line from stacking faults along the *c* axis.

The relationships between site occupancies of Fe atoms and *wR* values in each *M* site are given in Table 3. The significance tests on the *R* factor (Hamilton, 1965) (*R*-factor ratio $> \alpha_{b,\ n-m,\ 0.005}$) showed that Fe atoms do not sit in particular *M* sites. Thus, when we refined the structures we assumed that the Fe and Zn atoms were disordered.

Experimental

$LuFeO_3(ZnO)$

Crystal data

$LuFeO_3(ZnO)$
$M_r = 360.19$
Trigonal
$R\bar{3}m$
$a = 3.4185\ (1)$ Å
$c = 25.463\ (3)$ Å
$V = 257.71\ (3)$ Å^3
$Z = 3$
$D_x = 6.96$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 39$–$48°$
$\mu = 39.70$ mm^{-1}
$T = 295$ K
Sphere
0.0525 mm (radius)
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: spherical
$T_{\min} = 0.066$, $T_{\max} = 0.144$
558 measured reflections
558 independent reflections
484 observed reflections $[I > 1.5\sigma(I)]$
$\theta_{\max} = 60°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 61$
3 standard reflections
frequency: 240 min
intensity variation: −0.2%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.036$
$S = 2.3$
484 reflections
13 parameters
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 7.9$ e Å^{-3}
$\Delta\rho_{\min} = -11.9$ e Å^{-3}
Extinction correction: applied
Extinction coefficient: $7.0(1) \times 10^{-6}$

$LuFeO_3(ZnO)_4$

Crystal data

$LuFeO_3(ZnO)_4$
$M_r = 604.33$
Hexagonal
$P6_3/mmc$
$a = 3.3406(1)$ Å
$c = 32.51(2)$ Å
$V = 314.2(2)$ Å^3
$Z = 2$
$D_x = 6.39$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 35–44°$
$\mu = 33.27$ mm^{-1}
$T = 295$ K
Prism
$0.17 \times 0.16 \times 0.14$ mm
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.017$, $T_{\max} = 0.125$
926 measured reflections
926 independent reflections
733 observed reflections $[I > 1.5\sigma(I)]$
$\theta_{\max} = 60°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 79$
3 standard reflections
frequency: 240 min
intensity variation: −0.3%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.057$
$S = 2.6$
733 reflections
23 parameters
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 6.4$ e Å^{-3}
$\Delta\rho_{\min} = -6.2$ e Å^{-3}
Extinction correction: applied
Extinction coefficient: $1.06(2) \times 10^{-6}$

$LuFeO_3(ZnO)_5$

Crystal data

$LuFeO_3(ZnO)_5$
$M_r = 685.71$
Trigonal
$R\bar{3}m$
$a = 3.3291(1)$ Å
$c = 56.56(2)$ Å
$V = 542.8(2)$ Å^3
$Z = 3$
$D_x = 6.29$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 35–41°$
$\mu = 32.23$ mm^{-1}
$T = 295$ K
Prism
$0.17 \times 0.15 \times 0.08$ mm
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.023$, $T_{\max} = 0.182$
1171 measured reflections
1171 independent reflections
1060 observed reflections $[I > 1.5\sigma(I)]$
$\theta_{\max} = 60°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 136$
3 standard reflections
frequency: 240 min
intensity variation: −1.9%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.053$
$S = 4.2$
1060 reflections
25 parameters
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 8.1$ e Å^{-3}
$\Delta\rho_{\min} = -9.0$ e Å^{-3}
Extinction correction: applied
Extinction coefficient: $5.08(5) \times 10^{-6}$

$LuFeO_3(ZnO)_6$

Crystal data

$LuFeO_3(ZnO)_6$
$M_r = 767.09$
Hexagonal
$P6_3/mmc$
$a = 3.3220(1)$ Å
$c = 42.91(2)$ Å
$V = 410.1(2)$ Å^3
$Z = 2$
$D_x = 6.21$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 40–41°$
$\mu = 31.38$ mm^{-1}
$T = 295$ K
Prism
$0.13 \times 0.13 \times 0.07$ mm
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.026$, $T_{\max} = 0.214$
1195 measured reflections
1195 independent reflections
795 observed reflections $[I > 1.5\sigma(I)]$
$\theta_{\max} = 60°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 104$
3 standard reflections
frequency: 240 min
intensity variation: −0.6%

Refinement

Refinement on F
$R = 0.066$
$wR = 0.091$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 9.1$ e Å^{-3}
$\Delta\rho_{\min} = -9.8$ e Å^{-3}

S = 5.0
795 reflections
29 parameters
Unit weights applied
Extinction correction: applied
Extinction coefficient: 0.47 (2) × 10^{-6}

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

m = 1

	$x = y$	z	U_{eq}
Lu	0	0	0.184 (1)
M(1)	0	0.21564 (3)	0.0084 (1)
O(1)	0	0.1287 (3)	0.022 (1)
O(2)	0	0.2923 (2)	0.013 (1)

m = 4

	x	y	z	U_{eq}
Lu	0	0	0	0.0118 (1)
M(1)	1/3	2/3	1/4	0.0104 (2)
M(2)	0	0	0.17203 (4)	0.0117 (2)
M(3)	1/3	2/3	0.09352 (5)	0.0127 (2)
O(1)	0	0	1/4	0.049 (6)
O(2)	1/3	2/3	0.1827 (4)	0.023 (2)
O(3)	0	0	0.1088 (2)	0.014 (1)
O(4)	1/3	2/3	0.0330 (3)	0.014 (1)

m = 5

	$x = y$	z	U_{eq}
Lu	0	0	0.0105 (1)
M(1)	0	0.18921 (2)	0.0101 (1)
M(2)	0	0.09919 (2)	0.0119 (1)
M(3)	0	0.27952 (2)	0.0122 (1)
O(1)	0	0.1472 (3)	0.041 (3)
O(2)	0	0.2273 (2)	0.019 (1)
O(3)	0	0.0630 (1)	0.012 (1)
O(4)	0	0.3141 (1)	0.012 (1)

m = 6

	x	y	z	U_{eq}
Lu	0	0	0	0.0109 (1)
M(1)	0	0	1/4	0.0112 (4)
M(2)	1/3	2/3	0.19028 (7)	0.0122 (3)
M(3)	0	0	0.13094 (6)	0.0137 (3)
M(4)	1/3	2/3	0.07105 (6)	0.0125 (3)
O(1)	1/3	2/3	1/4	0.060 (10)
O(2)	0	0	0.1976 (6)	0.030 (4)
O(3)	1/3	2/3	0.1407 (3)	0.016 (2)
O(4)	0	0	0.0832 (3)	0.013 (2)
O(5)	1/3	2/3	0.0234 (5)	0.019 (3)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

		m = 1	*m* = 4	*m* = 5	*m* = 6
Lu—O^{i,ii}	(6 ×)	2.233 (2)	2.207 (4)	2.210 (3)	2.165 (10)
O^{i,ii}—O^{i,ii}	(6 ×)	3.419 (1)	3.341 (1)	3.329 (1)	3.322 (1)
O^{i,ii}—O^{ii,i}	(6 ×)	2.874 (5)	2.884 (9)	2.907 (7)	2.776 (21)
O^{i,ii}—Lu—O^{i,ii}	(6 ×)	99.9 (1)	98.4 (2)	97.8 (1)	100.2 (4)
O^{i,ii}—Lu—O^{ii,i}	(6 ×)	80.1 (1)	81.6 (2)	82.3 (1)	79.8 (4)
M(1)—O	(3 ×)	1.993 (1)	1.929 (1)	1.930 (1)	1.918 (1)
M(1)—O^{i}	(1 ×)	1.952 (5)	–	2.155 (9)	–
M(1)—O^{ii}	(1 ×)	2.215 (8)	–	2.377 (15)	–
M(1)—O^{i,ii}	(2 ×)	–	2.190 (13)	–	2.249 (24)
O—O	(3 ×)	3.419 (1)	3.341 (1)	3.329 (1)	3.322 (1)
O—O^{i}	(3 ×)	2.979 (7)	–	3.019 (13)	–
O—O^{ii}	(3 ×)	2.764 (8)	–	2.924 (16)	–
O—O^{i,ii}	(6 ×)	–	2.918 (9)	–	2.956 (18)
O—M(1)—O	(3 ×)	118.1 (1)	120	119.2 (1)	120
O—M(1)—O^{i}	(3 ×)	98.1 (2)	–	95.2 (4)	–
O—M(1)—O^{ii}	(3 ×)	81.9 (2)	–	84.9 (4)	–
O—M(1)—O^{i,ii}	(6 ×)	–	90	–	90
M(2)—O	(3 ×)	–	1.959 (2)	1.969 (2)	1.944 (4)
M(2)—O^{i}	(1 ×)	–	2.056 (8)	2.047 (6)	2.127 (15)
M(2)—O^{ii}	(1 ×)	–	2.535 (1)	2.714 (15)	2.563 (3)
O—O	(3 ×)	–	3.341 (1)	3.329 (1)	3.322 (1)
O—O^{i}	(3 ×)	–	3.080 (12)	3.101 (8)	3.104 (22)
O—O^{ii}	(3 ×)	–	2.918 (9)	3.019 (13)	2.956 (18)
O—M(2)—O	(3 ×)	–	117.0 (2)	116.2 (1)	117.4 (3)
O—M(2)—O^{i}	(3 ×)	–	100.1 (4)	101.4 (2)	99.3 (7)
O—M(2)—O^{ii}	(3 ×)	–	79.9 (4)	78.6 (2)	80.7 (7)
M(3)—O	(3 ×)	–	1.992 (2)	1.991 (2)	1.963 (3)
M(3)—O^{i}	(1 ×)	–	1.969 (9)	1.953 (6)	2.049 (14)
M(3)—O^{ii}	(1 ×)	–	2.897 (13)	2.953 (9)	2.860 (24)
O—O	(3 ×)	–	3.130 (9)	3.132 (7)	3.126 (16)
O—O^{ii}	(3 ×)	–	3.080 (12)	3.101 (8)	3.104 (22)
O—M(3)—O	(3 ×)	–	114.0 (1)	113.4 (1)	115.6 (2)
O—M(3)—O^{i}	(3 ×)	–	104.4 (2)	105.1 (2)	102.3 (4)
O—M(3)—O^{ii}	(3 ×)	–	75.6 (2)	74.9 (2)	77.7 (4)
M(4)—O	(3 ×)		–	–	1.987 (4)
M(4)—O^{i}	(1 ×)	–	–	–	2.046 (21)
M(4)—O^{ii}	(1 ×)			–	2.990 (15)
O—O	(3 ×)			–	3.322 (1)
O—O^{i}	(3 ×)		–	–	3.204 (20)
O—O^{ii}	(3 ×)	–	–		3.126 (16)
O—M(4)—O	(3 ×)	–	–		113.4 (2)
O—M(4)—O^{i}	(3 ×)	–	–	–	105.2 (4)
O—M(4)—O^{ii}	(3 ×)	–	–	–	74.8 (4)

Note: In Fig. 1, atoms on the same *c* plane have the same labels, M(1), O(1), *etc*. In the table, atoms with the same roman superscripts denote atoms on the same *c* plane and thus would carry common labels. In the LuO_6 octahedra, the labels of all O atoms are common. In the MO_5 bipyramids, superscript (i) denotes the shorter, and (ii) the longer, M—O distance.

Table 3. *Site occupancies of* Fe *atoms and wR values* (%)

m = 4

M(1)	1	0	0	1/3	1/3	0	1/5
M(2)	0	1	0	2/3	0	1/2	2/5
M(3)	0	0	1	0	2/3	1/2	2/5
wR	6.58	5.98	6.08	5.75	5.88	5.72	5.66

m = 5

M(1)	1	0	0	1/2	1/2	0	1/3
M(2)	0	1	0	1/2	0	1/2	1/3
M(3)	0	0	1	0	1/2	1/2	1/3
wR	5.53	5.61	5.96	5.23	5.44	5.49	5.28

m = 6

M(1)	1	0	0	0	1/3	1/3	1/3	0
M(2)	0	1	0	0	2/3	0	0	1/2
M(3)	0	0	1	0	0	2/3	0	1/2
M(4)	0	0	0	1	0	0	2/3	0
wR	9.61	9.32	9.31	9.33	9.18	9.18	9.20	9.15
M(1)	0	0	1/5	1/5	1/5	0	1/7	
M(2)	1/2	0	2/5	0	2/5	1/3	2/7	
M(3)	0	1/2	2/5	2/5	0	1/3	2/7	
M(4)	1/2	1/2	0	2/5	2/5	1/3	2/7	
wR	9.18	9.16	9.10	9.11	9.13	9.11	9.08	

The symmetry and approximate cell dimensions of the crystals were determined from both oscillation and Weissenberg photographs using Cu $K\alpha$ radiation. For compounds with m = odd (1 and 5), the only systematic absences occurred for reflections $-h + k + l$ with $3n \pm 1$. For compounds with m = even (4 and 6), the only systematic absences were hhl for $l = 2n + 1$. It was also found that only reflections with $h - k = 3n$ had observable intensities for $l = 2n$. From the possible space groups, $R\bar{3}m$ and $P6_3/mmc$ were adopted in later stages of structure determination for m = odd and even, respectively. The positions of the metal atoms, Lu, Fe and/or Zn, were found by direct methods. O atoms were located from the subsequent difference Fourier maps. The atomic scattering factors for neutral atoms and dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All of the calculations were performed using *SDP* (B. A. Frenz & Associates, Inc., 1985).

Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71533 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1025]

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Structure of $K_2Co_2(SeO_3)_3$

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Abstract

The structure of hexagonal dicobalt dipotassium triselenite, $K_2Co_2(SeO_3)_3$, is composed of CoO_6 octahedra, KO_9 polyhedra and two crystallographically different types of pyramidal SeO_3 groups. Pairs of face-sharing CoO_6 octahedra are linked *via* the SeO_3 groups forming $[Co_2(SeO_3)_3]^{2-}$ layers parallel to (0001), which are connected by the K atoms. This new structure type is closely related to the buetschliite-type compounds $K_2M(XO_3)_2$ (M = Ca, Mg with X = C, and M = Co, Mn with X = Se).

Comment

Single crystals of $K_2Co_2(SeO_3)_3$ were obtained as a by-product in experiments aimed at the hydrothermal synthesis of the zemannite-type compound $K_2Co_2(SeO_3)_3.2H_2O$ (Wildner, 1993), starting with appropriate mixtures of $Co(OH)_2$, K_2CO_3, SeO_2 and H_2O in synthesis (i) (giving both compounds) or Co powder, H_2SeO_3, KOH and H_2O in synthesis (ii) [giving only $K_2Co_2(SeO_3)_3$] in closed teflon-lined steel vessels at ~ 493 (5) K (6 d). X-ray intensity data were collected from a crystal obtained by synthesis (ii) and the structure was solved by interpretation of a three-dimensional Patterson function and a subsequent Fourier synthesis. The atomic arrangement is illustrated in Fig. 1.

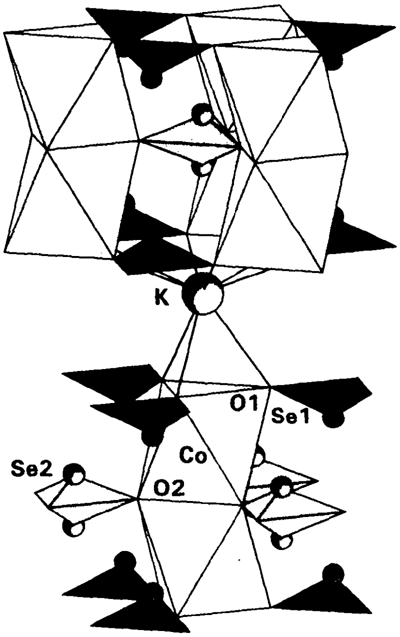

Fig. 1. Projection of the title structure along a direction slightly inclined to [11$\bar{2}$0], showing the environment of the K atom. Only one of the two Se2 positions related by the mirror plane parallel to (0001) is randomly occupied.

All cations occupy sites with $3m$ symmetry. The CoO_6 octahedra share faces *via* the O2 atoms forming Co_2O_9 dimers. The repulsion between two neighbouring Co atoms [Co···Co = 2.957 (1) Å] results in an off-centring of the Co atoms along the threefold axis and in markedly different distances to O1 and O2. The mean Co—O distance (2.123 Å) is in the usual range and correlates with the expectations from the observed bond-length distortion (Wildner, 1992*a*). The CoO_6 octahedra share all their corners with SeO_3 groups, thus forming $[Co_2(SeO_3)_3]^{2-}$ double-octahedral layers parallel to (0001). The Se1 atoms are one-sided pyramidally coordinated to three O1 atoms with usual interatomic bond lengths and angles (Hawthorne, Groat & Ercit, 1987; Fischer & Zemann, 1974); the Se apices and their lone-pair electrons point towards the centre of the layers. The Se2 atoms have an occupancy factor of only 0.5 and are randomly distributed on one of two positions [Se2···Se2′ = 1.237 (2) Å] symmetrically related by the mirror planes parallel to (0001) which contain the O2 atoms. The Se2—O2 distances are very short and the pyramids are extremely flattened compared to the average shapes of SeO_3 groups reported in the literature (Se—O = 1.709 Å, O—Se—O = 100.2°; Hawthorne, Groat & Ercit, 1987). This structural feature

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