[2·673 (2), 2·680 (4), 2·712 (5) and 2·808 (6) Å, respectively in In$_2$Mo$_{15}$Se$_{19}$]. Thus, the overall result is again an expansion of the Mo$_9$ cluster along the threefold axis [Δ(2)–Δ(3) 2·28 Å in In$_2$Mo$_{15}$Se$_{19}$]. Notable differences between the two parent structures also occur with respect to the separation of the Mo$_6$Se$_8$ and Mo$_9$Se$_{11}$ units. Indeed, as expected the removal of indium leads to a shortening of the Mo(1)—Mo(2) interunit bond which decreases from 3·389 (3) to 3·281 (1) Å. To a lesser extent, the Mo(1)—Se(2) and Mo(2)—Se(1) interunit bonds also shorten from 2·589 (6) to 2·569 (2) and from 2·641 (5) to 2·609 (2) Å, respectively.

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Structure of High-Pressure MnGeO$_3$ Ilmenite

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Abstract. A single-crystal X-ray study confirms that one of the high-pressure polymorphs of manganese germanate, MnGeO$_3$, has an ilmenite structure with MnO$_6$ and GeO$_6$ octahedra sharing edges to form fully ordered Mn and Ge layers of six-membered rings on (0001). The distortion and height of the GeO$_6$ octahedra in MnGeO$_3$ ilmenite are comparable with those observed in other germanate ilmenites. The crystal data for MnGeO$_3$ ilmenite are: $M_r = 175·55$, trigonal, $R\bar{3}$ [symmetry operators $(0,0,0)$, $(\frac{1}{3},\frac{2}{3},\frac{2}{3})$,$(\frac{2}{3},\frac{1}{3},\frac{1}{3})$ + $(x,y,z;\ -y,x-y,z;\ y-x,-x,z;\ -x,-y,z;\ y,y-x,-z;\ x-y,x,-z)]$, $a = 5·0148$ (5) Å, $c = 14·324$ (1) Å, $V = 311·97$ (7) Å^3, $Z = 6$, $D_x = 5·54$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7093$ Å, $\mu = 197·8$ cm^{-1}, $F(000) = 486$, $T = 298$ K, $R = 0·018$ ($wR = 0·017$), 187 unique reflections used for refinements, crystal synthesized at 1273 K and 4·87 GPa.

Introduction. Manganese germanate, MnGeO$_3$, crystallizes with the orthopyroxene structure under ambient conditions (Fang & Townes, 1969; Herpin, Whuler, Boucher & Sougi, 1971). With increasing pressure and temperature, the orthopyroxene form (MnGeO$_3$ I) transforms to a clinopyroxene form (MnGeO$_3$ II) and then to an ilmenite form (MnGeO$_3$ III) at 3·0 GPa and 987 K (Ringwood & Seabrook, 1963). The magnetic structure of MnGeO$_3$ III has been investigated in a powder neutron diffraction study with the TOF method (Tsuzuki, Ishikawa, Watanabe & Akimoto, 1974). Although that paper and another by Susaki, Konno & Akimoto (1985) include some structural data for MnGeO$_3$ ilmenite, to the best of the authors' knowledge, no structure refinement of this phase has ever been published. The purpose of this paper is to present details and results from a structure refinement of MnGeO$_3$ III using the method of single-crystal X-ray diffraction and to compare this compound with other germanate ilmenites.

Experimental. The crystals of MnGeO$_3$ ilmenite were grown from a powder sample of MnGeO$_3$ pyroxene that was packed in a Pt capsule and held at 4·87 GPa and 1273 K for three hours in a girdle-type apparatus (Ingrin & Liebermann, 1989). After careful examination of several crystals obtained from the

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Table 1. *Atomic positions and equivalent isotropic temperature factors* (Å^2)

The temperature factor is $\exp(-\beta_{ij}h_ih_j)$ and $B_{eq} = (\frac{4}{3})\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}/B_{iso}
Mn	0	0	0·36388 (7)	0·62
Ge	0	0	0·15687 (5)	0·47
O	0·3192 (6)	0·0367 (6)	0·2407 (2)	0·58

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Mn octahedron		Ge octahedron	
Mn^i—O1^i	2·327 (3) × (3)	Ge^i—O1^i	1·935 (3) × (3)
Mn^i—O4^{ii}	2·090 (3) × (3)	Ge^i—O^i	1·872 (3) × (3)
Mean ⟨Mn—O⟩	2·209	Mean ⟨Ge—O⟩	1·904
O1^i—O2^{iii}	2·628 (5) × (3)	O1^i—O2^{iii}	2·628 (5) × (3)
O1^i—O4^{ii}	3·113 (4) × (3)	O1^i—O7^{vi}	2·457 (5) × (3)
O1^i—O6^{iv}	3·227 (5) × (3)	O1^i—O9^{vii}	2·843 (4) × (3)
O4^{ii}—O5^v	3·278 (5) × (3)	O7^{vi}—O8^{viii}	2·823 (5) × (3)
Mean ⟨O—O⟩	3·062	Mean ⟨O—O⟩	2·688
O1^i—Mn^i—O2^{iii}	68·78 (10) × (3)	O1^i—Ge^i—O2^{iii}	85·52 (11) × (3)
O1^i—Mn^i—O4^{ii}	89·47 (13) × (3)	O1^i—Ge^i—O7^{vi}	80·37 (11) × (3)
O1^i—Mn^i—O6^{iv}	93·73 (9) × (3)	O1^i—Ge^i—O9^{vii}	96·60 (16) × (3)
O4^{ii}—Mn^i—O5^v	103·23 (8) × (3)	O7^{vi}—Ge^i—O8^{viii}	97·88 (11) × (3)
Mn^i—Ge^i	2·965 (1)	Ge^i—Ge^{vi}	2·9089 (2)
Mn^i—Mn^{ii}	3·0246 (6)		

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

experimental charge under the polarizing microscope, a plate-like crystal, free of inclusions, with a pseudohexagonal outline was chosen for the study. The dimensions of this (0001) plate were approximately 90 × 100 × 10 μm with edge lengths varying between 35 and 60 μm. Further examination of this crystal revealed that it was untwinned. The peak widths, however, were broad, typically 1·5° ω, similar to those of the high-pressure polymorph of $ZnGeO_3$ with the ilmenite structure (Ross & Leinenweber, 1990). This may be caused by small mosaic size formed upon quenching the sample from high pressure and temperature. The unit cell was determined from a least-squares fit to positions of 20 reflections in the range $40 \le 2\theta \le 45°$. Each reflection was centered at eight different equivalent positions of the Picker four-circle diffractometer. The intensity data from the four-circle diffractometer verified the Laue symmetry of the crystal as $\bar{3}$ and reflections with $-h + k + l \ne 3n$ were systematically absent.

Intensity data from ω scans were collected with a Picker four-circle diffractometer using filtered Mo $K\alpha$ radiation ($\lambda = 0·7093$ Å) out to $\sin\theta/\lambda = 0·7$ Å^{-1} with $-7 \le h \le 7$, $-7 \le k \le 7$, $0 \le l \le 19$. The 116 and $\bar{2}16$ reflections were monitored as intensity and orientation standards every 180 reflections; their intensities varied randomly by less than 0·5% from their means. A total of 672 symmetry-allowed reflections were measured, of which 576 were observed at $I > 2\sigma_I$. The reflections were corrected for Lorentz and polarization factors and absorption corrections were made with the program *ABSORB* (Burnham, 1966). Calculated transmission coefficients ranged from 30 to 81%. Equivalent reflections were averaged in Laue class $\bar{3}$ with $R_{int} = 0·020$ to give 187 unique reflections with $I > 2\sigma_I$ that were used for structure solution and refinement.

The systematic absences, intensity data and intensity statistics indicate that the space group is $R\bar{3}$. All parameters (scale factor, atom coordinates and anisotropic temperature factors) were refined simultaneously using the full-matrix least-squares program *RFINE6*, a version of *RFINE4* (Finger & Prince, 1975). Addition of an extinction correction resulted in a refined extinction parameter with an e.s.d. greater than the value of the parameter and was therefore omitted from the refinement. A weight of w

$= [\sigma^2(F_o)]^{-1}$ was assigned to each reflection, where $\sigma(F_o)$ is the e.s.d. derived from counting statistics, and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The refinement was terminated when the maximum least-squares shift of any parameter was less than 0·005 e.s.d. Final agreement indices on the observed reflections were $R = 0·018$, $wR = 0·017$ and goodness of fit = 2·75. Final atomic coordinates and equivalent isotropic temperature factors are reported in Table 1.* Difference Fourier syntheses calculated after the final refinement showed minimum and maximum values of $-0·6$ and $0·6$ e Å^{-3}, respectively.

Discussion. The structure of $MnGeO_3$ III is an isotype of the mineral ilmenite, $FeTiO_3$, obtained by substituting Mn for Fe and Ge for Ti. The ilmenite structure is an ordered corundum structure in which the two different cations occupy alternate (0001) layers of cationic sites. The heights of the Mn and Ge octahedral layers are 2·654 (6) and 2·121 (6) Å, respectively. Interatomic distances and angles for $MnGeO_3$ III are presented in Table 2. The mean Mn—O and Ge—O distances are 2·209 (3) and 1·904 (3) Å, respectively, compared with 2·22 and 1·94 Å calculated from effective ionic radii for relevant ions in sixfold coordination (Shannon & Prewitt, 1969). In the ilmenite structure, the size

difference between the two cations distorts the packing along [0001] from hexagonal close-packing. The O—O distances of the shared face and edges with neighboring cation octahedra are shortened whereas those with neighboring vacant octahedra are lengthened, resulting in a wide range of O—O distances (Table 2). In particular, the shortest O—O distance is the edge shared between two GeO_6 octahedra [2·457 (5) Å], which is even shorter than the O—O distance of the shared face between MnO_6 and GeO_6 octahedra [2·628 (5) Å]. In addition to the great variation in O—O separations, the departure from hexagonal close-packing is reflected in the c/a ratio which deviates from the ideal value of $8^{1/2} \simeq 2·828$. In MnGeO₃ III, c/a is 2·856. The axial ratio increases as the difference in size between the A^{2+} and B^{4+} cations increases, as shown in Fig. 1 for the germanate ilmenites MgGeO₃, ZnGeO₃, MnGeO₃ and CdGeO₃.

The mean quadratic elongation parameter, $\langle \lambda \rangle$, and bond angle variance, σ^2 (Robinson, Gibbs & Ribbe, 1971) provide a measure of the distortion of the MnO_6 and GeO_6 octahedra. The value of $\langle \lambda \rangle$ is equal to $\sum_i (l_i/l_0)^2/n$, where n is the coordination number, l_i is the distance from the central atom to the ith coordinating atom, and l_0 is the center-to-vortex distance of a regular polyhedron of the same volume. For a regular octahedron $\langle \lambda \rangle$ is equal to

1·000. The angle variance, σ^2, is equal to $\sum_i (\theta_i - \theta_0)^2/(n-1)$ where θ_0 is the ideal bond angle for a regular polyhedron (90° for an octahedron), n is the coordination number, and θ_i is the ith adjacent bond angle from outer-to-central-to-outer atoms. The angle variance is zero for a regular polyhedron. Among compounds with the ilmenite structure, $\langle \lambda \rangle$ ranges from 1·015 to 1·070 and σ^2 ranges from 50 to 222 (Ross & Leinenweber, 1990). The values of $\langle \lambda \rangle$ and σ^2 for the Mn octahedron in MnGeO₃ III are 1·058 and 175, respectively, and those for the Ge octahedron are 1·017 and 59. The values of $\langle \lambda \rangle$ and σ^2 for GeO_6 are comparable with those of other germanate ilmenites, indicating that distortion of the GeO_6 octahedra changes little upon substitution of different A^{2+} cations in the structure. In general, $\langle \lambda \rangle$ and σ^2 increase with cation size (Ross & Leinenweber, 1990) and therefore the octahedral distortion and shift of cations from the centers of octahedra is generally greater for larger cations.
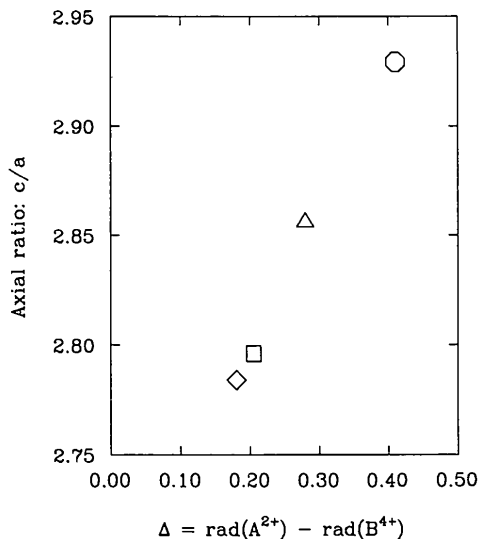
Fig. 1. The axial ratios, c/a, of the germanate ilmenites, MnGeO₃ – triangle (this study), MgGeO₃ – diamond (Kirfel, Hinze & Will, 1978), ZnGeO₃ – square (Ross & Leinenweber, 1990) and CdGeO₃ – circle (Susaki, Konno & Akimoto, 1985), as a function of Δ, the difference between the ionic radii for octahedrally coordinated A^{2+} and Ge^{4+} ions (Shannon & Prewitt, 1969).

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