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Structure of $(Ni,Mg)_{10}Ge_3O_{16}$

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Abstract. $(Ni_{0.45}Mg_{0.55})_{10}Ge_3O_{16}$, $M_r = 871{\cdot}7$, trigonal, $R\bar{3}$, $r = 10{\cdot}1250\ (5)$ Å, $\alpha = 33{\cdot}790\ (1)°$ [$a = 5{\cdot}8850\ (4)$, $c = 28{\cdot}6135\ (12)$ Å, hexagonal cell], $V = 286{\cdot}1$ Å^3, $Z = 1$, $D_x = 5{\cdot}060$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 152{\cdot}39$ cm^{-1}, $F(000) = 416$, room temperature, final $R = 0{\cdot}014$ for 1572 unique reflections. The structure consists of alternate {111} layers of spinel-like and rock-salt-like structures stacked in the ratio 3:1 in the direction of c_{hex}. Structural accommodation between the two structural units is made in the layer of O(3) atoms. Otherwise, coordination polyhedra are fairly regular and cation–oxygen distances correspond to ideal values. Ni is weakly partitioned into the rock-salt-like layers.

Introduction. The compound $(Ni_xMg_{1-x})_{10}Ge_3O_{16}$, $x \simeq 0{\cdot}4$–$0{\cdot}5$, was recently synthesized under dry conditions at atmospheric pressure by Barbier (1987*a*) and identified as a new phase in the NiO–MgO–GeO_2 system. Investigation by X-ray powder diffraction and transmission electron microscopy suggested a structure in space group $R3m$ formed of alternate triple and single {111} layers of spinel-like and rock-salt-like structures, which gave $R = 0{\cdot}15$ for ideal atomic positions and 41 powder lines. The present single-crystal study confirms this structure and reports on details of the Ni,Mg site ordering and stereochemistry.

Experimental. $(Ni,Mg)_{10}Ge_3O_{16}$ was prepared by crystallization from a flux of PbO composition. 1 g of nutrient and 4 g of flux in a platinum crucible with a well-fitting lid were cooled from 1573 to 1173 K at 4 K h^{-1}. The nutrient had the composition $(Ni_{0.50}Mg_{0.50})_{10}Ge_3O_{16}$ and was prepared by heating high-purity oxides under dry conditions at 1473 K. The product was recovered by dissolution of the flux in dilute HCl and hot water, and characterized as $(Ni_xMg_{1-x})_{10}Ge_3O_{16}$, $x < 0{\cdot}5$, with excess of a NiO-rich rock-salt-structure phase. Electron microprobe analysis using a JEOL JXA-8600 Superprobe with crystalline Mg_2GeO_4 and Ni_2GeO_4 standards yielded a composition of $(Ni_{0.41}Mg_{0.59})_{10}Ge_3O_{16}$ for the fine-grained matrix. However, the structure refinement indicated a composition of $(Ni_{0.45}Mg_{0.55})_{10}Ge_3O_{16}$ for the larger single crystals, which is assumed throughout this study. The crystal was rectangular in shape with approximate dimensions $0{\cdot}075 \times 0{\cdot}083 \times 0{\cdot}105$ mm and a calculated volume of $0{\cdot}65 \times 10^{-3}$ mm^3. It was trimmed from a 0·5 mm diameter composite crystal, and size reduced with 600 abrasive paper. X-ray precession study revealed that the Laue class was $\bar{3}$ and not $\bar{3}m$ (Barbier, 1987*a*), and restricted the possible space groups to $R3$ and $R\bar{3}$. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 20 reflections in 2θ range 53·0–65·3° for cell parameters. Data collected by θ–2θ scan; scan angle $(2\theta) = 2{\cdot}4°$, with dispersion correction. 4740 *hkl*, $-h-kl$ reflections (hexagonal indices) permitted by space group $R\bar{3}$ out to $2\theta = 90°$; $-11 \le h \le 11$, $-11 \le k \le 11$, $0 \le l \le 57$. Standard reflections 220, $\bar{2}40$, $0\bar{2}8$; $R_{\text{int}} = 0{\cdot}01$, no significant decline in intensity. Background, Lorentz, polarization and absorption corrections applied; transmission factors (by Gaussian integration with a $12 \times 12 \times 12$ grid) varied from 0·276 for $\bar{1}$,0,17 to 0·403 for 3,$\bar{5}$,50. 1572 unique reflections. 589 reflections considered unobserved [$I < 3\sigma(I)$].

Atomic positions in [$R3m$] (Barbier, 1987*a*) and $R\bar{3}$ are related in the following manner: [M(1)]M(1); [M(2)]M(2); [M(3),M(4)]M(3); [Ge(1)]Ge(1);

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Table 1. *Positional and isotropic thermal parameters* (Å^2) *for* (Ni,Mg)$_{10}$Ge$_3$O$_{16}$ *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	Equipoint	Occupancy*	x	y	z	B_{eq}
M(1)	1(b)	0·345 (4)	0·5	0·5	0·5	0·343 (3)
M(2)	3(e)	0·552 (2)	0·0	0·5	0·5	0·260 (4)
M(3)	6(f)	0·422 (2)	0·75735 (4)	0·24893 (4)	0·24897 (4)	0·300 (4)
Ge(1)	1(a)		0·0	0·0	0·0	0·208 (1)
Ge(2)	2(c)		0·18916 (1)	0·18916 (1)	0·18916 (1)	0·218 (1)
O(1)	2(c)		0·12714 (4)	0·12714 (4)	0·12714 (4)	0·391 (5)
O(2)	2(c)		0·37637 (4)	0·37637 (4)	0·37637 (4)	0·349 (5)
O(3)	6(f)		0·65950 (15)	0·11266 (15)	0·11284 (15)	0·374 (8)
O(4)	6(f)		0·12203 (13)	0·62622 (14)	0·62579 (14)	0·380 (8)

* Fraction of M site occupied by Ni, assuming (Ni + Mg) = 1·0.

Table 2. *Anisotropic thermal parameters* (Å^2 × 10^3) *for the refined structure of* (Ni,Mg)$_{10}$Ge$_3$O$_{16}$

Anisotropic temperature factors have the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
M(1)	352 (12)	352 (12)	352 (12)	−161 (6)	−161 (6)	−161 (6)
M(2)	228 (6)	251 (5)	251 (5)	−106 (3)	−111 (4)	−106 (3)
M(3)	284 (7)	323 (7)	309 (7)	−126 (5)	−119 (5)	173 (6)
Ge(1)	195 (4)	195 (4)	195 (4)	−87 (2)	−87 (2)	−87 (2)
Ge(2)	210 (3)	210 (3)	210 (3)	−94 (2)	−94 (2)	−94 (2)
O(1)	482 (21)	482 (21)	482 (21)	−232 (11)	−232 (11)	−232 (11)
O(2)	366 (21)	366 (21)	366 (21)	−169 (11)	−169 (11)	−169 (11)
O(3)	306 (16)	355 (18)	385 (18)	−135 (14)	−159 (14)	−169 (15)
O(4)	284 (19)	357 (19)	389 (19)	−103 (16)	−118 (16)	−230 (16)

Table 3. *Selected interatomic distances* (Å) *and bond angles* (°) *in* (Ni,Mg)$_{10}$Ge$_3$O$_{16}$

M(1)–O(4)	2·0918 (7)	M(2)–O(2)	2·0982 (4)
M(2)–O(3^{i})	2·0943 (7)	M(2)–O(3^{ii})	2·0935 (8)
M(3)–O(4^{i})	2·0604 (7)	M(3)–O(4^{ii})	2·0588 (7)
M(3)–O(2)	2·1051 (4)	M(3)–O(1)	2·0587 (4)
M(3)–O(3^{iv})	2·0923 (7)	M(3)–O(3^{v})	2·0928 (8)
Ge(1)–O(3)	1·8907 (7)	Ge(2)–O(1)	1·7746 (4)
Ge(2)–O(4^{iii})	1·7753 (7)		

O(4)–M(1)–O(4^{i})	90·30 (3)	O(4)–M(1)–O(4^{iii})	180·0
O(4)–M(1)–O(4^{iv})	89·70 (3)	O(2)–M(2)–O(2^{iii})	180·0
O(2)–M(2)–O(3^{i})	90·54 (2)	O(2)–M(2)–O(3^{ii})	90·57 (2)
O(2)–M(2)–O(3^{iv})	89·46 (2)	O(2)–M(2)–O(3^{v})	89·43 (2)
O(3)–M(2)–O(3^{ii})	100·41 (4)	O(3)–M(2)–O(3^{v})	79·59 (4)
O(4^{i})–M(3)–O(4^{ii})	92·11 (4)	O(4^{i})–M(3)–O(2)	88·10 (2)
O(4^{i})–M(3)–O(1)	91·27 (2)	O(4^{i})–M(3)–O(3^{iv})	173·01 (3)
O(4^{i})–M(3)–O(3^{v})	94·29 (3)	O(4^{ii})–M(3)–O(2)	88·15 (2)
O(4^{ii})–M(3)–O(1)	91·21 (2)	O(4^{ii})–M(3)–O(3^{iv})	94·28 (3)
O(4^{ii})–M(3)–O(3^{v})	173·03 (3)	O(2)–M(3)–O(1)	179·09 (1)
O(2)–M(3)–O(3^{iv})	89·28 (2)	O(2)–M(3)–O(3^{v})	89·31 (2)
O(1)–M(3)–O(3^{iv})	91·42 (2)	O(1)–M(3)–O(3^{v})	91·40 (2)
O(3^{iv})–M(3)–O(3^{v})	79·19 (4)	O(3)–Ge(1)–O(3^{i})	89·72 (3)
O(3)–Ge(1)–O(3^{iii})	180·0	O(3)–Ge(1)–O(3^{iv})	90·28 (3)
O(1)–Ge(2)–O(4^{iii})	108·3 (2)	O(4^{iii})–Ge(2)–O(4^{iv})	110·60 (2)

Symmetry code: (i) z, x, y; (ii) y, z, x; (iii) $-x, -y, -z$; (iv) $-z, -x, -y$; (v) $-y, -z, -x$.

[Ge(2),Ge(3)]Ge(2); [O(1),O(4)]O(1); [O(2),O(3)]O(2); [O(5),O(6)]O(3); [O(7),O(8)]O(4), with Ni and Mg disordered on M sites. $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma^2$; weak reflections $[|F_o| < (|F_o|)_{max}/20)]$ were given a low weight ($\sigma = 1000$). Refinement using all data out to $2\theta = 90°$ and 49 variable parameters converged to $R = 0·014$, $wR = 0·017$, $S = 0·109$, $(\Delta/\sigma)_{max} = 6 \times 10^{-7}$, $\Delta\rho = -0·9$ to 4·2 e Å^{-3}. The low value of S reflects the low weight given to the weak reflections. The maximum residual electron density corresponded to a spike well above background at equipoint 2(c) with $x \simeq 0·32$. However, investigation of it as a possible interstitial point defect (*cf.* Fleet, 1981, 1982) did not result in a reduction in R. The isotropic extinction parameter for type I extinction (g; Coppens & Hamilton, 1970) is 0·182 (5) × 10^{-4}. Scattering factors for neutral atomic species and f',f'' taken from Tables 2.2B and 2.3.1, respectively, of *International Tables for X-ray Crystallography* (1974). Computations carried out with *DATAP*77 and *LINEX*77 (State University of New York at Buffalo).

Discussion. Positional and M-site occupancy parameters for (Ni,Mg)$_{10}$Ge$_3$O$_{16}$ are given in Table 1, anisotropic thermal parameters in Table 2, and selected interatomic distances and bond angles in Table 3.*

In the structure proposed by Barbier (1987*a*), the O atoms form a cubic close-packed array, and {111} triple layers of spinel-like structure alternate with single layers of rock-salt-like structure in the direction of c_{hex} (Fig. 1). The structure of (Ni,Mg)$_{10}$Ge$_3$O$_{16}$ may be viewed also as formed of alternate layers of olivine-like

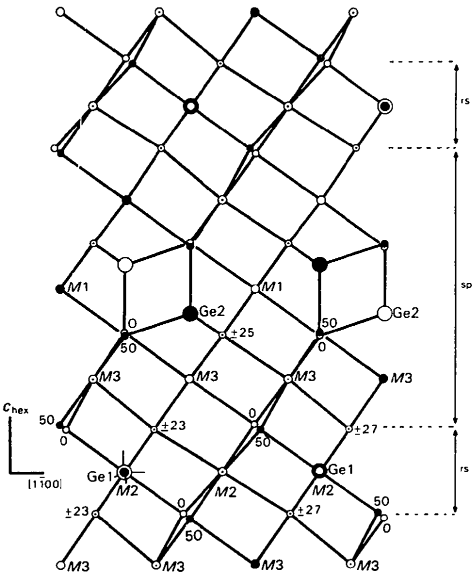

Fig. 1. Structure of (Ni,Mg)$_{10}$Ge$_3$O$_{16}$ projected along [11$\bar{2}$0]$_{hex}$. Large, medium and small circles represent Ge, (Ni,Mg) and O atoms, respectively. Open, filled and dotted circles are at heights 0, 50 and ±25, respectively (in units of 1/100 of the projection axis). Only part of the unit cell is drawn showing the stacking along c_{hex} of the triple spinel (sp) layers and single rock-salt (rs) layers. Note the presence of six-coordinated Ge atoms within the rock-salt layers and the distortion of the cubic-close-packed oxygen array due to the shorter Ge–O octahedral bond (*cf.* Table 3).

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44429 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and rock-salt-like structures stacked parallel to $(01\bar{1})_{\mathrm{trig}}$, and has been shown to belong to a new structural family $M_{4n+6}\mathrm{Ge}_{2n+1}\mathrm{O}_{(n+1)}$ built from the regular intergrowth of n olivine layers with a single rock-salt-like layer (Barbier, 1987*b*).

Barbier's (1987*a*) structure is confirmed by the present structural analysis and is essentially unaffected by revision of the space group to $R\bar{3}$. Spinel-like layers are formed from 7[M(1)M(3)]2[Ge(2)]8[O(1)O(4)]-3[O(2)O(3)] and rock-salt-like layers from 3[M(2)]-[Ge(1)]5[O(2)O(3)] (Fig. 1, Table 1). Refined atomic positions (Table 1) differ only slightly from the ideal values as anticipated from the close dimensional agreement between the corresponding unit cells (Barbier, 1987*a*). The cation coordination polyhedra are all fairly regular (Table 3). In fact, only the $M(3)\mathrm{O}_6$ octahedron is significantly distorted from ideal geometry: it appears that the slight structural accommodation between the spinel-like and rock-salt-like layers is made within the layers of O(3) atoms (Table 1, Fig. 1).

Mean cation—oxygen bond distances compare favorably with ideal values compiled with the data of Shannon (1976), and shown in parentheses (roman superscripts refer to cation coordination): ${}^{\mathrm{VI}}M(1)\text{—}\mathrm{O} = 2{\cdot}092$ $(2{\cdot}110)$; ${}^{\mathrm{VI}}M(2)\text{—}\mathrm{O} = 2{\cdot}095$ $(2{\cdot}103)$; ${}^{\mathrm{VI}}M(3)\text{—}\mathrm{O} = 2{\cdot}078$ $(2{\cdot}107)$; ${}^{\mathrm{VI}}\mathrm{Ge}(1)\text{—}\mathrm{O} = 1{\cdot}891$ $(1{\cdot}914)$; ${}^{\mathrm{IV}}\mathrm{Ge}(2)\text{—}\mathrm{O} = 1{\cdot}775$ Å $(1{\cdot}766$ Å).

The refined structure of $(\mathrm{Ni,Mg})_{10}\mathrm{Ge_3O_{16}}$ indicates little tendency for ordering of the divalent cations on the M sites (Table 1), compared to the marked M(1),-M(2) site ordering in olivine-structure $(\mathrm{Ni,Mg})_2\mathrm{SiO_4}$ (Rajamani, Brown & Prewitt, 1975). However, this is readily attributable to the similarity in size and stereochemistry of all three $M\mathrm{O}_6$ octahedra in $(\mathrm{Ni,Mg})_{10}\mathrm{Ge_3O_{16}}$, which have the same number (six) and configuration of shared edges. $M(1)\mathrm{O}_6$ and $M(2)\mathrm{O}_6$ octahedra in the olivine structure are slightly different in size (Rajamani *et al.*, 1975) and distinctly different in stereochemistry (Fleet, 1974). In $(\mathrm{Ni,Mg})_{10}\mathrm{Ge_3O_{16}}$, Ni does have a preference for the M(2) site (or the rock-salt-like layer, Table 1, Fig. 1) and this is consistent with the selective partitioning of Ni into the rock-salt-structure phase in the $\mathrm{NiO\text{–}MgO\text{–}GeO_2}$ system (Navrotsky, 1972; Fig. 1 of Barbier, 1987*a*).

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Affinement sur Monocristal de la Structure du Polytype 2*H* du Séléniure de Gallium GaSe Forme *β*

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Abstract. 2*H*-*β*-GaSe, $M_r = 148{\cdot}68$, hexagonal, $P6_3/mmc$, $a = 3{\cdot}750\,(4)$, $c = 15{\cdot}995\,(7)$ Å, $V = 194{\cdot}8\,(5)$ Å^3, $Z = 4$, $D_x = 5{\cdot}07$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 34{\cdot}4$ mm^{-1}, $F(000) = 260{\cdot}0$, $T = 293$ K, $R = 0{\cdot}057$ and $wR = 0{\cdot}054$ for 119 independent reflections. The structure, isotypic with *β*-GaS, has been refined on measurements made on a single crystal. In contrast to the interlayer distances, the intralayer distances do not deviate significantly from those previously obtained by extrapolation from the solid solution $\mathrm{GaSe}_x\mathrm{S}_{1-x}$ $(0 < x < 0{\cdot}7)$.

Introduction. Les structures des variétés ε et γ (Schubert, Dörre & Kluge, 1955) et β (Jellinek & Hahn, 1961) du séléniure de gallium GaSe ont été déterminées à partir des diffractogrammes de poudre, avec une

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