INORGANIC COMPOUNDS

Normal and inverse garnets: Ca₃Fe₂Ge₃O₁₂, Ca₃Y₂Ge₃O₁₂ and Mg₃Y₂Ge₃O₁₂

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Abstract

The structures of three garnets, namely, tricalcium diiron(III) trigermanium dodecaoxide, tricalcium diyttrium trigermanium dodecaoxide and trimagnesium diyttrium trigermanium dodecaoxide, have been determined by X-ray diffraction using flux-grown single crystals. The cation distributions correspond to a normal garnet structure for $Ca_3^{[8]}Fe_2^{[6]}Ge_3^{[4]}O_{12}$ and $Ca_3^{[8]}Y_2^{[6]}Ge_3^{[4]}O_{12}$, and to an inverse garnet structure for $(MgY_2)^{[8]}Mg_2^{[6]}Ge_3^{[4]}O_{12}$.

Comment

The crystal structure of the garnet analogue $Ca_3Fe_2Ge_3O_{12}$, (I), has been refined previously by powder neutron diffraction using a very limited dataset of only nine reflections (Lipin & Nozik, 1971). A new refinement has now been carried out by single-crystal X-ray diffraction to obtain more accurate bond distances for the purpose of comparison with the new tetragonal compound $(Ca,Fe,Mg)_{0.92}^{[8]}(Mg,Fe)_4^{[6]}(Ge,Fe)_3^{[4]}O_{12}$ (Lévy & Barbier, 1999); superscript values in square brackets designate the coordination numbers, following standard mineralogical nomenclature. The $Ca_3Y_2Ge_3O_{12}$ garnet, (II), has been synthesized previously in microcrystalline form and studied for its spectroscopic properties (Oudet, 1973), but its crystal structure has not been refined previously. Similarly, only lattice parameters have been reported to date for the $Mg_3Y_2Ge_3O_{12}$ garnet, (III) (Bayer, 1971). The crystal structures of all three title compounds are presented here.

The present refinements of the three garnet structures yield the following cation distributions: $Ca_3^{[8]}Fe_2^{[6]}Ge_3^{[4]}O_{12}$, $Ca_3^{[8]}Y_2^{[6]}Ge_3^{[4]}O_{12}$ and $(MgY_2)^{[8]}Mg_2^{[6]}Ge_3^{[4]}O_{12}$. By analogy with the nomenclature used for normal and inverse spinels, (I) and (II) are normal garnets, whereas (III) is an inverse garnet with a mixed
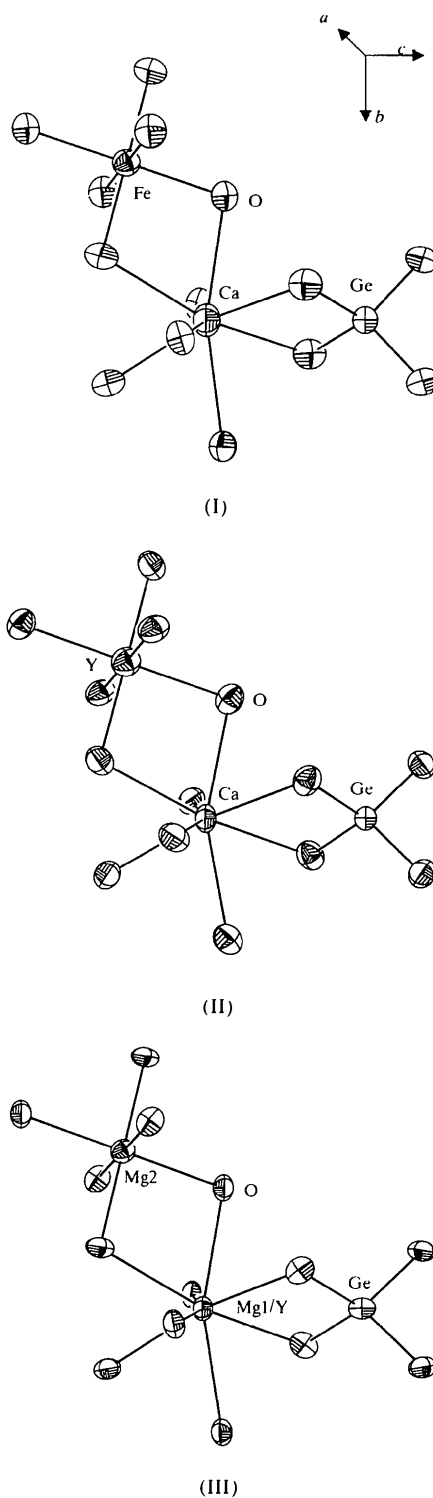

Fig. 1. Displacement ellipsoid diagrams of the three title garnet structures viewed along the [001] direction. Displacement ellipsoids are drawn at the 90% probability level.

Mg^{2+}/Y^{3+} occupancy of the dodecahedral site. In view of the small size difference between Ca^{2+} and Y^{3+}, viz. 1.12 versus 1.02 Å for eightfold coordination (Shannon, 1976), the normal distribution in (II) was checked by introducing Y^{3+} and Ca^{2+} on the dodecahedral and octahedral sites, respectively. After a few cycles of refinement with a constraint on the global composition of the crystal, their populations converged to zero, thus confirming the normal cation distribution. A similar procedure also confirmed the inverse distribution in (III).

As indicated by the formulae, the Ca$_3$Fe$_2$[6]Ge$_3$O$_{12}$ and Ca$_3$Y$_2$[6]Ge$_3$O$_{12}$ structures only differ by their octahedral site contents. The mean Ge—O distances are equivalent in both structures [mean Ge—O = 1.765 (2) Å in (I) and 1.766 (3) Å in (II)], whereas the mean Ca—O distances are not [mean Ca—O = 2.449 (2) Å in (I) and 2.516 (3) Å in (II)]. The difference is significant and seems to indicate that the size of the dodecahedral sites in the garnet structure is mainly imposed by the framework of corner-sharing tetrahedra and octahedra. The bond valence around Ca^{2+} in (I) sums to 2.26, indicating that the average Ca—O bond length is too short, whereas it sums to 1.88 in (II), indicating this time that the average Ca—O bond is too long. These bond-valence sums, however, differ only slightly from the theoretical value of 2 for Ca^{2+}, and the Ca garnet phases are expected to be stable compounds. Indeed, no difficulties were encountered during the syntheses of these compounds.

In the case of garnet (III), the bond valences sum to 2.97 for dodecahedral Y^{3+}, 1.25 for dodecahedral Mg^{2+} and 2.19 for octahedral Mg^{2+}. This clearly indicates that the presence of dodecahedral Mg^{2+} may be a destabilizing factor for the structure. In that respect, it is noteworthy that the garnet mineral pyrope, Mg$_3$Al$_2$Si$_3$O$_{12}$, is metastable at a pressure of 1 atm (1 atm = 101325 Pa) (Liu & Bassett, 1986).

Finally, (III) is the third confirmed member of the family of inverse garnets (the first two are Co$_3$Y$_2$Ge$_3$O$_{12}$ and Co$_3$Gd$_2$Ge$_3$O$_{12}$; Geller & Miller, 1960), where the larger trivalent cation shifts from the octahedral to the dodecahedral site.

Experimental

Single crystals of compounds (I), (II) and (III) were obtained by the flux method. For (I), 3 g of the starting oxide mixture were dissolved in 5 g of a K$_2$Mo$_2$O$_7$ flux. The melt was kept at 1523 K for 12 h and cooled slowly to 1223 K. For (II), 3 g of the starting oxide mixture were dissolved in 10 g of K$_2$MoO$_4$. The melt was kept at 1523 K for 24 h and cooled slowly to 1123 K. For (III), 4 g of the starting oxide mixture were dissolved in 10 g of K$_2$Mo$_2$O$_7$. The melt was kept at 1623 K for 24 h and cooled to 1425 K. In all cases, the melts were contained in covered Pt crucibles and cooled at a rate of 3 K h^{-1}.

Compound (I)

Crystal data

Ca$_3$Fe$_2$Ge$_3$O$_{12}$	Mo $K\alpha$ radiation
M_r = 641.71	λ = 0.71073 Å
Cubic	Cell parameters from 2873
$Ia\bar{3}d$	reflections
a = 12.321 (9) Å	θ = 4.05–36.34°
V = 1870 (2) Å^3	μ = 14.277 mm^{-1}
Z = 8	T = 300 (2) K
D_x = 4.558 Mg m^{-3}	Prism
D_m not measured	0.12 × 0.12 × 0.12 mm
	Brown

Data collection

Siemens SMART 1K CCD area detector and Siemens P4 diffractometer	9916 measured reflections
	382 independent reflections
	R_{int} = 0.050
Area-detector scans	θ_{max} = 36.33°
Absorption correction:	$h = -19 \rightarrow 12$
multi-scan (Sheldrick, 1996)	$k = -20 \rightarrow 20$
	$l = -19 \rightarrow 20$
T_{min} = 0.200, T_{max} = 0.259	Intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$R[F^2 > 2\sigma(F^2)]$ = 0.030	$\Delta\rho_{min}$ = −0.58 e Å^{-3}
$wR(F^2)$ = 0.068	Extinction correction:
S = 1.253	SHELXL97 (Sheldrick,
382 reflections	1997)
18 parameters	Extinction coefficient:
$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 9.5751P]$	0.00095 (10)
where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from International Tables for
$(\Delta/\sigma)_{max} < 0.001$	Crystallography (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ge	0	1/4	3/8	0.00571 (16)
Fe	0	0	0	0.00611 (19)
Ca	0	1/4	1/8	0.00804 (18)
O	−0.03415 (14)	0.05099 (14)	0.15172 (14)	0.0076 (3)

Compound (II)

Crystal data

Ca$_3$Y$_2$Ge$_3$O$_{12}$	Mo $K\alpha$ radiation
M_r = 707.83	λ = 0.71073 Å
Cubic	Cell parameters from 1467
$Ia\bar{3}d$	reflections
a = 12.8059 (8) Å	θ = 3.90–28.83°
V = 2100.1 (2) Å^3	μ = 20.952 mm^{-1}
Z = 8	T = 299 (2) K
D_x = 4.478 Mg m^{-3}	Prism
D_m not measured	0.05 × 0.04 × 0.03 mm
	Colourless

Data collection

Siemens SMART 1K CCD area detector and Siemens P4 diffractometer
Area-detector scans
Absorption correction: multi-scan (Sheldrick, 1996)
$T_{min} = 0.289$, $T_{max} = 0.487$

4744 measured reflections
234 independent reflections
$R_{int} = 0.063$
$\theta_{max} = 28.83°$
$h = -16 \rightarrow 14$
$k = -16 \rightarrow 15$
$l = -9 \rightarrow 17$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.087$
$S = 1.179$
234 reflections
18 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 22.9720P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.89$ e Å^{-3}
$\Delta\rho_{min} = -1.17$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.00066 (11)
Scattering factors from International Tables for Crystallography (Vol. C)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Ge	0	1/4	3/8	0.0049 (4)
Y	0	0	0	0.0075 (4)
Ca	0	1/4	1/8	0.0063 (5)
O	-0.0363 (2)	0.0567 (3)	0.1609 (3)	0.0073 (8)

Compound (III)

Crystal data

$Mg_3Y_2Ge_3O_{12}$
$M_r = 660.52$
Cubic
$Ia\bar{3}d$
$a = 12.2489 (12)$ Å
$V = 1837.8 (3)$ Å^3
$Z = 8$
$D_x = 4.775$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3474 reflections
$\theta = 4.04–36.04°$
$\mu = 22.473$ mm^{-1}
$T = 299 (2)$ K
Prism
$0.07 \times 0.05 \times 0.04$ mm
Colourless

Data collection

Siemens SMART 1K CCD area detector and Siemens P4 diffractometer
Area-detector scans
Absorption correction: multi-scan (Sheldrick, 1996)
$T_{min} = 0.266$, $T_{max} = 0.377$

12 155 measured reflections
378 independent reflections
$R_{int} = 0.047$
$\theta_{max} = 36.38°$
$h = -17 \rightarrow 20$
$k = -19 \rightarrow 6$
$l = -20 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.075$
$S = 1.187$
378 reflections
18 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 18.3164P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.00056 (8)
Scattering factors from International Tables for Crystallography (Vol. C)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Y†	0	1/4	1/8	0.00755 (19)
Mg1‡	0	1/4	1/8	0.00755 (19)
Mg2	0	0	0	0.0084 (4)
Ge	0	1/4	3/8	0.00778 (19)
O	-0.03093 (19)	0.05582 (19)	0.15607 (18)	0.0094 (4)

† Site occupancy = 0.67.   ‡ Site occupancy = 0.33.

Table 4. Selected bond lengths (Å) and oxygen coordinates for (I), (II) and (III)

	(I)	(II)	(III)
Ge—O × 4	1.765 (2)	1.766 (3)	1.766 (2)
M—O† × 6	2.016 (2)	2.333 (3)	2.065 (2)
A—O × 4	2.389 (2)	2.469 (3)	2.332 (2)
A—O × 4	2.510 (3)	2.561 (3)	2.438 (2)
x	-0.03415 (14)	-0.0363 (2)	-0.03093 (19)
y	0.05099 (14)	0.0567 (3)	0.05582 (19)
z	0.15172 (14)	0.1609 (3)	0.15607 (18)

† In (I), M = Fe and A = Ca; in (II), M = Y and A = Ca; and in (III), M = Mg2 and A = Mg1/Y.   Note: Ge in $(0,\frac{1}{4},\frac{3}{8})$, M in $(0,0,0)$ and A in $(0,\frac{1}{4},\frac{1}{8})$.

For all compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990a); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL97*.

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