Crystal structure of manganese gallium germanium silicon oxide (garnet type), $Mn_3(Ga_{2-y}Mn_y)(Ge_{3-z}Si_z)O_{12}$ ($y = 0.6$, $z = 0.14$; $y = 0.44$, $z = 0$), and of manganese gallium germanium silicon oxide (braunite type), $Mn(Mn_{6-y}Ga_y)(Si_{1-z}Ge_z)O_{12}$ ($y = 0.7$, $z = 0.4$)

R. Wartchow*, L. Müller and M. Binnewies

Universität Hannover, Institut für Anorganische Chemie, Callinstr. 9, D-30167 Hannover, Germany

Received June 26, 2003, accepted in revised form and available online September 19, 2003; CSD-No. 409715, 409716, 409717

Abstract

$Ga_{1.4}Ge_{2.86}Mn_{3.6}O_{12}Si_{0.14}$ (**1**), cubic, $Ia\bar{3}d$ (No. 230), $a = 12.043(3)$ Å, $V = 1746.6$ Å^3, $Z = 8$, $R_{gt}(F) = 0.028$, $wR_{ref}(F^2) = 0.062$, $T = 300$ K.

$Ga_{1.56}Ge_3Mn_{3.44}O_{12}$ (**2**), cubic, $Ia\bar{3}d$ (No. 230), $a = 12.049(3)$ Å, $V = 1749.3$ Å^3, $Z = 8$, $R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.052$, $T = 300$ K.

$Ga_{0.7}Ge_{0.4}Mn_{6.3}O_{12}Si_{0.6}$ (**3**), tetragonal, $I4_1/acd$ (No. 142), $a = 9.464(4)$ Å, $c = 18.78(3)$ Å, $V = 1682.1$ Å^3, $Z = 8$, $R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.053$, $T = 300$ K.

Source of material

Solid solution compounds of garnet and braunite type in the system $MnO/Mn_2O_3/Ga_2O_3/GeO_2/SiO_2$ were obtained accidentally by annealing Mn_2O_3 (99.9 %, ChemPur), Ga_2O_3 (99.5 %, Merck) and GeO_2 (99.9 %, Merck) in the stoichiometric ratio of 2:1:6. The experiment was performed inside a closed quartz tube at 1273 K which contained the amount of hydrochloric acid gas corresponding to the pressure of 500 mbar at reaction temperature. The reaction time was 145 h. Aiming at a selective preparation of $Mn_3Ga_2Ge_3O_{12}$ the corresponding stoichiometric mixture of MnO, Ga_2O_3 (99.5 %, Merck) and GeO_2 (99.9 %, Merck) was annealed in an open corundum cup inserted in a closed quartz tube. Reaction temperature and the pressure of hydrochloric acid gas were chosen as in the previous experiment. The reaction time was 315 h. MnO was prepared by decomposing $MnCO_3$ under hydrogen flow at 823 K. Red single crystals of garnet type were obtained and a second non single crystalline phase which was not identified.

Experimental details

For **1**, six crystals in random orientation were measured with similar results. Therefore, the merged reflections of the six measurements were combined for the last refinement. For **2** and **3** two crystals were measured with similar results, and the merged reflections of the two measurements were combined for the last refinement. The compositions of the crystals were derived from the refined occupation factors, and the results of EDX analyses were only used qualitatively.

For **1**, in more detail, the differences of most of the parameters of each individual result lie in the range 2 to 4 e.s.d. Although one can expect crystals of variable composition in a solid solution synthesis, in our case the observed differences in the composition are not significant. We therefore consider the differences in the results as random and believe that merging of the reflection data for the final refinement is justified in order to obtain a result which is more representative for the whole sample. The merged F^2_{obs} data set of each single measurement was scaled against F^2_{calc}, therefore, it can be expected that the relative scale factors for the various data sets are nearly 1.0. In an empirical way, relative scale factors in the range 0.97 – 1.03 were tested, and the scale factor chosen was the one that improved both the R_{int} as well as the final residual $wR_{ref}(F^2)$. Other data reported in the CIF (e.g. lattice parameters) were averaged too. The reported number of 'measured' reflections in Table 1 is the sum of the merged reflections of the six crystals. Similarly, for **2** and **3** cases, for the final refinement the merged reflection data sets of the two measured crystals were compiled in one file and merged again. Lattice parameters were averaged too. The data relevant for the absorption correction reported in the CIF file are taken from the larger crystal. The reported number of reflections in Tables 3 and 5 is the sum of the merged reflections of the two crystals. Details of each individual measurement are contained in the deposited CIF.

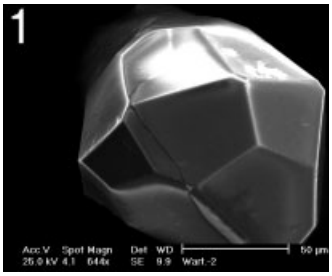
Discussion

The next end-member garnet nearest in composition to our garnets (compound **1** and **2**) is $Mn_3Ga_2Ge_3O_{12}$, of which the lattice constant is known from powder diffraction data (PDF 13-5) as $a = 12.043$ Å in good agreement with our average value of compound **1**. Its colour is described as beige. A single crystal structure refinement is not available. The comparison with $Mn_3Fe_2Ge_3O_{12}$ instead (see [1]) is in good agreement as regards interatomic distances taking into account that the ionic radius of Ga^{+3} is assumed to be 2-3% smaller than that of Fe^{+3}. The anisotropic displacement ellipsoid of Mn^{+2} ($U_3/U_1 = 2.6$ to 2.8, this work) agrees fairly well with that of spessartine ($U_3/U_1 = 3.1$, ICSD #83458) and its longest half axis points to the midpoint of two oxygen neighbours with the longest Mn—O distances within the peculiar 4 + 4 coordination sphere as one would expect. The refinement shows that the electron density at the Ga^{+3} site is reduced. We assume that Ga^{+3} is partially substituted by Mn^{+3}. This was not proven by other means, but we believe that the red colour of our garnet crystals is caused by this substitution. The observation of crystals of braunite type (compound **3**) confirms the statement on the stability of braunite $Mn^{2+}Mn_6^{3+}SiO_{12}$ (see [2]) and shows that in braunite Mn^{+3} can be partially substituted by Ga^{+3} and Si^{+4} by Ge^{+4}. The situation of the Mn^{+2} ion in braunite is quite similar to that in garnet. The anisotropy of the displacement ellipsoid ($U_3/U_1 = 4.7$) is still more pronounced because there are larger differences in the Mn^{+2}—O

* Correspondence author (e-mail: wartchow@aca.uni-hannover.de)

distances of the 4 + 4 coordination polyhedron. The Mn^{+2}—O distances are : 2.30 Å (4×) and 2.42 Å (4×) in **1**, 2.30 Å (4×) and 2.43 Å (4×) in **2**, and 2.18 Å (4×) and 2.52 Å (4×) in **3**.

1. Manganese gallium germanium silicon oxide (garnet type), $Mn_3(Ga_{2-y}Mn_y)(Ge_{3-z}Si_z)O_{12}$ ($y = 0.6$, $z = 0.14$)



Projection along [100]

Table 1. Data collection and handling.

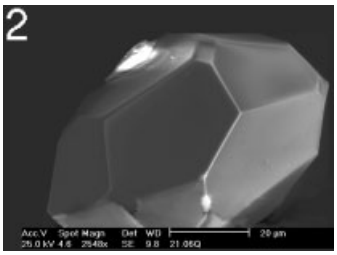
Crystals:	six red {211}-ikositetrahedra, average size 0.10 × 0.12 × 0.13 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	191 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 240 exposures, $\Delta\phi = 1.5°$
$2\theta_{max}$:	61.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1375, 231
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 212
$N(param)_{refined}$:	19
Program:	SHELXL-93 [3]

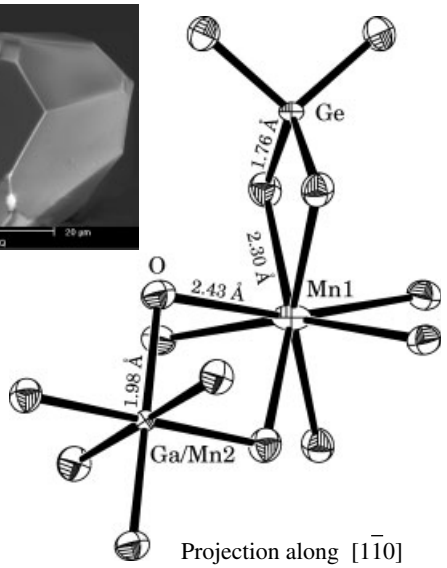
Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	24*c*	0	1/4	1/8	0.0114(4)	U_{11}	0.0054(5)	0.0024(3)	0	0
Ga/Mn(2) [a]	16*a*	0	0	0	0.0037(3)	U_{11}	U_{11}	0.0001(1)	U_{12}	U_{12}
Ge/Si [b]	24*d*	0	1/4	3/8	0.0053(3)	U_{11}	0.0031(3)	0	0	0
O(1)	96*h*	–0.0301(2)	0.0528(2)	0.1522(2)	0.010(1)	0.010(1)	0.0073(9)	–0.0001(8)	0.0009(8)	0.0001(7)

a: Ga/Mn(2) = 0.70(2)Ga + 0.30Mn
b: Ge/Si = 0.954(8)Ge + 0.046Si

2. Manganese gallium germanium oxide (garnet type), $Mn_3(Ga_{2-y}Mn_y)Ge_3O_{12}$ ($y = 0.44$)





Projection along [1$\bar{1}$0]

Table 3. Data collection and handling.

Crystals:	two red {211}-ikositetrahedra, average size 0.082 × 0.098 × 0.105 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	198 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 240 exposures, $\Delta\phi = 1.5°$
$2\theta_{max}$:	56.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	364, 182
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 153
$N(param)_{refined}$:	18
Program:	SHELXL-93 [3]

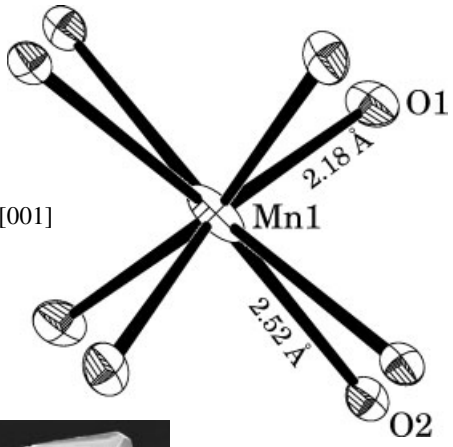
Table 4. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	24*c*	0	1/4	1/8	0.0117(3)	U_{11}	0.0049(5)	0.0022(3)	0	0
Ga/Mn(2) [a]	16*a*	0	0	0	0.0040(4)	U_{11}	U_{11}	–0.0001(1)	U_{12}	U_{12}
Ge(1)	24*d*	0	1/4	3/8	0.0054(3)	U_{11}	0.0037(3)	0	0	0
O(1)	96*h*	–0.0300(2)	0.0526(2)	0.1524(2)	0.010(1)	0.012(1)	0.0076(9)	0.0003(8)	0.0005(7)	–0.0006(7)

a: Ga/Mn(2) = 0.78(2)Ga + 0.22Mn

3. Manganese gallium germanium silicon oxide (braunite type), $Mn(Mn_{6-y}Ga_y)(Si_{1-z}Ge_z)O_{12}$ ($y = 0.7$, $z = 0.4$)

Projection along [001]



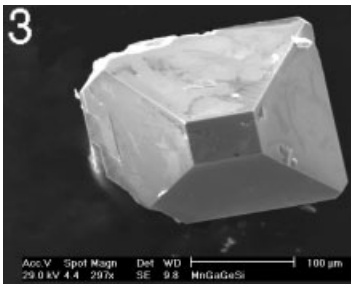


Table 5. Data collection and handling.

Crystals:	two black octahedra, average size 0.100 × 0.130 × 0.132 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	129.24 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 240/300 exposures, $\Delta\phi$ = 1.5°/1.2°
$2\theta_{max}$:	60.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1286, 646
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 507
$N(param)_{refined}$:	53
Program:	SHELXL-93 [3]

Acknowledgments. The help of Dipl. Chem. J. Mattik in preparing the figures is gratefully acknowledged. Computing facilities of RRZN (Hannover) were used.

References

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2. Ohmann, S.; Abs-Wurmbach, I.; Stüßer, N.; Sabine, T. M.; Westerholt, K.: The magnetic structure of braunite $Mn^{2+}Mn^{3+}{}_6O_8/SiO_4$. Z. Kristallogr. **213** (1998) 19-27.
3. Sheldrick, G. M.: SHELXL-93, a program for refining crystal structures, University of Göttingen, Germany 1993.

Table 6. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	8*b*	0	1/4	1/8	0.0110(3)	U_{11}	0.0053(4)	–0.0071(3)	0	0
Mn/Ga(2) [a]	16*c*	0	0	0	0.0046(2)	0.0059(2)	0.0031(3)	–0.0026(2)	–0.0010(2)	0.0006(2)
Mn/Ga(3) [b]	16*e*	0.03454(6)	0	1/4	0.0035(3)	0.0047(3)	0.0034(3)	0	0	0.0012(2)
Mn/Ga(4) [c]	16*f*	0.23238(4)	*x*+1/4	1/8	0.0043(2)	U_{11}	0.0022(3)	–0.0011(1)	0.0004(1)	$-U_{13}$
Ge/Si [d]	8*a*	0.0	1/4	3/8	0.0037(3)	U_{11}	0.0031(4)	0	0	0
O(1)	32*g*	0.1492(2)	0.3551(2)	0.05406(9)	0.0093(7)	0.0068(7)	0.0065(7)	–0.0013(6)	0.0027(6)	–0.0028(6)
O(2)	32*g*	0.1443(2)	0.0723(2)	0.05691(8)	0.0060(7)	0.0064(7)	0.0046(7)	–0.0011(6)	–0.0024(6)	0.0012(6)
O(3)	32*g*	0.0808(2)	0.1320(2)	0.92627(9)	0.0087(8)	0.0095(8)	0.0095(8)	–0.0010(6)	0.0003(7)	0.0024(6)

a: Mn/Ga(2) = 0.79(1)Mn + 0.21Ga
b: Mn/Ga(3) = 0.96(1)Mn + 0.04Ga
c: Mn/Ga(4) = 0.90(1)Mn + 0.10Ga
d: Ge/Si = 0.406(5)Ge + 0.594Si