



Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

Garnet-type  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$ 

Christian Lipp, Sabine Strobel, Falk Lissner and Rainer Niewa\*

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Correspondence e-mail: rainer.niewa@iac.uni-stuttgart.de

Received 11 April 2012; accepted 17 April 2012

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{Ge}-\text{O}) = 0.002$  Å;  $R$  factor = 0.025;  $wR$  factor = 0.068; data-to-parameter ratio = 15.4.

Single crystals of garnet-type trimanganese(II) dichromium(III) tris[orthogermanate(IV)],  $\text{Mn}^{\text{II}}_3\text{Cr}^{\text{III}}_2(\text{GeO}_4)_3$ , were obtained by utilizing a chemical transport reaction. Corresponding to the mineral garnet with the general formula  $A^{\text{II}}_3B^{\text{III}}_2(\text{SiO}_4)_3$ , each of the four elements occupies only one crystallographically distinct position.  $\text{Mn}^{2+}$  occupies the respective  $A$  position (Wyckoff site 24c, site symmetry 2.22), being surrounded by eight O atoms that form a distorted cube [ $d(\text{Mn}-\text{O}) = 2.291$  (2) and 2.422 (2) Å,  $4 \times$  each], while  $\text{Cr}^{3+}$  on the  $B$  position (Wyckoff site 16a, site symmetry  $\bar{3}$ ) is situated in a slightly distorted octahedron of six  $\text{O}^{2-}$  anions [ $d(\text{Cr}-\text{O}) = 1.972$  (2) Å,  $6 \times$ ]. In addition, the O atoms on general site 96h form isolated  $[\text{GeO}_4]^{4-}$  tetrahedra with Ge<sup>4+</sup> on site 24d [site symmetry  $\bar{4}$ .;  $d(\text{Ge}-\text{O}) = 1.744$  (2) Å,  $4 \times$ ].

## Related literature

For general background to garnets, see: Geller (1967); Geusic *et al.* (1964); Menzer (1925, 1926, 1928); Nishikawa (1917); Novak & Gibbs (1971). For synthetic details, see: Binnewies *et al.* (2011); Pajczkowska & Majcher (1985, 1986); Pajczkowska *et al.* (1986). For isotypic structures, see: Andrut & Wildner (2002); Belov *et al.* (1972); Fursenko (1981); Geller *et al.* (1960); Golosovskii *et al.* (1976); Lind & Geller (1969); Prandl (1973); Tauber *et al.* (1958a,b, 1961); Wildner & Andrut (2001).

## Experimental

## Crystal data

$\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$   
 $M_r = 678.59$   
 Cubic,  $Ia\bar{3}d$   
 $a = 12.0001$  (3) Å  
 $V = 1728.04$  (7) Å<sup>3</sup>

$Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 17.01$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.18 \times 0.15 \times 0.09$  mm

## Data collection

Nonius KappaCCD diffractometer  
 Absorption correction: numerical  
 (HABITUS; Herrendorf &

Bärnighausen, 1997)  
 $T_{\text{min}} = 0.063$ ,  $T_{\text{max}} = 0.201$   
 7635 measured reflections

277 independent reflections  
 265 reflections with  $I > 2\sigma(I)$

 $R_{\text{int}} = 0.084$ 

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$   
 $wR(F^2) = 0.068$   
 $S = 1.26$   
 277 reflections

18 parameters  
 $\Delta\rho_{\text{max}} = 0.63$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.72$  e Å<sup>-3</sup>

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg & Putz, 2012); software used to prepare material for publication: publCIF (Westrip, 2010).

We thank the state of Baden-Württemberg (Stuttgart) for financial support. This work was also supported by the German Research Foundation (DFG) within the funding program Open Access Publishing.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2621).

## References

- Andrut, M. & Wildner, M. (2002). *Phys. Chem. Miner.* **29**, 595–608.  
 Belov, K. P., Mamsurova, D. G., Mill', B. V. & Sokolov, V. I. (1972). *Pis'ma Zh. Eksp. Teor. Fiz.* **16**, 173–176.  
 Binnewies, M., Glaum, R., Schmidt, M. & Schmidt, P. (2011). *Chemische Transportreaktionen*, 1st ed. Berlin: de Gruyter.  
 Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
 Fursenko, B. A. (1981). *Bull. Miner.* **104**, 418–422.  
 Geller, S. (1967). *Z. Kristallogr.* **125**, 1–47.  
 Geller, S., Miller, C. E. & Treuting, R. G. (1960). *Acta Cryst.* **13**, 179–186.  
 Geusic, J. E., Marcos, H. M. & van Uitert, L. G. (1964). *Appl. Phys. Lett.* **4**, 182–184.  
 Golosovskii, I. V., Plakhii, V. P., Smirnov, O. P., Chernenkov, Yu. P., Kovalev, A. V. & Bedrizova, M. N. (1976). *Pis'ma Zh. Eksp. Teor. Fiz.* **24**, 461–464.  
 Herrendorf, W. & Bärnighausen, H. (1997). *HABITUS*. Universities of Karlsruhe and Giessen, Germany.  
 Lind, M. D. & Geller, S. (1969). *Z. Kristallogr.* **129**, 427–434.  
 Menzer, G. (1925). *Centralbl. Mineral. A*, pp. 344–345.  
 Menzer, G. (1926). *Z. Kristallogr.* **63**, 157–158.  
 Menzer, G. (1928). *Z. Kristallogr.* **69**, 300–396.  
 Nishikawa, Sh. (1917). *Proc. Math. Phys. Soc. Tokyo*, **9**, 194–197.  
 Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.  
 Novak, G. A. & Gibbs, G. V. (1971). *Am. Mineral.* **56**, 791–825.  
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.  
 Pajczkowska, A., Jasiolek, G. & Majcher, K. (1986). *J. Cryst. Growth*, **79**, 417–420.  
 Pajczkowska, A. & Majcher, K. (1985). *J. Cryst. Growth*, **71**, 810–812.  
 Pajczkowska, A. & Majcher, K. (1986). *J. Mater. Sci. Lett.* **5**, 487–488.  
 Prandl, W. (1973). *Phys. Status Solidi B*, **55**, K159–K163.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Tauber, A., Banks, E. & Kedesdy, H. (1958a). *Acta Cryst.* **11**, 893–894.  
 Tauber, A., Banks, E. & Kedesdy, H. H. (1958b). *J. Appl. Phys.* **29**, 385–387.  
 Tauber, A., Whinfrey, C. G. & Banks, E. (1961). *J. Phys. Chem. Solids*, **21**, 25–32.  
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.  
 Wildner, M. & Andrut, M. (2001). *Am. Mineral.* **86**, 1231–1251.

## supplementary materials

*Acta Cryst.* (2012). E68, i35 [doi:10.1107/S1600536812016832]

**Garnet-type  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$** **Christian Lipp, Sabine Strobel, Falk Lissner and Rainer Niewa****Comment**

Garnet can be found among the very early attempts to solve crystal structures with the help of X-ray diffraction (Nishikawa, 1917), soon being followed by the understanding of the regular structure (Menzer, 1925, 1926) and the variability of garnet in a systematic way (Menzer, 1928; Geller, 1967; Novak & Gibbs, 1971). The variability of the garnet-type structure led for example to the well known Nd:YAG lasers ( $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Nd}^{3+}$ ; Geusic *et al.*, 1964). A much more apparent variation is of course the replacement of Si by Ge (Tauber *et al.*, 1961; Geller, 1967), resulting in germanate garnets that are accessible *via* chemical transport reactions. The latter are an elegant way to grow crystals (Binnewies *et al.*, 2011) when other methods deliver only fine powders or require very high temperatures if the growth from melts is necessary.

The formation of garnet-type  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$  by chemical transport reactions was already successfully demonstrated for transporting agents like  $\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{SCL}_4$  and  $\text{TeCl}_4$  (Pajączkowska & Majcher, 1985, Pajączkowska *et al.* 1986;  $\text{Mn}_3\text{Fe}_2(\text{GeO}_4)_3$ : Pajączkowska & Majcher, 1986). While only 0.5 mm edge length as a maximum crystal size was stated when  $\text{TeCl}_4$  was used as a transporting agent, we achieved sizes of up to 4 mm within twelve days with the same agent. Quite interestingly Pajączkowska & Majcher (1985) determined only the unit-cell dimensions by using powder X-ray diffraction ( $a = 12.030$  (1) Å), but not the structural details. The same germanate  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$  was already presented before, but each time again only by mentioning the unit-cell dimensions, being obtained by powder diffraction (Tauber *et al.*, 1958a ( $a = 12.027$  Å); Tauber *et al.*, 1958b ( $a = 12.027$  Å); Geller *et al.*, 1960 ( $a = 12.027$  (3) Å); Belov *et al.*, 1972 ( $a = 12.028$  (4) Å)). In addition some experiments on the magnetic properties have been conducted (Tauber *et al.*, 1958b; Belov *et al.*, 1972; Golosovskii *et al.* 1976), but again without the determination of structural details of  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$ . Golosovskii *et al.* (1976) conducted neutron diffraction experiments and discussed the magnetic structure. They achieved results similar to the ones obtained for the spessartite-type germanate garnet  $\text{Mn}_3\text{Al}_2(\text{GeO}_4)_3$  by Prandl (1973), thus finding confirmation for  $\text{Mn}^{2+}$  on site 24i where it is eightfold coordinated by oxygen.

The obtained dark green garnet-type  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$  (see Fig. 1) crystallizes isotypically with regular garnets. While  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ge}^{4+}$  are located on the special sites 24c, 16a and 24d, oxygen is found on general site 96h. Manganese(II) is eightfold coordinated by oxygen in a distorted cube (Fig. 2) with Mn–O distances of 2.291 (2) and 2.422 (2) Å (4× each). These values are in good agreement with those reported for  $\text{Mn}_3\text{Fe}_2(\text{GeO}_4)_3$  (2.303 (7) and 2.421 (7) Å; Lind & Geller, 1969). For additional comparison the analogous garnet  $\text{Mn}_3\text{Cr}_2(\text{SiO}_4)_3$  would be of interest, but once more only the unit-cell parameters, determined by powder diffraction, are mentioned ( $a = 11.766$  (2) Å; synthesis at 80 kbar/1273 K; Fursenko, 1981). The green color of  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$  may be taken as an indicator for the +III oxidation state of chromium. Oxygen surrounds chromium(III) in a slightly distorted octahedron (Fig. 3) with  $d(\text{Cr}—\text{O}) = 1.972$  (2) Å (6×), whereas 1.9942 (6) Å is reported for chromium on the same position in synthetic uvarovite ( $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ ; Andrut & Wildner, 2002; for natural uvarovite, see: Wildner & Andrut, 2001). Due to the slight distortion, the (O—Cr—O) angles within the  $[\text{CrO}_6]$  octahedra deviate from 90°, viz 86.33 (8)° and 93.67 (8)°. Completing the description of the cation

environments,  $\text{Ge}^{4+}$  is situated in slightly elongated tetrahedra of four  $\text{O}^{2-}$  anions where  $d(\text{Ge—O}) = 1.744$  (2) Å, and the angles (O—Ge—O) are found to be  $99.02$  (14)° (2×) and  $114.93$  (7)° (4×). This is again similar to the values detected for  $\text{Mn}_3\text{Fe}_2(\text{GeO}_4)_3$  ( $d(\text{Ge—O}) = 1.766$  (7) Å, (O—Ge—O) =  $98.8$  (5)° (2×) and  $115.1$  (3)° (4×); Lind & Geller, 1969).

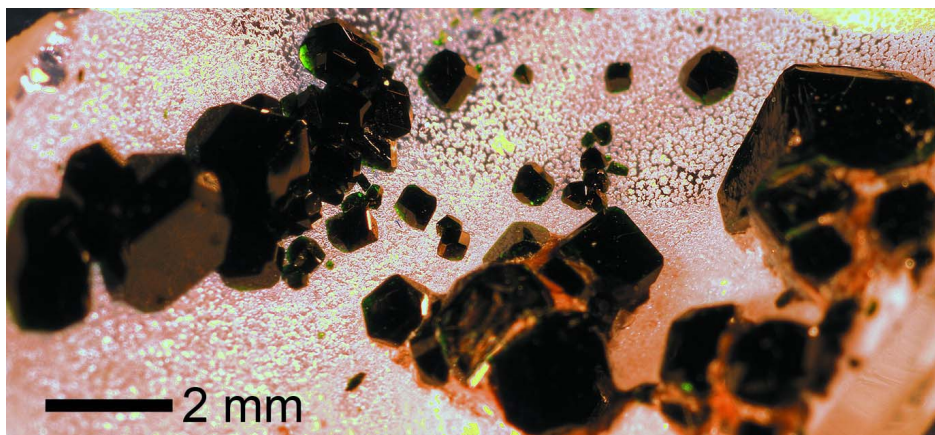
Keeping in mind only a single site is occupied by oxygen, the structure of garnets might be described as two interpenetrating networks in  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$ , the first made up of edge sharing  $[\text{CrO}_6]$  octahedra and  $[\text{GeO}_4]^{4-}$  tetrahedra (Fig. 2 & 3), while the second consists of groups of three edge sharing  $[\text{MnO}_8]$  polyhedra (see Fig. 2), with each distorted  $[\text{MnO}_8]$  cube being part of two of these units of three polyhedra. Therefore, each  $[\text{MnO}_8]$  polyhedron shares four edges with four  $[\text{MnO}_8]$  polyhedra, four edges with four  $[\text{CrO}_6]$  octahedra, and two edges and four vertices with six  $[\text{GeO}_4]^{4-}$  tetrahedra.

### Experimental

$\text{MnO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{GeO}_2$  (molar ratios of 3:1:3;  $\text{MnO}$  (Riedel-de Haën, *rein*): 212.8 mg,  $\text{Cr}_2\text{O}_3$  (Riedel-de Haën, *rein*): 152.0 mg,  $\text{GeO}_2$  (ChemPur, 99.999%): 313.8 mg) and the transporting agent  $\text{TeCl}_4$  (Alfa-Aesar, 99.9%; 8.5 mg ml<sup>-1</sup>) were brought into a fused silica ampule (length: 120 mm, inner diameter: 16 mm) and sealed under vacuum. The following transport reaction was conducted within twelve days in a two-zone tube furnace with a temperature gradient of 70 K ( $T_2 = 1293$  K,  $T_1 = 1223$  K, with the transport direction  $T_2 \rightarrow T_1$ ). Subsequent to the cooling to a temperature of 673 K within five hours, ambient temperature was reached by quenching in water. The obtained crystals had a size of up to 4 mm and shapes that are typically observed in garnets, *i.e.* derived from rhombic dodecahedra with often truncated edges. Larger crystals appear virtually black and opaque while smaller ones are transparent and dark green in color (see Fig. 1).

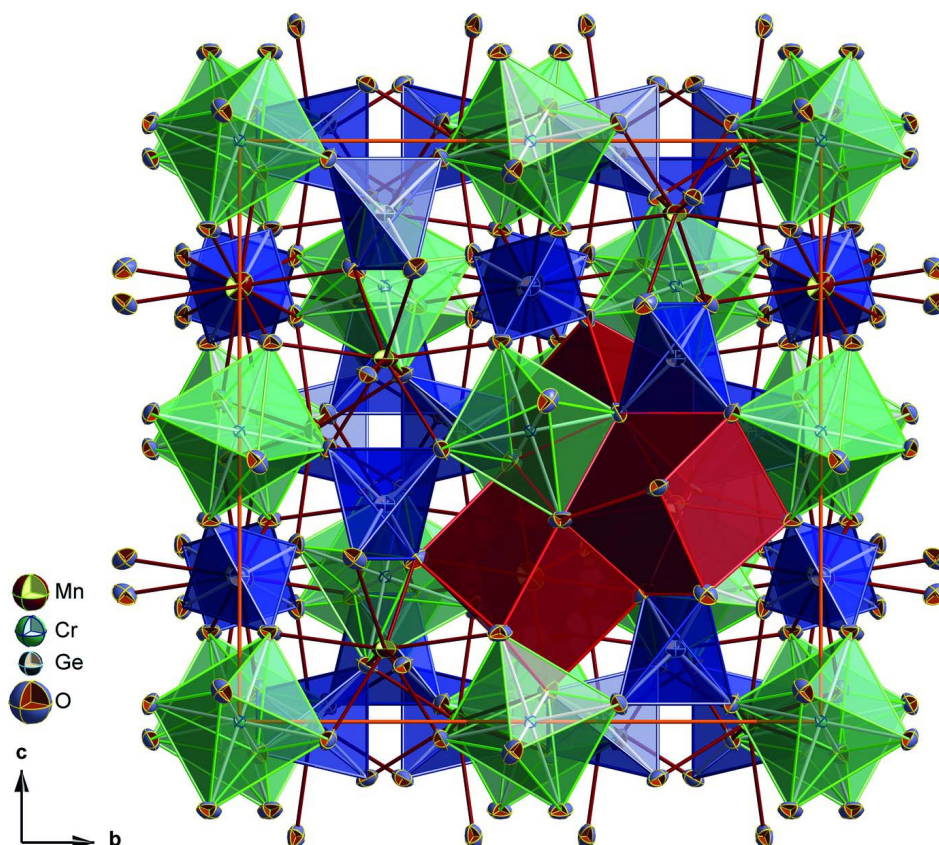
### Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *pubCIF* (Westrip, 2010).



**Figure 1**

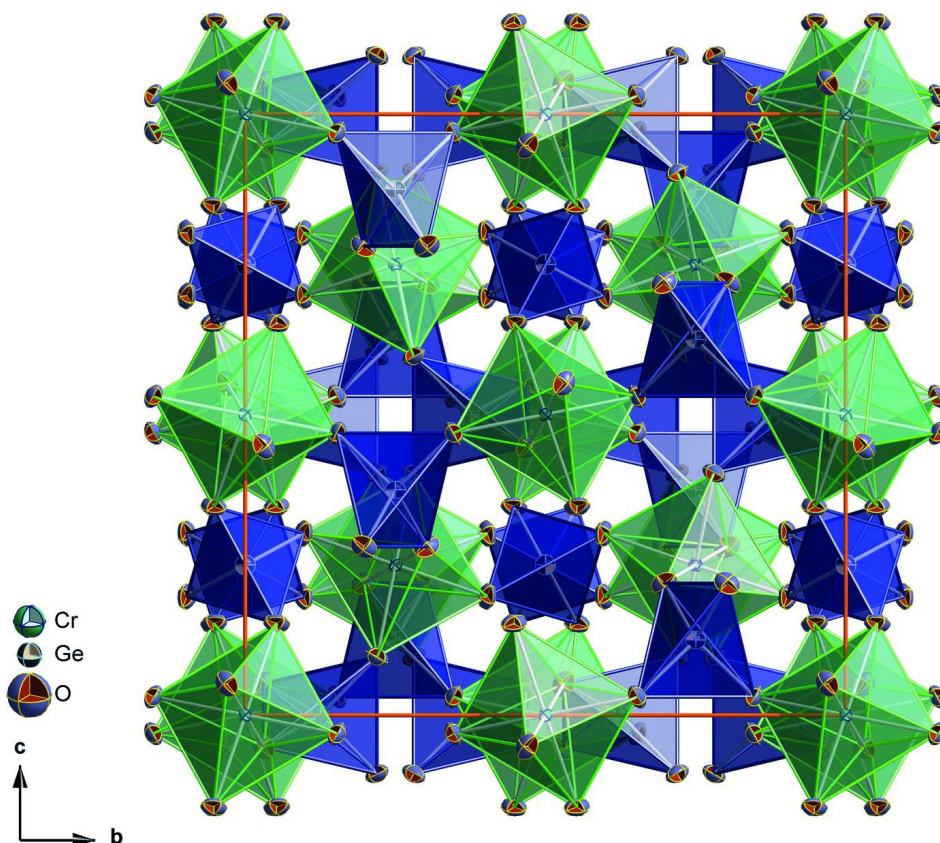
Dark green crystals of garnet-type  $\text{Mn}^{\text{II}}_3\text{Cr}^{\text{III}}_2(\text{GeO}_4)_3$  in the shape of rhombic dodecahedra, often with truncated edges. The photograph shows the crystals as they were grown after twelve days.



**Figure 2**

Overview of the structure of  $\text{Mn}^{\text{II}}_3\text{Cr}^{\text{III}}_2(\text{GeO}_4)_3$ . For a better understanding only a group of three edge-connected distorted cubes  $[\text{MnO}_8]$ , representing the polyhedra about  $\text{Mn}^{2+}$ , are drawn besides  $[\text{CrO}_6]$  octahedra and  $[\text{GeO}_4]^{4-}$  tetrahedra (displacement ellipsoids are drawn at the 95% probability level).





**Figure 3**

The network of vertex sharing  $[\text{CrO}_6]$  octahedra and  $[\text{GeO}_4]^{4-}$  tetrahedra in the *neso* germanate  $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$  (displacement ellipsoids are drawn at the 95% probability level).

### Trimanganese(II) dichromium(III) tris[orthogermanate(IV)]

#### Crystal data

$\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$

$M_r = 678.59$

Cubic,  $Ia\bar{3}d$

Hall symbol:  $-I\ 4bd\ 2c\ 3$

$a = 12.0001(3)\ \text{\AA}$

$V = 1728.04(7)\ \text{\AA}^3$

$Z = 8$

$F(000) = 2520$

$D_x = 5.217\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 6052 reflections

$\theta = 0.4\text{--}40.3^\circ$

$\mu = 17.01\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Truncated rhombic dodecahedron, dark green

$0.18 \times 0.15 \times 0.09\ \text{mm}$

#### Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: numerical

(*HABITUS*; Herrendorf & Bärnighausen, 1997)

$T_{\min} = 0.063$ ,  $T_{\max} = 0.201$

7635 measured reflections

277 independent reflections

265 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.084$

$\theta_{\max} = 33.1^\circ$ ,  $\theta_{\min} = 4.2^\circ$

$h = -18 \rightarrow 16$

$k = -18 \rightarrow 15$

$l = -17 \rightarrow 15$

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.068$

$S = 1.26$

277 reflections

18 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

$w = 1/[\sigma^2(F_o^2) + (0.0115P)^2 + 25.1758P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.63 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.72 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0031 (2)

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn	0.1250	0.0000	0.2500	0.0080 (3)
Cr	0.0000	0.0000	0.0000	0.0023 (3)
Ge	0.3750	0.0000	0.2500	0.0045 (2)
O	0.03061 (17)	0.05245 (18)	0.65268 (17)	0.0065 (4)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn	0.0039 (4)	0.0100 (3)	0.0100 (3)	0.000	0.000	0.0019 (3)
Cr	0.0023 (3)	0.0023 (3)	0.0023 (3)	0.00006 (17)	0.00006 (17)	0.00006 (17)
Ge	0.0036 (3)	0.0050 (3)	0.0050 (3)	0.000	0.000	0.000
O	0.0068 (9)	0.0082 (9)	0.0044 (8)	0.0016 (7)	-0.0018 (7)	-0.0006 (7)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Mn—O <sup>i</sup>	2.291 (2)	Cr—O <sup>xi</sup>	1.972 (2)
Mn—O <sup>ii</sup>	2.291 (2)	Cr—O <sup>xii</sup>	1.972 (2)
Mn—O <sup>iii</sup>	2.291 (2)	Cr—O <sup>ii</sup>	1.972 (2)
Mn—O <sup>iv</sup>	2.291 (2)	Ge—O <sup>xiii</sup>	1.744 (2)
Mn—O <sup>v</sup>	2.422 (2)	Ge—O <sup>iii</sup>	1.744 (2)
Mn—O <sup>vi</sup>	2.422 (2)	Ge—O <sup>i</sup>	1.744 (2)
Mn—O <sup>vii</sup>	2.422 (2)	Ge—O <sup>xiv</sup>	1.744 (2)
Mn—O <sup>viii</sup>	2.422 (2)	O—Ge <sup>xv</sup>	1.744 (2)
Cr—O <sup>viii</sup>	1.972 (2)	O—Cr <sup>x</sup>	1.972 (2)
Cr—O <sup>ix</sup>	1.972 (2)	O—Mn <sup>iv</sup>	2.291 (2)
Cr—O <sup>x</sup>	1.972 (2)	O—Mn <sup>xvi</sup>	2.422 (2)

O <sup>i</sup> —Mn—O <sup>ii</sup>	112.61 (10)	O <sup>v</sup> —Mn—Ge <sup>xvii</sup>	97.88 (5)
O <sup>i</sup> —Mn—O <sup>iii</sup>	70.78 (10)	O <sup>vi</sup> —Mn—Ge <sup>xvii</sup>	82.12 (5)
O <sup>ii</sup> —Mn—O <sup>iii</sup>	160.86 (10)	O <sup>vii</sup> —Mn—Ge <sup>xvii</sup>	82.12 (5)
O <sup>i</sup> —Mn—O <sup>iv</sup>	160.86 (10)	O <sup>viii</sup> —Mn—Ge <sup>xvii</sup>	97.88 (5)
O <sup>ii</sup> —Mn—O <sup>iv</sup>	70.78 (10)	O <sup>viii</sup> —Cr—O <sup>ix</sup>	180.00 (17)
O <sup>iii</sup> —Mn—O <sup>iv</sup>	112.61 (10)	O <sup>viii</sup> —Cr—O <sup>x</sup>	93.67 (8)
O <sup>i</sup> —Mn—O <sup>v</sup>	94.58 (6)	O <sup>ix</sup> —Cr—O <sup>x</sup>	86.33 (8)
O <sup>ii</sup> —Mn—O <sup>v</sup>	124.69 (4)	O <sup>viii</sup> —Cr—O <sup>xi</sup>	93.67 (8)
O <sup>iii</sup> —Mn—O <sup>v</sup>	72.34 (8)	O <sup>ix</sup> —Cr—O <sup>xi</sup>	86.33 (8)
O <sup>iv</sup> —Mn—O <sup>v</sup>	69.78 (10)	O <sup>x</sup> —Cr—O <sup>xi</sup>	86.33 (8)
O <sup>i</sup> —Mn—O <sup>vi</sup>	124.69 (4)	O <sup>viii</sup> —Cr—O <sup>xii</sup>	86.33 (8)
O <sup>ii</sup> —Mn—O <sup>vi</sup>	94.58 (6)	O <sup>ix</sup> —Cr—O <sup>xii</sup>	93.67 (8)
O <sup>iii</sup> —Mn—O <sup>vi</sup>	69.78 (10)	O <sup>x</sup> —Cr—O <sup>xii</sup>	93.67 (8)
O <sup>iv</sup> —Mn—O <sup>vi</sup>	72.34 (8)	O <sup>xi</sup> —Cr—O <sup>xii</sup>	180.00 (17)
O <sup>v</sup> —Mn—O <sup>vi</sup>	108.41 (10)	O <sup>viii</sup> —Cr—O <sup>ii</sup>	86.33 (8)
O <sup>i</sup> —Mn—O <sup>vii</sup>	69.78 (10)	O <sup>ix</sup> —Cr—O <sup>ii</sup>	93.67 (8)
O <sup>ii</sup> —Mn—O <sup>vii</sup>	72.34 (8)	O <sup>x</sup> —Cr—O <sup>ii</sup>	180.00 (17)
O <sup>iii</sup> —Mn—O <sup>vii</sup>	124.69 (4)	O <sup>xi</sup> —Cr—O <sup>ii</sup>	93.67 (8)
O <sup>iv</sup> —Mn—O <sup>vii</sup>	94.58 (6)	O <sup>xii</sup> —Cr—O <sup>ii</sup>	86.33 (8)
O <sup>v</sup> —Mn—O <sup>vii</sup>	73.85 (10)	O <sup>xiii</sup> —Ge—O <sup>iii</sup>	114.93 (7)
O <sup>vi</sup> —Mn—O <sup>vii</sup>	164.23 (10)	O <sup>xiii</sup> —Ge—O <sup>i</sup>	114.93 (7)
O <sup>i</sup> —Mn—O <sup>viii</sup>	72.34 (8)	O <sup>iii</sup> —Ge—O <sup>i</sup>	99.02 (14)
O <sup>ii</sup> —Mn—O <sup>viii</sup>	69.78 (10)	O <sup>xiii</sup> —Ge—O <sup>xiv</sup>	99.02 (14)
O <sup>iii</sup> —Mn—O <sup>viii</sup>	94.58 (6)	O <sup>iii</sup> —Ge—O <sup>xiv</sup>	114.93 (7)
O <sup>iv</sup> —Mn—O <sup>viii</sup>	124.69 (4)	O <sup>i</sup> —Ge—O <sup>xiv</sup>	114.93 (7)
O <sup>v</sup> —Mn—O <sup>viii</sup>	164.23 (10)	O <sup>xiii</sup> —Ge—Mn	130.49 (7)
O <sup>vi</sup> —Mn—O <sup>viii</sup>	73.85 (10)	O <sup>iii</sup> —Ge—Mn	49.51 (7)
O <sup>vii</sup> —Mn—O <sup>viii</sup>	108.41 (10)	O <sup>i</sup> —Ge—Mn	49.51 (7)
O <sup>i</sup> —Mn—Ge	35.39 (5)	O <sup>xiv</sup> —Ge—Mn	130.49 (7)
O <sup>ii</sup> —Mn—Ge	144.61 (5)	O <sup>xiii</sup> —Ge—Mn <sup>xviii</sup>	49.51 (7)
O <sup>iii</sup> —Mn—Ge	35.39 (5)	O <sup>iii</sup> —Ge—Mn <sup>xviii</sup>	130.49 (7)
O <sup>iv</sup> —Mn—Ge	144.61 (5)	O <sup>i</sup> —Ge—Mn <sup>xviii</sup>	130.49 (7)
O <sup>v</sup> —Mn—Ge	82.12 (5)	O <sup>xiv</sup> —Ge—Mn <sup>xviii</sup>	49.51 (7)
O <sup>vi</sup> —Mn—Ge	97.88 (5)	Ge <sup>xv</sup> —O—Cr <sup>x</sup>	128.90 (11)
O <sup>vii</sup> —Mn—Ge	97.88 (5)	Ge <sup>xv</sup> —O—Mn <sup>iv</sup>	95.10 (9)
O <sup>viii</sup> —Mn—Ge	82.12 (5)	Cr <sup>x</sup> —O—Mn <sup>iv</sup>	103.54 (9)
O <sup>i</sup> —Mn—Ge <sup>xvii</sup>	144.61 (5)	Ge <sup>xv</sup> —O—Mn <sup>xvi</sup>	122.92 (10)
O <sup>ii</sup> —Mn—Ge <sup>xvii</sup>	35.39 (5)	Cr <sup>x</sup> —O—Mn <sup>xvi</sup>	99.02 (8)
O <sup>iii</sup> —Mn—Ge <sup>xvii</sup>	144.61 (5)	Mn <sup>iv</sup> —O—Mn <sup>xvi</sup>	102.43 (8)
O <sup>iv</sup> —Mn—Ge <sup>xvii</sup>	35.39 (5)		

Symmetry codes: (i)  $x+1/4, -z+3/4, -y+1/4$ ; (ii)  $-x, y, z-1/2$ ; (iii)  $x+1/4, z-3/4, y+1/4$ ; (iv)  $-x, -y, -z+1$ ; (v)  $z-1/2, x, -y+1/2$ ; (vi)  $-z+3/4, y-1/4, -x+1/4$ ; (vii)  $-z+3/4, -y+1/4, x+1/4$ ; (viii)  $z-1/2, -x, y$ ; (ix)  $-z+1/2, x, -y$ ; (x)  $x, -y, -z+1/2$ ; (xi)  $-y, -z+1/2, x$ ; (xii)  $y, z-1/2, -x$ ; (xiii)  $-x+1/2, y, -z+1$ ; (xiv)  $-x+1/2, -y, z-1/2$ ; (xv)  $-x+1/2, -y, z+1/2$ ; (xvi)  $-y, z, x+1/2$ ; (xvii)  $x-1/2, y, -z+1/2$ ; (xviii)  $x+1/2, y, -z+1/2$ .