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The crystal structure of brunogeierite, Fe_2GeO_4 spinel

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ABSTRACT

Brunogeierite, Fe_2GeO_4, a = 8.4127(7) Å , V = 595.4(1) Å^3, is a rare germanate spinel from Tsumeb, Namibia. Its structure has been refined to an R index of 2.2%. The oxygen parameter, u, is 0.2466(1), indicating nearly ideal cubic close-packing of oxygen atoms. There is exact agreement between the observed a unit-cell dimension and that calculated from the observed Ge–O and Fe–O bond lengths. The cations Ge and Fe are fully ordered at tetrahedral (A) and octahedral (B) sites, respectively, in keeping with synthetic germanate spinels, all of which are fully-ordered normal spinels.

KEYWORDS: brunogeierite, spinel, crystal structure.

Introduction

GERMANATES are frequently used as structural analogues of high-pressure silicates because they allow phase transformations and structural behaviour to be studied at pressures that are more routinely accessible experimentally than those for the corresponding silicate systems. The spinel Mg_2GeO_4 is the low-pressure analogue of ringwoodite, γ-Mg_2SiO_4, and has been used to model high-pressure behaviour of the latter. There was some debate about the state of Mg-Ge order (degree of inversion) in this spinel, until Von Dreele *et al*. (1977) showed that it is completely ordered on the normal scheme (A = Ge, B = Mg). The present study was undertaken to determine the state of order in the natural germanate analogue of γ-Fe_2SiO_4: brunogeierite, Fe_2GeO_4.

Almost all recent structural studies of germanate spinels have been done on powder samples, reflecting both the difficulty of synthesizing crystals of sufficient quality for single-crystal work and the rarity of good natural samples. We acquired a high-quality specimen of brunogeierite (Tsumeb, Namibia) from Mr William Pinch, and we report the structure refinement of this crystal here.

Experimental

X-ray diffraction

Brunogeierite from Tsumeb occurs as 40–50 μm thick crusts on tennantite cores (Otteman and Nuber, 1972), the aggregates forming octahedra. A partial octahedron was removed from the sample and a 37 μm thick {111} plate prepared by grinding away the attached tennantite. The bounding faces of the plate form an equilateral triangle 170 μm on each side. Zero-level precession photographs down two a axes revealed a very minor secondary component (<5%). This component had a diffraction pattern similar to that of the main portion of the brunogeierite and represents a second single crystal. The diffraction maxima of this secondary component are displaced sufficiently from those of the main crystal so as not to interfere; careful examination of all background regions adjacent to the diffraction maxima of the main crystal confirmed this.

The crystal plate was attached to a glass fibre and mounted on a Siemens P4 automated four-circle diffractometer equipped with Mo-$K\alpha$ radiation (λ = 0.71073 Å). All twelve Laue equivalents of {440} were centred and the unit-cell parameter was refined by least-squares to give a = 8.4127(7) Å, V = 595.4(1) Å^3. A whole sphere of data was collected in the range 4–60°2θ ($\bar{1}\bar{1}$ $\bar{1}\bar{1}$ $\bar{1}\bar{1}$ → 11 11 11). Reflections were scanned in ω–2θ mode at a variable speed of 2–19°2θ/min;

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TABLE 1. Miscellaneous information relating to structure determination and refinement.

Space group	$Fd\bar{3}m$	crystal size (mm)	{111} triangular plate 0.17 × 0.17 × 0.17 × 0.037
a (Å)	8.4127(7)	radiation/monochromator	Mo-$K\alpha$/graphite
V (Å^3)	595.4(1)	total no. of intensities	1668
Cell content: 8 [Fe_2GeO_4]		no. of unique intensities	61
		μ (mm^{-1})	19.5
		absorption correction	Gaussian
		min. transmission	0.1625
		max. transmission	0.4955
		R_{merge} (%)	4.0
$R_1 = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$		R_1 (%)	2.2
$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$		wR_2 (%)	3.0
$w = 1/\sigma^2(F_o^2)$			

one check reflection was measured every 50 reflections. A total of 1668 intensities was collected, of which 61 were unique. A Gaussian absorption correction was applied and the crystal was modelled as a triangular plate with minimum and maximum transmission values of 0.1625 and 0.4955, respectively. Background, Lorentz polarization and absorption corrections were applied to the raw intensities which were then reduced to structure factors. Sixteen reflections violating the *d* glide were observed ($F^2/\sigma F^2 > 20$), but psi scans of these reflections showed that their presence is due to double diffraction. Consequently, $Fd\bar{3}m$ was confirmed as the correct space group. The structure of brunogeierite was refined in space group $Fd\bar{3}m$ using the Siemens SHELXTL PLUS software package, F^2 values for all data, ionic scattering factors and a minor extinction correction. The refined site occupancies indicate that Ge and Fe are fully ordered at the *A* and *B* sites, respectively, i.e. Fe_2GeO_4 is a normal spinel. Therefore, the final stages of refinement were performed with site occupancies fixed at A = Ge and B = Fe.

The structure refined smoothly to an *R* index of 2.2% for an anisotropic-displacement model. Details relating to the structure solution and refinement are summarized in Table 1. Atom coordinates and displacement parameters are given in Table 2, and structure factors in Table 3.

Results and discussion

The Ge–O and Fe–O bond-lengths for brunogeierite are 1.771(2) and 2.132(1) Å, respectively. The value for the oxygen parameter *u* in brunogeierite is 0.2466(1). The *u* value for ideal cubic close-packing of oxygen is 0.25; hence, brunogeierite has nearly perfect cubic close-packing of oxygen anions. The Ge–O bond length is equal to the sum of the ionic radii (0.39 + 1.38 = 1.77 Å; Shannon, 1976). The Fe–O bond is slightly shorter than the sum of the ionic radii (0.78 + 1.38 = 2.16 Å). The *A* site refined to full occupancy by Ge; hence, there is no evidence for a magnetite component in solid solution in brunogeierite – it has Ge and Fe completely ordered at the *A* and *B* sites, respectively. This cation distribution is in keeping with synthetic germanate spinels Mg_2GeO_4, Co_2GeO_4 and Ni_2GeO_4 (Von Dreele *et al*., 1977; Hill *et al*., 1979). The synthetic high-pressure phase γ-Fe_2SiO_4 is also fully ordered on the normal scheme and has $u = 0.2409$ (Finger *et*

TABLE 2. Atom coordinates and displacement parameters (× 10^4 Å^2) for brunogeierite.

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ge	1/8	1/8	1/8	46(3)	46(3)	46(3)	46(3)	–	–	–
Fe	1/2	1/2	1/2	61(3)	61(3)	61(3)	61(3)	4(2)	4(2)	4(2)
O	0.2466(1)	0.2466(1)	0.2466(1)	62(5)	62(5)	62(5)	62(5)	−15(7)	−15(7)	−15(7)

TABLE 3. Observed and calculated structure factors for brunogeierite.

h k l	10Fo	10Fc	10s	*h k l*	10Fo	10Fc	10s	*h k l*	10Fo	10Fc	10s	*h k l*	10Fo	10Fc	10s	*h k l*	10Fo	10Fc	10s
1 1 1	224	221	1	3 3 5	2114	2137	7	1 3 7	1923	1925	4	2 6 8	978	964	3	0 2 10	981	968	3
0 2 2	2114	2067	9	1 5 5	86	86	4	3 3 7	105	104	2	4 6 8	70	15	5	2 2 10	816	821	2
2 2 2	1341	1335	10	3 5 5	1815	1793	6	1 5 7	1621	1634	4	6 6 8	806	811	4	2 4 10	883	877	2
1 1 3	3076	3048	9	5 5 5	1538	1547	16	3 5 7	83	37	5	0 8 8	2424	2452	11	4 4 10	41	7	9
1 3 3	224	213	2	0 2 6	1494	1527	4	5 5 7	100	51	7	2 8 8	124	27	11	0 6 10	803	801	3
3 3 3	2620	2631	22	2 2 6	1245	1257	4	1 7 7	99	78	5	1 1 9	85	85	3	2 6 10	702	697	2
0 0 4	2728	2705	25	2 4 6	1340	1344	3	3 7 7	1397	1434	5	1 3 9	1416	1420	3	1 1 11	1249	1254	4
2 2 4	1754	1764	6	4 4 6	76	10	12	5 7 7	1259	1259	6	3 3 9	67	47	4	1 3 11	65	70	3
0 4 4	4874	5148	56	0 6 6	1205	1196	5	0 0 8	3700	3716	15	1 5 9	1263	1253	3	3 3 11	1193	1208	5
2 4 4	135	15	16	2 6 6	1006	1002	4	2 2 8	1186	1192	3	3 5 9	125	75	6				
4 4 4	1472	1447	17	4 6 6	1056	1063	4	0 4 8	1042	1032	3	5 5 9	100	87	3				
1 1 5	2434	2417	6	6 6 6	824	822	6	2 4 8	61	18	4	1 7 9	54	42	4				
1 3 5	76	36	4	1 1 7	78	60	3	4 4 8	2910	2941	12	3 7 9	1126	1118	3				

al., 1979), reflecting the smaller size of the *A* cation (Si) and shortening of shared octahedral edges. There is no shortening of shared octahedral edges in brunogeierite; in fact, the unshared octahedral edges (2.98 Å) are slightly shorter than the shared edges (3.05 Å). We note that there is perfect agreement between the observed unit-cell parameter and that calculated from the Ge–O and Fe–O bond lengths using the formulae of Hill *et al.* (1979), indicating that the unit-cell parameter and atom positions are fully consistent in the brunogeierite structure.

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