

LETTER

Crystal structure of single-crystal CaGeO_3 tetragonal garnet synthesized at 3 GPa and 1000 °C

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ABSTRACT

Single crystals of CaGeO_3 garnet were synthesized at 3 GPa and 1000 °C using a cubic anvil type of high pressure apparatus and the crystal structure was refined from single crystal X-ray diffraction data. This garnet is tetragonal with lattice parameters of $a = 12.535(2)$ Å, $c = 12.370(2)$ Å, $V = 1943.5(5)$ Å³ and belongs to space group $I4_1/a$. Two dodecahedral sites are occupied only by Ca with mean Ca–O bond lengths of 2.480(4) and 2.467(4) Å. The Ca and Ge cations are completely ordered at two octahedral sites with mean Ca–O = 2.301(3) Å and mean Ge–O = 1.910(3) Å. Three tetrahedral sites are occupied only by Ge, and their mean Ge–O bond lengths are 1.753(3), 1.787(4), and 1.764(4) Å. Furthermore, the present tetragonal garnet has an unusual feature in that the mean value [2.704(5) Å] of the shared edge lengths of GeO_6 octahedron is larger than that [2.699(5) Å] of the unshared ones, as has also been observed for other tetragonal garnets with $I4_1/a$.

INTRODUCTION

Garnets are major constituents in the earth's crust and upper mantle and commonly crystallize in cubic symmetry with space group $Ia\bar{3}d$. However, optically anisotropic garnets are sometimes found in the grossular-andradite series (grandite garnet) and they have an orthorhombic ($Fddd$) or triclinic ($\bar{1}$) structure (Takéuchi et al. 1982). According to Takéuchi et al. (1982), noncubic garnets with similar-sized octahedral cations, such as the grossular-andradite series, favor an orthorhombic ($Fddd$) or triclinic ($\bar{1}$) structure, whereas those with different-sized octahedral cations favor a tetragonal ($I4_1/a$) structure. The $I4_1/a$ structure is often found in high-pressure phases and has two dodecahedral sites (X1 and X2), two octahedral sites (Y1 and Y2), three tetrahedral sites (Z1–Z3), and six oxygen sites (O1–O6). Such a typical example is MgSiO_3 majorite (Angel et al. 1989), which is considered a major constituent of the transition zone in the earth's mantle between the 400 and 670 km seismic discontinuities (e.g., Ringwood 1967; Liu 1977; Akaogi and Akimoto 1977; Ito and Takahashi 1987).

CaGeO_3 (Prewitt and Sleight 1969), CdGeO_3 (Prewitt and Sleight 1969), and MnSiO_3 (Fujino et al. 1986) garnets have tetragonal symmetry, of which the last two were substantiated to have the $I4_1/a$ structure by single-crystal X-ray diffraction analyses. CaGeO_3 garnet is also probably isostructural with majorite (Prewitt and Sleight 1969) and will be of importance as the best analogue of majorite, but its detailed structure has not been published to date because no crystals large enough for single-crystal examination have been synthesized. Here we present the results of the first single-crystal X-ray diffraction study of CaGeO_3 garnet and describe its structural features.

EXPERIMENTS AND ANALYSES

Synthesis under high pressure

Single crystals of CaGeO_3 garnet were synthesized at 3 GPa and 1000 °C using a 700 ton cubic anvil type high-pressure apparatus. A 12.5 mm cube of pyrophyllite and cylindrical graphite were used as a pressure medium and heater, respectively. The starting material was powdered CaGeO_3 wollastonite prepared by solid-state reaction of special grade reagents (99.99%) of CaO and GeO_2 . The CaGeO_3 wollastonite was sealed in a gold capsule to prevent the reduction of Ge^{4+} during heating by the graphite heater. The sealed gold capsule was put into a born nitride (BN) capsule, and then it was inserted into the cylindrical graphite heater embedded in the pyrophyllite cube, and the BN capsule was used as an insulator between the gold capsule and the graphite heater. The sample temperature was monitored by a Pt–Pt13%Rh thermocouple. The junction of the thermocouple was put at the midpoint of the outer surface of the gold capsule. No correction was made for the pressure effect on emf. After being kept under a desired condition (3 GPa and 1000 °C) for 2 hours, the sample was quenched by shutting off the electric power supply. The pressure was released slowly and the sample was recovered to the ambient condition. Numerous transparent single-crystals of CaGeO_3 garnet were present in the recovered sample.

Single crystal X-ray diffraction

A single crystal with a size of $80 \times 80 \times 60$ µm was selected for X-ray diffraction measurements. The unit-cell parameters and diffraction intensity data were measured at room temperature using a four circle diffractometer (Rigaku AFC-5S) operated at 45 kV and 35 mA. The graphite-monochromatized $\text{MoK}\alpha$ ($\lambda = 0.71069$ Å) radiation was used for the measurements. The unit-cell parameters were determined by a least-squares method from a set of 25 reflections within the range of $40^\circ \leq 2\theta \leq 70^\circ$. The intensity data within $\sin\theta/\lambda \leq 0.904$, corresponding to $0 \leq h, k, l \leq 22$, were collected in continuous ω - 2θ scan mode. Lorentz and polarization corrections were applied and a correction for absorption was made based on the ψ -scan technique. From the systematic absences, the space group was identified as $I4_1/a$; this was also confirmed by precession photography. A total of 3016 reflections were measured, of which 860 observed reflections with $|F_o| \geq 3\sigma(|F_o|)$ were used in the structure refinements.

The structure refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$ using the full matrix least-squares program RADY (Sasaki 1987). Atomic scattering factors for neutral atoms and anomalous dispersion coefficients were taken from the *International Tables for X-ray Crystallography* (Ibers and Ham-

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ilton 1974). During the refinements, a correction for the isotropic extinction effect (Becker and Coppens 1974a, 1974b) was made. After several cycles of refinements, displacement parameters were converted to the anisotropic thermal vibration model. The occupancy parameters were preliminarily constrained between two octahedral sites (Y1 and Y2) on the basis of the formula $\text{Ca}_3^{Y1}(\text{Ca}_p\text{Ge}_{1-p})^{Y2}[\text{Ca}_{1-p}\text{Ge}_p]\text{Ge}_2\text{O}_{12}$. The occupancy parameter p converged to the value of 1.008(6), which demonstrates complete cation-ordering between the two octahedral sites. Accordingly, the parameter p was fixed at unity in the final refinement.

The crystallographic data, data collection parameters, and refinement parameters

TABLE 1. Crystallographic data, data collection parameters, and refinement parameters

Space group	$I4_1/a$	Scan type	ω -2 θ
a (Å)	12.535(2)	2 θ range (°)	2–80
c (Å)	12.370(2)	No. of measured reflections	3016
V (Å ³)	1943.5(5)	No. of observed reflections	860
		with $ F_o \geq 3\sigma(F_o)$	
Crystal size (μm)	80 × 80 × 60	R	0.023
Radiation used	MoK α	R_w	0.020
μ (cm ⁻¹)	150.47	Weighting scheme	$1/\sigma^2(F_o)$

TABLE 2. Refined positional parameters and equivalent isotropic displacement parameters

Site	Atom	x	y	z	B_{eq} (Å ²)
X1	Ca	0.62459(9)	0.00296(7)	0.25307(8)	0.449(5)
X2	Ca	0.5	0.25	0.62325(12)	0.453(6)
Y1	Ca	0.5	0	0.5	0.420(7)
Y2	Ge	0.5	0	0	0.288(4)
Z1	Ge	0.5	0.25	0.375	0.315(3)
Z2	Ge	0.5	0.25	0.875	0.381(3)
Z3	Ge	0.62647(5)	0.01509(4)	0.75723(5)	0.266(2)
O1	O	0.53087(28)	0.06623(29)	0.67127(26)	0.482(17)
O2	O	0.54303(27)	-0.04195(28)	0.86141(26)	0.407(17)
O3	O	0.72260(29)	0.11082(28)	0.80554(25)	0.288(10)
O4	O	0.71030(29)	-0.07756(29)	0.69968(28)	0.503(17)
O5	O	0.43278(27)	0.16676(28)	0.46628(26)	0.426(17)
O6	O	0.39650(29)	0.20977(28)	0.78439(28)	0.560(18)

eters are summarized in Table 1. The refined parameters are listed in Tables 2 and 3. The selected interatomic distances are given in Table 4. Observed and calculated structure factors are listed in the supplemental table¹.

RESULTS AND DISCUSSION

MnSiO_3 (Fujino et al. 1986), CdGeO_3 (Prewitt and Sleight 1969), and the present CaGeO_3 tetragonal garnets show complete cation-ordering between the two octahedral sites (Y1 and Y2). These garnets have almost the same axial ratio [$c/a = 0.9868(3)$ for CaGeO_3 ; 0.9883(3) for MnSiO_3 (Fujino et al. 1986); 0.9879(2) for CdGeO_3 (Prewitt and Sleight 1969)]. On the other hand,

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TABLE 3. Refined anisotropic displacement parameters ($\times 10^4$)

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
X1	36(5)	60(5)	75(4)	-9(4)	5(4)	11(4)
X2	85(8)	38(7)	49(4)	-11(6)	0	0
Y1	40(6)	55(8)	65(6)	1(5)	4(5)	0(5)
Y2	25(3)	34(4)	50(3)	1(3)	2(3)	-5(3)
Z1	43(3)	43	35(4)	0	0	0
Z2	44(3)	44	57(5)	0	0	0
Z3	24(3)	28(2)	48(2)	-1(2)	2(2)	-3(2)
O1	46(18)	67(19)	71(15)	23(15)	-9(12)	-2(12)
O2	41(17)	61(18)	53(15)	-19(13)	12(12)	-16(12)
O3	29(16)	7(14)	73(13)	9(13)	4(12)	19(12)
O4	57(18)	41(18)	94(15)	33(15)	12(12)	-10(13)
O5	32(18)	55(18)	75(14)	-20(14)	-6(12)	12(12)
O6	49(18)	46(19)	118(16)	31(14)	8(13)	-24(13)

TABLE 4. Selected interatomic distances (Å)

X1 dodecahedron				Y2 octahedron			
Ca-O1	2.329(4)	O1-O2*	2.719(5)	Ge-O2	1.873(3) × 2	O2-O3†	2.651(5) × 2
Ca-O2	2.581(4)	O3-O4*	2.704(5)	Ge-O3	1.906(3) × 2	O2-O6†	2.718(5) × 2
Ca-O3	2.475(4)	O1-O4†	3.240(5)	Ge-O6	1.951(4) × 2	O3-O6†	2.744(5) × 2
Ca-O3	2.480(3)	O2-O3†	2.651(5)	Ave.	1.910(3)	O2-O3	2.693(5) × 2
Ca-O4	2.365(4)	O4-O5†	3.085(5)			O2-O6	2.691(5) × 2
Ca-O4	2.547(4)	O3-O6†	2.744(5)			O3-O6	2.712(5) × 2
Ca-O5	2.344(4)	O3-O4†	2.910(5)				
Ca-O6	2.719(4)	O2-O5†	2.974(5)	Z1 tetrahedron			
Ave.	2.480(4)	O1-O6†	2.834(5)	Ge-O5	1.753(3) × 4	O5-O5†	2.682(7) × 2
		O3-O4†	2.910(5)			O5-O5	2.949(6) × 4
		O4-O5	2.946(5)	Z2 tetrahedron			
		O3-O6	3.057(5)	Ge-O6	1.787(4) × 4	O6-O6†	2.784(7) × 2
						O6-O6	2.983(6) × 4
X2 dodecahedron				Z3 tetrahedron			
Ca-O1	2.410(4) × 2	O5-O5*	2.682(7)	Ge-O1	1.726(4)	O1-O2†	2.719(5)
Ca-O2	2.667(4) × 2	O6-O6*	2.784(7)	Ge-O2	1.807(3)	O3-O4†	2.704(5)
Ca-O5	2.360(4) × 2	O1-O5†	3.087(5) × 2	Ge-O3	1.802(4)	O1-O3	2.974(5)
Ca-O6	2.431(4) × 2	O2-O6†	2.718(5) × 2	Ge-O4	1.720(4)	O1-O4	2.904(5)
Ave.	2.467(4)	O1-O6†	2.834(5) × 2	Ave.	1.764(4)	O2-O3	3.035(5)
		O2-O5†	2.974(5) × 2			O2-O4	2.932(5)
		O1-O2	2.931(5) × 2				
Y1 octahedron							
Ca-O1	2.308(3) × 2	O1-O5†	3.087(5) × 2				
Ca-O4	2.304(4) × 2	O1-O4†	3.240(5) × 2				
Ca-O5	2.292(3) × 2	O4-O5†	3.085(5) × 2				
Ave.	2.301(3)	O1-O5	3.411(5) × 2				
		O1-O4	3.282(5) × 2				
		O5-O4	3.406(5) × 2				

* Edge-sharing with tetrahedron.

† Edge-sharing with octahedron.

‡ Edge-sharing with dodecahedron.

MgSiO_3 tetragonal garnet with about 40% disorder at the two octahedral sites (Angel et al. 1989) has a c/a value of 0.9982(2), which is considerably larger than that for CaGeO_3 , CdGeO_3 , and MnSiO_3 tetragonal garnets. Thus, the axial ratio c/a , which is an indicator of the degree of deviation from cubic symmetry, seems to depend on the degree of cation ordering between the Y1 and Y2 sites.

The mean bond lengths of the CaGeO_3 tetragonal garnet are nearly equal to the value calculated from Shannon's radii (Shannon 1976), except for the Y1 octahedron (Table 4). The mean $^{\text{VI}}\text{Ca-O}$ bond length of the Y1 octahedron is 2.301(3) Å, which is considerably shorter than the calculated value (2.38 Å). This large difference is also observed in MnSiO_3 (Fujino et al. 1986) and CdGeO_3 (Prewitt and Sleight 1969) tetragonal garnets with complete cation-ordering. The anomalous Y1-O lengths are, thus, probably a fundamental feature of tetragonal garnet with $I4_1/a$ symmetry and may result from geometric constraints of the $I4_1/a$ structure.

Another notable feature is that the mean value [2.704(5) Å] of the shared edge lengths of the Y2 octahedron is larger than that [2.699(5) Å] of the unshared ones (Table 4). The same observation has also been reported for CdGeO_3 (Prewitt and Sleight 1969), MnSiO_3 (Fujino et al. 1986), and MgSiO_3 (Angel et al. 1989) tetragonal garnets, but no explanation has been provided for these unusually long shared edges. Here we give a possible interpretation to this unusual feature. The mean $^{\text{VI}}\text{Ge}^{4+}\text{-}^{\text{VIII}}\text{Ca}^{2+}$ distance [3.514(1) Å] between the Y2 octahedral site and the dodecahedral sites is longer than the mean $^{\text{VI}}\text{Ca}^{2+}\text{-}^{\text{VIII}}\text{Ca}^{2+}$ distance [3.463(1) Å] between the Y1 octahedral site and the dodecahedral sites. This probably arises from the necessity of minimizing the $^{\text{VI}}\text{Ge}^{4+}\text{-}^{\text{VIII}}\text{Ca}^{2+}$ repulsion across the dodecahedral-octahedral shared edge owing to the higher charge of Ge^{4+} . This weakened repulsion would not need to be largely shielded by O^{2-} ions forming the shared edges. Hence it follows that the shared edges of the Y2 octahedron are allowed to become longer than the unshared ones under the geometric constraints.

Finally, in view of the significance of CaGeO_3 tetragonal garnet as an analogue of MgSiO_3 majorite, we are planning

crystal-chemical studies of the present single crystal under high pressures and temperatures.

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