

## LETTERS

### Structure refinement of a birefringent Cr-bearing majorite $\text{Mg}_3(\text{Mg}_{0.34}\text{Si}_{0.34}\text{Al}_{0.18}\text{Cr}_{0.14})_2\text{Si}_3\text{O}_{12}$

AKIHIKO NAKATSUKA,<sup>1</sup> AKIRA YOSHIASA,<sup>2</sup> TAKAMITSU YAMANAKA,<sup>2</sup> AND EIJI ITO<sup>3</sup>

<sup>1</sup>Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755-8611, Japan

<sup>2</sup>Department of Earth and Space Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

<sup>3</sup>Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori 682-0193, Japan

#### ABSTRACT

A single crystal of a birefringent Cr-bearing majorite,  $\text{Mg}_3(\text{Mg}_{0.34}\text{Si}_{0.34}\text{Al}_{0.18}\text{Cr}_{0.14})_2\text{Si}_3\text{O}_{12}$ , was synthesized at 20 GPa and 2000 °C using “6–8” type uniaxial split-sphere apparatus. This garnet is tetragonal with the unit-cell parameters  $a \approx c$  and deviates slightly from cubic symmetry. The structure refinements using single-crystal X-ray diffraction intensity data were carried out by assuming three space groups (one cubic and two tetragonal) to determine the most probable symmetry. The most probable space group is  $I4_1/a$  (tetragonal). The Cr ions show a disordered distribution between the two nonequivalent octahedral sites in the  $I4_1/a$  structure.

#### INTRODUCTION

The seismic discontinuities in the Earth's mantle are controlled by changes in the physical properties of the constituent mineral phases. Therefore, the investigation of the symmetry of mantle minerals is important because the physical properties are very sensitive to the crystal structure. The majorite solid-solution in the system  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{MgSiO}_3$  having the garnet structure is considered to be 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). It has been reported that the symmetry of the majorite solid-solution with 20–100 mol%  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  component is cubic (space group  $Ia\bar{3}d$ ), whereas that of garnet having a  $\text{MgSiO}_3$  composition is tetragonal (space group  $I4_1/a$ ) (e.g., Kato and Kumazawa 1985; Sawamoto 1987; Angel et al. 1989; Parise et al. 1996; Heinemann et al. 1997). The cubic phase ( $Ia\bar{3}d$ ) has one unique dodecahedral (X), octahedral (Y), tetrahedral (Z), and oxygen (O) site, whereas the tetragonal phase ( $I4_1/a$ ) has two nonequivalent dodecahedral (X1 and X2), two octahedral (Y1 and Y2), three tetrahedral (Z1–Z3), and six oxygen (O1–O6) sites. The end-member  $\text{MgSiO}_3$  garnet exhibits ordering of Mg and Si between Y1- and Y2-sites in the  $I4_1/a$  structure (Angel et al. 1989).

The upper mantle contains about 0.4 wt%  $\text{Cr}_2\text{O}_3$  (Ringwood 1979) and most of the Cr ions in transition zone in the Earth's mantle are expected from high-pressure experiments by Irifune (1994) to be distributed to the high-pressure garnet phase, i.e., the majorite solid-solution. Hence, the behavior of Cr ions in the majorite solid-solution in the Earth's mantle cannot be neglected. In the present study, we examine the symmetry of Cr-

bearing majorite and the distribution of Cr ions between atomic sites in the crystal structure using the single-crystal X-ray diffraction method.

#### EXPERIMENTAL DETAILS

##### Material

A single crystal of Cr-bearing majorite,  $\text{Mg}_3(\text{Mg}_{0.34}\text{Si}_{0.34}\text{Al}_{0.18}\text{Cr}_{0.14})_2\text{Si}_3\text{O}_{12}$ , was synthesized under high pressure and high temperature (20 GPa and 2000 °C) using a 1000 ton “6–8” type uniaxial split-sphere apparatus (USSA-1000) installed at the ISEI of Okayama University. Special grade reagents (99.99%) of  $\text{MgO}$ ,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{Cr}_2\text{O}_3$  were used as starting materials. These oxides were mixed together in a stoichiometric molar ratio. A flux of  $\text{PbO}$  (15 mol%) was mixed with the starting materials. The anvil assembly of tungsten carbide cubes with a truncated edge length of 5 mm was compressed with the aid of USSA-1000. A 10 mm regular octahedron of a sintered  $\text{MgO}$  containing 5%  $\text{Cr}_2\text{O}_3$  was used as pressure medium. The powder mixtures were put into a cylindrical rhenium heater embedded in the  $\text{MgO}$  octahedron. Because  $\text{MgO}$  has a high thermal conductivity, a  $\text{LaCrO}_3$  sleeve was inserted outside of the rhenium heater. The sample temperature was monitored by a W25%Re-W3%Re thermocouple with 0.05 mm in diameter. The junction of the thermocouple was put at the midpoint of the outer surface of the cylindrical rhenium heater. No correction was made for the pressure effect on emf. After being kept at 20 GPa and 2000 °C for an hour, the product was quenched by shutting off the electric power supply. The pressure was released slowly and the product was recovered under ambient conditions. Composition of the single crystal was determined using a JEOL JCMA-733II electron microprobe analyzer (EPMA). No contamination of Pb into the single crystal was detected from

\*E-mail: tuka@po.cc.yamaguchi-u.ac.jp

TABLE 1. Chemical analysis by electron microprobe analyzer

	Weight percent	Cation ratio
SiO <sub>2</sub>	53.91	3.68
Al <sub>2</sub> O <sub>3</sub>	4.49	0.36
MgO	36.13	3.68
Cr <sub>2</sub> O <sub>3</sub>	5.21	0.28
Total	99.74	8.00

qualitative analysis by EPMA. The result of the chemical analysis is shown in Table 1.

### Data collection and structure refinements

The unit-cell parameters and diffraction intensity data of the synthesized single crystal were measured at room temperature using a four circle diffractometer (Rigaku AFC-5FOS) equipped with a rotating-anode generator operated at 50 kV and 200 mA. Graphite-monochromatized MoK $\alpha$  ( $\lambda = 0.71069$  Å) radiation was used for the measurements. The unit-cell parameters were determined by least-squares refinement of 25 reflections within the range of  $40^\circ \leq 2\theta \leq 50^\circ$ . A silicon single crystal was used as a standard material for the measurements of the unit-cell parameters. Intensity data within  $(\sin\theta)/\lambda \leq 0.807$  with  $0 \leq h, k, l \leq 18$  were collected in a continuous  $\omega$  scan mode. A total of 1892 reflections were measured and 555 reflections with  $|F_o| \geq 3\sigma(|F_o|)$  were used for the structure refinements. Lorentz and polarization corrections were applied, but no absorption correction was made because of sufficiently small  $\mu_{\max}$ , where  $\mu = 15.57$  cm<sup>-1</sup> and the crystal size is 0.10 mm  $\times$  0.08 mm  $\times$  0.07 mm. The unit-cell parameters were also measured using synchrotron X-ray radiation with the four circle diffractometer installed at BL-10A in the Photon Factory of the National Laboratory for High Energy Physics. Synchrotron radiation of wavelength  $\lambda = 1.000$  Å was obtained from the 2.5 GeV storage ring using a double Si(111) monochromator crystal.

The crystal-structure refinements were carried out by mini-

TABLE 3. Selected bond lengths (Å)

X1-O1	2.203(5)	X2-O1	2.356(5) $\times 2$	Y2-O2	1.912(5) $\times 2$
X1-O2	2.200(6)	X2-O2	2.346(5) $\times 2$	Y2-O3	1.907(4) $\times 2$
X1-O3	2.198(5)	X2-O5	2.193(6) $\times 2$	Y2-O6	1.913(4) $\times 2$
X1-O3	2.354(6)	X2-O6	2.196(6) $\times 2$	Average	1.911
X1-O4	2.204(5)	Average	2.273	Z1-O5	1.642(5) $\times 4$
X1-O4	2.361(6)	Y1-O1	1.912(5) $\times 2$	Z2-O6	1.642(5) $\times 4$
X1-O5	2.348(6)	Y1-O4	1.901(4) $\times 2$	Z3-O1	1.628(5)
X1-O6	2.340(6)	Y1-O5	1.911(4) $\times 2$	Z3-O2	1.642(5)
Average	2.276	Average	1.908	Z3-O3	1.634(5)
				Z3-O4	1.637(5)
				Average	1.635

mizing the function  $\Sigma w(|F_o| - |F_c|)^2$  using a full matrix least-squares program RADY (Sasaki 1987). A weight of  $w = 1/\sigma^2(|F_o|)$  was assigned to each observed reflection. Atomic scattering factors for neutral atoms and anomalous dispersion coefficients were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). During the least-squares refinements, the correction for the isotropic extinction effect (Type II) by Becker and Coppens (1974a, 1974b) was performed. The space group adopted in the present study is *I4<sub>1</sub>/a* with  $Z = 8$ . From a consideration of the discussion of the cation distribution described below, the final refinement in *I4<sub>1</sub>/a* was based on a disordered model for the cations. Cation occupancies on respective sites were fixed on the basis of the result from the chemical analysis.

Final reliability factors are  $R = 3.63\%$  and  $wR = 2.11\%$ . The *a* cell parameter is 11.512(1) Å and *c* is 11.515(1) Å. Cell volume *V* is 1526.0(2) Å<sup>3</sup>, corresponding to a density of 3.562 g/cm<sup>3</sup>. The chemical formula weight is 409.062. Atomic coordinates and anisotropic displacement parameters are listed in Table 2. Selected bond lengths are given in Table 3.

## RESULTS AND DISCUSSION

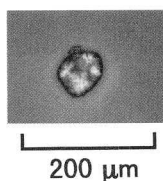
The single crystal of Cr-bearing majorite obviously shows birefringence ( $<0.003$ ) under crossed polars (Fig. 1). No compositional zoning was observed by EPMA. Moreover, the single crys-

TABLE 2. Atomic coordinates and anisotropic displacement parameters

Site	Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>	U <sub>eq</sub> (Å <sup>2</sup> ) <sup>*</sup>
X1	Mg	0.1250(2)	-0.0003(3)	0.2497(3)	0.006(1)	0.020(2)	0.024(2)	-0.000(1)	0.003(2)	0.011(2)	0.0164(2)
X2	Mg	0	1/4	0.6246(5)	0.019(3)	0.023(3)	0.005(2)	-0.011(2)	0	0	0.0155(4)
Y1	0.34 Mg	0	0	1/2	0.006(2)	0.004(2)	0.003(2)	0.001(1)	-0.001(2)	-0.000(2)	0.0044(3)
	0.34 Si										
	0.18 Al										
	0.14 Cr										
Y2	0.34 Mg	0	0	0	0.004(2)	0.005(2)	0.006(2)	-0.001(1)	-0.001(2)	0.003(2)	0.0049(3)
	0.34 Si										
	0.18 Al										
	0.14 Cr										
Z1	Si	0	1/4	3/8	0.008(2)	0.008	0.009(3)	0	0	0	0.0082(2)
Z2	Si	0	1/4	7/8	0.008(2)	0.008	0.005(3)	0	0	0	0.0071(2)
Z3	Si	0.1251(2)	0.0001(2)	0.7497(3)	0.007(1)	0.009(1)	0.008(1)	0.001(1)	0.000(1)	-0.000(1)	0.0080(2)
O1	O	0.0331(4)	0.0503(4)	0.6547(4)	0.007(2)	0.014(3)	0.009(3)	-0.001(2)	-0.004(2)	0.006(2)	0.0101(4)
O2	O	0.0326(4)	-0.0510(4)	0.8454(4)	0.006(2)	0.017(3)	0.021(3)	-0.003(2)	0.006(2)	0.012(2)	0.0147(4)
O3	O	0.2173(4)	0.0955(4)	0.8000(4)	0.006(2)	0.010(3)	0.019(3)	-0.002(2)	0.000(2)	-0.007(2)	0.0115(4)
O4	O	0.2172(4)	-0.0961(4)	0.7000(4)	0.007(2)	0.013(3)	0.014(3)	-0.001(2)	0.002(2)	-0.001(2)	0.0111(4)
O5	O	-0.0511(4)	0.1546(4)	0.4679(4)	0.016(3)	0.014(2)	0.008(2)	-0.007(2)	0.001(2)	0.003(2)	0.0125(4)
O6	O	-0.0951(4)	0.1989(4)	0.7819(4)	0.014(2)	0.015(3)	0.006(2)	-0.002(2)	-0.001(2)	0.001(2)	0.0117(4)

Note: The origin of atomic coordinates is shifted by 1/2, 0, 0 relative to the standard origin at the Wyckoff position 8c, to conform with previous descriptions of tetragonal garnets (*I4<sub>1</sub>/a*).

\*  $U_{eq} = (1/3)\Sigma\Sigma U_{ij}a_i^*a_j^*$



**FIGURE 1.** The photomicrograph of the Cr-bearing majorite single crystal. The crystal is in immersion liquid and was photographed under crossed polars with a sensitive color plate inserted (RT = 530 nm), where RT represents retardation.

tal shows not undulatory extinction but “normal” extinction under crossed polars, and the patchy interference colors observed in Figure 1 are due to the variations of crystal thickness. This strongly suggests that the appearance of birefringence in the Cr-bearing majorite is due to not ferroelastic strain but to reduction of symmetry from cubic. The unit-cell parameters measured by the conventional X-ray source have values  $a = 11.512(1)$  Å,  $b = 11.512(1)$  Å, and  $c = 11.515(1)$  Å with interaxial angles statistically equal to  $90^\circ$ . In addition, the unit-cell parameters obtained using synchrotron radiation, which yields higher resolution for  $2\theta$  angle than conventional radiation sources, have values  $a = 11.537(1)$  Å,  $b = 11.536(1)$  Å, and  $c = 11.543(1)$  Å. (The discrepancy between the absolute values of the unit-cell parameters obtained using both X-ray sources may be due to the uncertainty of wavelength of synchrotron X-ray radiation used.) Both results indicate that this garnet has a tetragonal unit cell with  $a \approx c$  and deviates slightly from cubic symmetry. Among the subgroups of  $Ia\bar{3}d$ , the possible tetragonal space groups that allow the garnet structure to be maintained are  $I4_1/acd$  and  $I4_1/a$ . Therefore, structure refinements assuming space groups  $Ia\bar{3}d$  (model 1),  $I4_1/acd$  (model 2), and  $I4_1/a$  (model 3) were attempted to determine the most probable symmetry. Structure refinements in models 1, 2, and 3 resulted in  $R = 3.86\%$  with  $wR = 2.33\%$ ,  $R = 3.80\%$  with  $wR = 2.19\%$ , and  $R = 3.63\%$  with  $wR = 2.11\%$ , respectively. Among these models, the final  $R$ - and  $wR$ -values were lowest for the refinement in model 3 although the improvement in  $R$ -values was slight. Moreover, the bond lengths and the equivalent isotropic displacement parameters ( $U_{eq}$ ) regarded as symmetry equivalent in model 1, are obviously more distinguishable in model 3 than in model 2. Particularly, the remarkable difference between models 2 and 3 can be found in the  $U_{eq}$  values of O atoms. The  $U_{eq}$  values of three nonequivalent O atoms in model 2 are  $0.0121(2)$  Å<sup>2</sup>,  $0.0111(2)$  Å<sup>2</sup>, and  $0.0120(2)$  Å<sup>2</sup>, which do not show significant difference. On the other hand, the most remarkable nonequivalency can be found between  $U_{eq}$  values of O1 [ $0.0101(4)$  Å<sup>2</sup>] and O2 [ $0.0147(4)$  Å<sup>2</sup>] in model 3 (Table 2). Therefore, we conclude that the most probable space group of this birefringent garnet is  $I4_1/a$ , which is the same as that of  $MgSiO_3$  majorite. The two different types of merohedral and pseudomerohedral twins have been invariably observed in the tetragonal majorite ( $I4_1/a$ ) by several researchers (e.g., Angel et al. 1989; Wang et al. 1993; Heinemann et al. 1997). However, it was very difficult to observe these twins in the Cr-bearing majorite under the polarization microscope. This may be because the twin domains produced are very fine owing to a very small deviation from cubic, as reported in majorite in the system  $Mg_3Al_2Si_3O_{12}$ - $MgSiO_3$  by Heinemann et al. (1997). In further study, the obser-

vation of twinning by transmission electron microscopy (TEM) will be necessary to gain the conclusive proof that the Cr-bearing majorite has the tetragonal space group  $I4_1/a$ .

The result of the chemical analysis (Table 1) shows that the single crystal is stoichiometric and Cr ions exist in the trivalent state. Moreover, in consideration of the general formula of garnets ( $^{VIII}X_3^{VI}Y_2^{IV}Z_3O_{12}$ ) and cation sizes, this result indicates that the mixing of cations (Mg, Al, Si, and Cr) occurs only on the two nonequivalent octahedral sites (Y1 and Y2) in the  $I4_1/a$  structure. However, it is very difficult to determine the site occupancies of Mg, Al, and Si on the octahedral sites because these atoms have similar atomic scattering factors. Therefore, the occupancy refinement for Cr ions on Y1- and Y2-sites was performed by substitution of the atomic scattering factor of Al for those of Mg and Si because the average of atomic scattering factors of Mg and Si is approximately equal to that of Al. This procedure for the occupancy refinement will be sufficiently worth attempting for the purpose of the occupancy determination of only Cr ions whose scattering power is much greater than the remaining cations (Mg, Al, and Si). The occupancy refinement indicated that the Cr ions occupy 14.1(9)% of the Y1-site and 14.6(9)% of the Y2-site. This result is consistent with Cr content obtained by chemical analysis (Table 1) and, moreover, indicates complete disordering of Cr ions between Y1- and Y2-sites. Therefore, among the constituent cations, at least the Cr ions do not show the ordered distribution with the symmetry reduction from cubic to tetragonal. Although it is very difficult to know the exact distribution of the remaining cations (Mg, Al, and Si) between Y1- and Y2-sites, comparison of mean  $\langle Y1-O \rangle$  and  $\langle Y2-O \rangle$  distances may provide some insights into the distribution of these cations. In Table 3, the difference between  $\langle Y1-O \rangle$  and  $\langle Y2-O \rangle$  distances is only 0.003 Å, which is not significant. This suggests that the ordering of Mg, Al, and Si between Y1- and Y2-sites will not be present at all or a degree of the ordering will be very slight even if it is present.

#### ACKNOWLEDGMENTS

We thank T. Katsura of ISEL, Okayama University, for his help in the high-pressure experiments and T. Tanaka of ISIR, Osaka University, for his help in the operation of the X-ray equipment. A portion of this work has been done under the approval of the Photon Factory Program Advisory Committee (Proposal no. 94 G314).

#### REFERENCES CITED

- Akaogi, M. and Akimoto, S. (1977) Pyroxene-garnet solid-solution equilibria in the system  $Mg_4Si_4O_{12}$ - $Mg_3Al_2Si_3O_{12}$  and  $Fe_4Si_4O_{12}$ - $Fe_3Al_2Si_3O_{12}$  at high pressure and temperature. *Physics of Earth and Planetary Interiors*, 15, 90–104.
- Angel, R.J., Finger, L.W., Hazen, R.M., Kanzaki, M., Weidner, D.J., Liebermann, R.C., and Veblen, D.R. (1989) Structure and twinning of single crystal  $MgSiO_3$  garnet synthesized at 17 GPa and 1800 °C. *American Mineralogist*, 74, 509–512.
- Becker, P.J. and Coppens, P. (1974a) Extinction within the limit of validity of the Darwin transfer equations. I. General formalisms for primary and secondary extinction and their application to spherical crystals. *Acta Crystallographica*, A30, 129–147.
- (1974b) Extinction within the limit of validity of the Darwin transfer equations. II. Refinement of extinction in spherical crystals of  $SrF_2$  and  $LiF$ . *Acta Crystallographica*, A30, 148–153.
- Heinemann, S., Sharp, T.G., Seifert, F., and Rubie, D.C. (1997) The cubic-tetragonal phase transition in the system majorite ( $Mg_3Si_3O_{12}$ )-pyrope ( $Mg_3Al_2Si_3O_{12}$ ), and garnet symmetry in the Earth's transition zone. *Physics and Chemistry of Minerals*, 24, 206–221.
- Ibers, J.A. and Hamilton, W.C., Eds. (1974) *International Tables for X-ray Crystallography*, vol. IV, 366 p. Kynoch, Birmingham, U.K.
- Irifune, T. (1994) Absence of an aluminous phase in the upper part of the earth's lower mantle. *Nature*, 370, 131–133.
- Ito, E. and Takahashi, E. (1987) Ultrahigh-pressure phase transformations and the constitution of the deep mantle. In M.H. Manghni and Y. Syono, Eds., *High-pressure*

- research in mineral physics, p. 221–230. Terra Scientific Publishing Company, Tokyo.
- Kato, T. and Kumazawa, M. (1985) Garnet phase of  $\text{MgSiO}_3$  filling the pyroxene-ilmenite gap at very high temperature. *Nature*, 316, 803–805.
- Liu, L. (1977) The system enstatite-pyroxene at high pressures and temperatures and the mineralogy of the earth's mantle. *Earth and Planetary Science Letters*, 36, 237–245.
- Parise, J.B., Wang, Y., Gwanmesia, G.D., Zhang, J., Sinelev, Y., Chmielowski, J., Weidner, D.J., and Liebermann, R.C. (1996) The symmetry of garnets on the pyroxene ( $\text{Mg}, \text{Al}_2\text{Si}_2\text{O}_{12}$ )-majorite ( $\text{MgSiO}_3$ ) join. *Geophysical Research Letters*, 23(25), 3799–3802.
- Ringwood, A.E. (1967) The pyroxene-garnet transformation in the earth's mantle. *Earth and Planetary Science Letters*, 2, 255–263.
- (1979) *Origin of the Earth and Moon*, p. 295. Springer-Verlag, New York.
- Sasaki, S. (1987) RADY. A Fortran Program for the Least-Squares Refinement of Crystal Structures. National Laboratory for High Energy Physics, Japan.
- Sawamoto, H. (1987) Phase diagram of  $\text{MgSiO}_3$  at pressures up to 24 GPa and temperatures up to 2200 °C: Phase stability and properties of tetragonal garnet. In M.H. Manghnani and Y. Syono, Eds., *High-pressure research in mineral physics*, p. 209–219. Terra Scientific Publishing Company, Tokyo.
- Wang, Y., Gasparik, T., and Liebermann, R.C. (1993) Modulated microstructure in synthetic majorite. *American Mineralogist*, 78, 1165–1173.

MANUSCRIPT RECEIVED MAY 27, 1998

MANUSCRIPT ACCEPTED SEPTEMBER 7, 1998

PAPER HANDLED BY JAMES W. DOWNS