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Flux growth of single crystals of $MgGeO_3$ polymorphs (orthopyroxene, clinopyroxene, and ilmenite) and their phase relations and crystal structures

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Abstract

Three kinds of $MgGeO_3$ pyroxene single crystals of 1–10 mm size were grown by the flux method: an orthopyroxene, a clinopyroxene and a "clino-from proto" phase. The lattice parameters and the space groups are (1) orthopyroxene: $a = 18.8099(12)$, $b = 8.9484(8)$, $c = 5.3451(4)$Å, *Pbca*, (2) clinopyroxene and (3) "clino-from proto" phase: $a = 9.6010(8)$, $b = 8.9323(6)$, $c = 5.1592(5)$Å, $\beta = 101.034(9)°$, *C2/c*. The phase relations of $MgGeO_3$ were studied in the temperature range 655–1030°C and in the pressure range 0–55 kbar. The boundary between orthopyroxene and clinopyroxene was determined as $T = 810°C + 3.8\,P$(kbar), where the high-pressure and low-temperature phase is monoclinic. Single crystals of ilmenite-type $MgGeO_3$ (up to 100 μm in size) were also grown in association with the pyroxene → ilmenite transformation at 55 kbar, using the flux-grown mm-size orthopyroxene or clinopyroxene $MgGeO_3$ single crystals as starting materials.

Introduction

Pyroxene is one of the important constituent minerals of the earth's crust and upper mantle. Ito (1975) has established a crystal-growth technique particularly suitable for growing enstatite ($MgSiO_3$). Orthoenstatite single crystals provided by Ito have been successfully used for detailed structure analyses (Sasaki *et al.*, 1982) and for Brillouin scattering measurements (Weidner *et al.*, 1978). Germanates are generally used as geochemical models of silicates. They often display the same phases as silicates but at lower pressures more easily achieved in the laboratory. However, the phase relationships of germanate pyroxenes such as $MgGeO_3$ have not been studied in detail nor has the growth of single crystals of germanate pyroxenes been reported. Large single crystals of germanate pyroxene are useful as starting materials to obtain single crystals of high-pressure phases as well as for physical property measurements.

Previous studies have demonstrated that $MgGeO_3$ exhibits phases isomorphic to those of $MgSiO_3$. Roth (1955) reported the synthesis of an orthorhombic phase isomorphic to orthoenstatite. Robbins and Levin (1959) reported the synthesis of a monoclinic polymorph of $MgGeO_3$ in addition to the orthorhombic form. In contrast to the $MgSiO_3$ system, they concluded that the monoclinic phase is the high-temperature phase (above 1555°C). Furthermore, they reported that the germanate melts congruently at 1700°C which also differs from the behavior of the silicate pyroxene.

High-pressure transformation of $MgGeO_3$ pyroxene into the ilmenite structure was first reported by Ringwood and Seabrook (1963), and later by Kirfel and Neuhaus (1974) who determined phase boundaries among orthorhombic, monoclinic and hexagonal (ilmenite structure) phases.

This paper reports growth of large single crystals (1–10 mm size) of $MgGeO_3$ pyroxene in air by the flux method. Based on morphological observation and X-ray diffraction measurements on the synthesized single crystals, phase relations at atmospheric pressure between orthorhombic (two orthorhombic phases) and monoclinic polymorphs in $MgGeO_3$ pyroxene are discussed in detail. Preliminary results of high-pressure and high-temperature experiments using single-crystal $MgGeO_3$ pyroxene prepared in the present study as starting materials are also reported.

Crystal growth and phase relations

We adopted a flux method to grow single crystals of orthorhombic phase of $MgGeO_3$. Single crystals of $MgSiO_3$ orthoenstatite have already been grown by Ito (1975) using such a method. We followed his procedure, including the chemical composition of the flux (Li_2O = 51.7 mol%, MoO_3 = 42.3 mol%, V_2O_5 = 6.0 mol%) and the temperature range for growth.

Reagent grade MoO_3, Li_2CO_3, V_2O_5, MgO, and GeO_2 of 99.999% were used as starting materials. MoO_3, Li_2CO_3, and V_2O_5 were for flux and MgO and GeO_2 were for nutrient. Mixtures of these were heated in air at 955°C in platinum crucibles for several days, slowly cooled to

Table 1. Crystal growth data for $MgGeO_3$ pyroxene

Charge composition	flux	Li_2CO_3	7.35 g(Li_2O:2.97g)
		MoO_3	11.70
		V_2O_5	2.08
	nutrient	MgO	0.232
		GeO_2	0.602
Mg/Ge atomic ratio			1.0
Nutrient/Flux			5 wt%
Soaking temperature			955°C
Soaking time			7 days
Cooling rate			1.6°C/hr
Crucible size			10 ml
Cut-off temperature			650°C
Crystal size(length)			1 - 10 mm
Products			Orthoenstatite-type Clinoenstatite-type "Clino-from proto"

655°C, and quenched to room temperature. After the flux was dissolved in water, the residual materials were collected as products. In Table 1, an example of the growth conditions is shown. According to Robbins and Levin (1959) this temperature range should yield only one orthorhombic phase (orthoenstatite-type). However, we have obtained three kinds of $MgGeO_3$ crystals in the temperature range 955–655°C, *i.e.*, single crystals of orthorhombic $MgGeO_3$, single crystals of monoclinic $MgGeO_3$ with or without twinning, and "clino-from proto" $MgGeO_3$ with very fine twinning. Morphological features of these three kinds of crystals are described below.

(1) *Orthorhombic $MgGeO_3$ (orthoenstatite-type, Pbca)*

A number of single crystals of orthorhombic $MgGeO_3$ were grown. These are transparent and colorless with either an octagonal needle-like shape elongated along the *c*-axis (0.5 mm× 0.5 mm × 10 mm) or a platelet shape (3 mm × 5 mm × 0.5 mm). The crystal habit for this orthorhombic $MgGeO_3$ is completely the same as that of flux-grown orthoenstatite, *i.e.*, the axis of elongation is *c*, {100}, {010}, and {210} faces form an octagonal column, and {111} and {211} build up a peculiar feature at the top of the needle (Takei *et al.*, 1982). The (010) faces develop to make a flat surface in the platelet crystals.

(2) *Type A monoclinic $MgGeO_3$ (clinoenstatite-type, C2/c)*

According to Robbins and Levin (1959), monoclinic $MgGeO_3$ is reported to be stable above 1555°C at atmospheric pressure. In this study, however, a number of single crystals (with or without twinning) of the monoclinic phase of $MgGeO_3$ were obtained simultaneously with the orthorhombic phase in a single run. This indicates that single crystals of monoclinic $MgGeO_3$ were grown in the temperature range 955 to 655°C. These crystals are transparent and colorless and plate-like or needle-like with dimensions about 3 mm × 5 mm × 0.5 mm or 0.5 mm × 0.5 mm × 10 mm. When the solution was cooled very slowly around 800°C, twinning-free single crystals of plate-like monoclinic $MgGeO_3$ were grown (Fig. 1). As the shapes of the needle-like and plate-like monoclinic $MgGeO_3$ are very similar to those of orthorhombic $MgGeO_3$, *i.e.*, octagonal column composed of {110}, {100}, and {010} and elongated in the *c*-axis and (010) plate, it is difficult to distinguish the monoclinic $MgGeO_3$ crystals from the orthorhombic $MgGeO_3$ using only the crystal habit. When we observe these crystals under a petrographic microscope with crossed nicols, the orthorhombic phase shows a straight extinction, while the monoclinic phase extinguishes obliquely (about 25–28°). Twins in the monoclinic phase are easy to recognize. The (100) twinning (occasionally only a single twin in a grain) seems not to be essential for crystal growth, and furthermore, this twinning is completely different from those for the type B monoclinic phase discussed below. This latter group is interpreted as resulting from phase transitions upon quenching. Therefore, these type A monoclinic $MgGeO_3$ crystals can be regarded as having grown as a primary phase in this temperature range.

(3) *Type B monoclinic $MgGeO_3$ (clino-from proto-type, C2/c)*

In the temperature range 955 to 655°C, a number of opaque, white and thick octagonal columnar crystals were also produced. Precession photographs and microscopic observation revealed that these are mostly monoclinic $MgGeO_3$ single crystals with very fine (100) twinning (plus a small amount of the orthorhombic phase). Because of their similarity to "proto-inverted-clinoenstatite" (Ito, 1975), these are considered to be an inversion product from unquenchable proto-type $MgGeO_3$ single crystals, *i.e.*, "clino-from proto"-$MgGeO_3$. As will be discussed later, this type B monoclinic $MgGeO_3$ (*C2/c*) is crystallographically identical to the type A monoclinic $MgGeO_3$ (*C2/c*). However, the appearance of these two geneses of monoclinic $MgGeO_3$ crystals is completely different. That is, the former is opaque due to the extensively developed twinning and cracks, and the latter is transparent with at most a small amount of twinning. A small amount of orthorhombic phase was also found to coexist within or on the surface of these type B monoclinic crystals. This orthorhombic phase is regarded as the inversion product of the protophase and/or newly grown crystals which formed on the surface during the process of cooling.

In order to elucidate further these complicated relations of the synthesis of $MgGeO_3$ crystals, several different kinds of heat treatments were carried out. Slow-cooling of the solution from 908°C did not yield any type B monoclinic $MgGeO_3$ crystals, while cooling from 935°C produced a number of type B monoclinic $MgGeO_3$ crystals. Therefore, the stability field of proto-type $MgGeO_3$ at atmospheric pressure is indicated to be above about 920°C and this temperature is very close to that for enstatite (950°C). On slow-cooling from 908°C to 810°C,

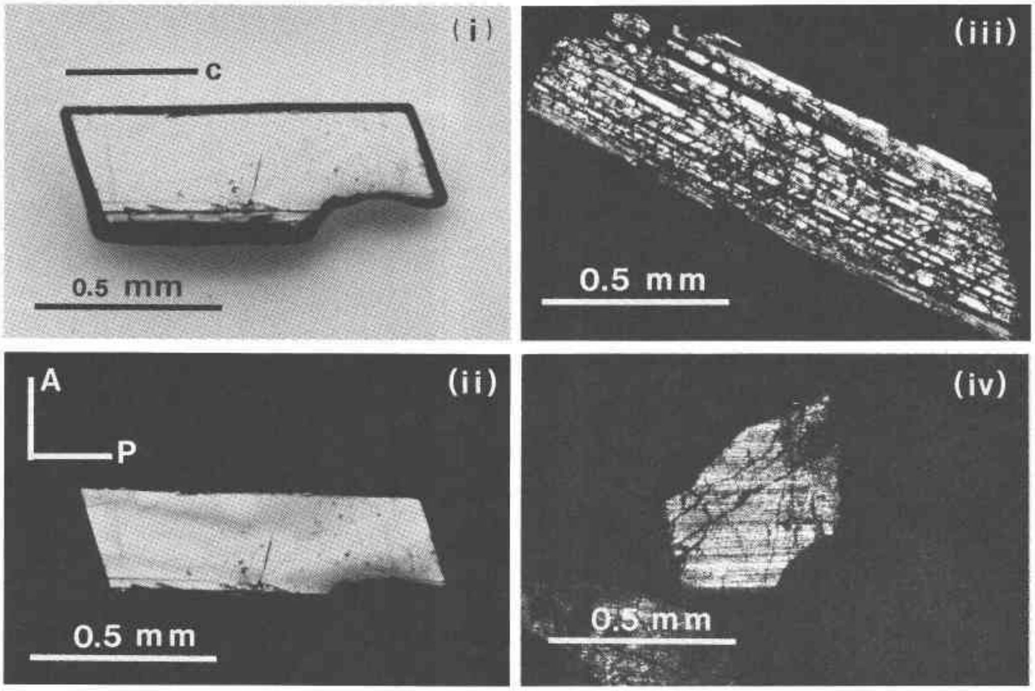

Fig. 1.(i),(ii) An (010) plate of type A monoclinic $MgGeO_3$ single crystal (twinning-free). (i) uncrossed nicols, (ii) crossed nicols. A small single crystal of orthoenstatite-type $MgGeO_3$ is attached at the lower part which shows straight extinction under crossed nicols (ii). (iii) thin section of type B monoclinic $MgGeO_3$ (''clino-from proto'' $MgGeO_3$) under crossed nicols. (iv) An (010) plate of ''clino-from ortho'' $MgGeO_3$ (31 kbar, 850°C) under crossed nicols.

no monoclinic $MgGeO_3$ phase grew at all; rather only orthorhombic $MgGeO_3$ was obtained. Cooling to 795°C produced both type A monoclinic $MgGeO_3$ and orthorhombic $MgGeO_3$. These results imply that single crystals of orthorhombic $MgGeO_3$ (orthoenstatite-type) are stable only between 920°C and about 810°C, and monoclinic $MgGeO_3$ grows below 810°C.

The present phase relations are completely discordant with those given by Robbins and Levin (1959). They concluded monoclinic $MgGeO_3$ is the high-temperature phase (above 1555°C), while we conclude that it is the low-temperature phase (below 810°C). The present phase relations at atmospheric pressure are very similar to those for $MgSiO_3$ enstatite (for example, Boyd and England (1965)), except that the boundary between the monoclinic and orthorhombic phase in $MgGeO_2$ is higher by about 200–250°C than that for $MgSiO_3$ (566°C by Grover (1972); 630°C by Boyd and England (1965)). In this context, note that it should be possible to grow single crystals of clinoenstatite of $MgSiO_3$ at atmospheric pressure if we can find a solvent which dissolves considerable amounts of MgO and SiO_2 below 566°C. In Figure 1, both type A and type B monoclinic $MgGeO_3$ crystals are shown. If our phase relations are correct, the structural identities of all those $MgGeO_3$ samples studied by Roth (1955), Robbins and Levin (1959), and Kirfel and Neuhaus (1974) should be suspected. Further discussion of this point is given in the following sections.

High-pressure and high-temperature experiments

High-pressure and high-temperature experiments were carried out in the pressure range 31–55 kbar and in the temperature range 850–1030°C, with the aim of elucidating the phase relations between orthoenstatite- and clinoenstatite-type $MgGeO_3$ at high pressures. Both a tetrahedral anvil apparatus and a cubic anvil apparatus were used. In experiments using the tetrahedral anvil apparatus, tungsten-carbide anvils with 15 mm edges and baked pyrophyllite tetrahedra with 20 mm edges were used. For the cubic anvil apparatus, a combination of 16 mm-edge anvils with 21 mm-edge cubes was adopted. Single crystals of orthoenstatite-type and clinoenstatite-type $MgGeO_3$ were used as the starting materials. A tubular graphite heater was used for heating these crystal samples. NaCl was adopted as the pressure-transmitting medium surrounding these crystals inside the graphite heater. Since the temperature-pressure conditions of the present study are close to the melting curve of NaCl, the NaCl insert was softened markedly although not melted. This produced a uniform stress condition for the crystals.

Pressure values were calibrated against press load at room temperature based on the well-established pressure-fixed points of low-Bi (25.5 kbar), low-Ba (55 kbar) and high-Bi (77 kbar). A conventional quenching technique was used for investigating the phase relations. After the pressure was applied to the sample, temperature was brought to the desired value and held there for 30 to 90 minutes. The sample was then quenched by turning off the heating power under the working pressure. After releasing the pressure, the single crystals were collected by dissolving the NaCl insert with water. Before and after the high-pressure and high-temperature treatment, the phases of the samples were examined with a petrographic microscope and a precession camera.

At 40 kbar and 900°C, no change was observed in the type A monoclinic single crystals of $MgGeO_3$. On the other hand, orthorhombic single crystals of $MgGeO_3$ changed to a monoclinic structure after the same treatment. These run-products, "clino-from ortho"-$MgGeO_3$ crystals were confirmed to be crystallographically identical to the type A monoclinic $MgGeO_3$, except for the presence of a large number of twins developed through the phase transformation. This twin texture was the same as observed in the "clino-from proto"-$MgGeO_3$, type B monoclinic $MgGeO_3$ (Fig. 1). At 39 and 44 kbar and 1020°C, the type A monoclinic phase changed to an orthorhombic phase, while at 31 kbar, 850°C; 38 kbar, 900°C; and 44 kbar, 940°C; the orthorhombic phase changed to a monoclinic phase with very fine twinning. At 51 kbar and 1030°C, the orthorhombic phase did not change. Summarizing all our results including the phase relations at atmospheric pressure, the ortho-clino phase boundary is shown in Figure 2. The boundary curve is approximately determined as T = 810°C + 3.8 P (kbar). The high-temperature and low-pressure phase is the orthorhombic orthoenstatite-type and the low-temperature and high-pressure phase is the monoclinic clinoenstatite-type.

The present result is entirely different from the determination of Kirfel and Neuhaus (1974). They reported a narrow stability field for the orthoenstatite-type below 10 kbar and gave a steep negative slope for the phase boundary. The unit cell volumes of the orthoenstatite-type and the clinoenstatite-type are 899.69(12)$Å^3$ (Z = 16) and 434.27(6)$Å^3$ (Z = 8), respectively. The smaller cell volume of the clinoenstatite-type supports our conclusion that the clinoenstatite-type is the high-pressure phase. It is noted that Kirfel and Neuhaus (1974) did not consider the possibility of the appearance of a proto-phase and consequently did not distinguish "clino-from proto" $MgGeO_3$ (type B) from the primary monoclinic $MgGeO_3$ (type A) and from the "clino-from ortho" $MgGeO_3$. Furthermore, their identification of phases based on their polycrystalline powder sample could have resulted in an erroneous conclusion. In the next section we critically discuss their powder data on the basis of our own measurements on powdered samples. The present phase relations of $MgGeO_3$ at high-pressures and high-temperatures are similar to those of $MgSiO_3$ reported by Boyd and England (1965); whose ortho-clino boundary is T = 630°C + 2.6 P (kbar), although their experiments were claimed to be carried out under the existence of some shearing stress (Grover, 1972).

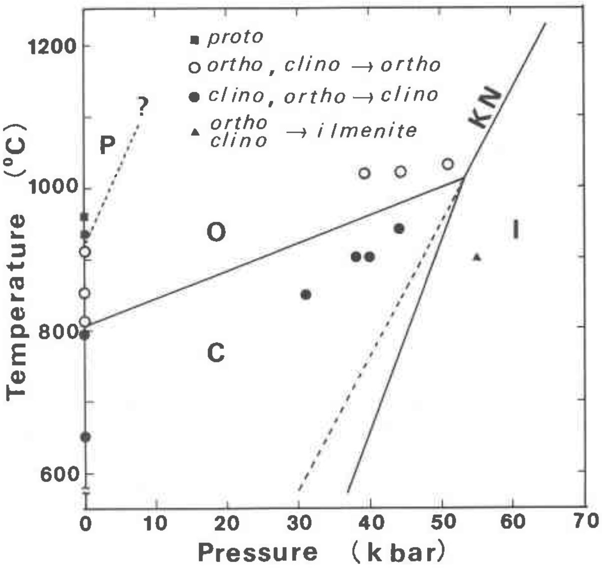

Fig. 2. Phase diagram of $MgGeO_3$. P: protoenstatite-type region; O: orthoenstatite-type region; C: clinoenstatite-type region; I: ilmenite-type region; KN: pyroxene-ilmenite phase boundary by Kirfel and Neuhaus (1974).

At 55 kbar and 900°C, small single crystals of hexagonal ilmenite-type $MgGeO_3$ (up to 100 μm in size) partly replaced single crystals of both the ortho- and clino-phase (Fukizawa *et al.*, 1982). This condition is located within the ilmenite-type region given by Kirfel and Neuhaus (1974) and not far from the phase boundary between pyroxene and ilmenite. The crystal orientation of this hexagonal phase with respect to the parent phase was examined with a precession camera. It was found that the (100) plane of the ortho- or clino-phase coincides with the (001) plane of the ilmenite phase, *i.e.*, the oxygen-close-packed plane is conserved through the transition. Although we did not determine the boundary between the pyroxene and ilmenite phases, Kirfel and Neuhaus's straight line should have a kink at the triple point (ortho, clino, ilmenite) and the estimated boundary lines are shown in Figure 2.

Conservation of the oxygen-close-packed plane through the phase transformation has recently been reported for the olivine–spinel transformation (Lacam *et al.*, 1980; Hamaya and Akimoto, 1982). Hamaya and Akimoto (1982) also demonstrated the successful growth of high-quality single crystals of Ni_2SiO_4 spinel (up to 300 μm in size) using mm-size single crystals of olivine as starting materials. This suggests a possibility of growing sub-mm size high-quality single crystals of $MgGeO_3$ ilmenite using the mm-size single crystals of $MgGeO_3$ pyroxene synthesized in the present study as starting materials.

Crystal structure

Crystal structure of single crystals of both orthorhombic and monoclinic $MgGeO_3$ were studied with a preces-

Table 2. X-ray powder diffraction data of orthoenstatite-type $MgGeO_3$

h	k	l	$d_{obs.}$	$d_{calc.}$	Intensity
2	1	0	6.4840	6.4829	m
4	0	0	4.7024	4.7025	m
0	2	0	4.4756	4.4742	m
4	1	0	4.1630	4.1627	vw
1	2	1	3.3750	3.3752	w
4	1	1	3.2846	3.2842	vw
4	2	0	3.2412	3.2414	vs
3	2	1	3.0089	3.0097	w
6	1	0	2.9601	2.9587	s
5	1	1	2.9111	2.9093	w
4	2	1	2.7713	2.7716	w
1	3	1	2.5747	2.5801	w
2	0	2	2.5747	2.5708	w
5	2	1	2.5348	2.5350	m
3	1	2	2.3704	2.3707	vw
6	2	1	2.3161	2.3143	vw
0	4	0	2.2371	2.2371	w
5	0	2	2.1781	2.1787	vw
8	1	1	2.0928	2.0925	vw
1	4	1	2.0509	2.0513	w
4	4	0	2.0204	2.0202	m
2	4	1	2.0170	2.0157	m
3	4	1	1.9604	1.9602	w
10	1	0	1.8405	1.8408	m
5	4	1	1.8091	1.8093	w
8	3	1	1.7451	1.7453	w
7	2	2	1.7451	1.7449	w
8	1	2	1.7314	1.7319	w
0	2	3	1.6551	1.6553	vw
9	0	2	1.6472	1.6463	vw
9	3	1	1.6297	1.6301	w
8	4	0	1.6210	1.6207	w
6	5	0	1.5542	1.5542	m
10	3	1	1.5244	1.5249	m
1	3	3	1.5244	1.5246	m
6	5	1	1.4923	1.4924	m
9	4	1	1.4685	1.4684	vw
3	5	2	1.4461	1.4469	vw
7	4	2	1.4461	1.4459	vw
11	0	2	1.4395	1.4404	vw
11	3	1	1.4297	1.4295	w
11	1	2	1.4221	1.4221	vw
4	5	2	1.4179	1.4178	vw
12	3	1	1.3431	1.3430	w
12	1	2	1.3371	1.3369	w
1	0	4	1.3331	1.3329	vw
14	1	0	1.3289	1.3287	w
10	5	0	1.2969	1.2966	m

orthorhombic *Pbca*
a = 18.8099(12) Å, b = 8.9484(8) Å, c = 5.3451(4) Å,
V = 899.69(12) $Å^3$, Z = 16, $\rho_{calc.}$ = 4.278 g/cm^3

sion camera and a four-circle diffractometer. Powdered samples were examined by a diffractometer.

The orthorhombic phase was confirmed to have the orthoenstatite structure (space group *Pbca*) with cell parameters a = 18.8099(12), b = 8.9484(8), c = 5.3451(4)Å. These cell parameters were determined for a single crystal using only strong reflections at high 2θ angle selectively peak-refined with a four-circle diffractometer. In Table 2 are shown observed d-spacings for a powdered sample together with the calculated ones based on the refined unit cell parameters. Our data are generally close to that by Robbins and Levin (1959). In Table 3, the crystal data are compared to those of other authors.

Table 3. Crystal data of orthoenstatite-type $MgGeO_3$

	Roth(1975)	Kirfel & Neuhaus(1974)	This study
a /Å	18.661	18.859(6)	18.8099(12)
b /Å	8.954	8.958(2)	8.9484(8)
c /Å	5.346	5.334(1)	5.3451(4)
V /$Å^3$	893.27	901.17(35)	899.69(12)
Space Group	*Pbca*	*Pbca*	*Pbca*

Table 4. X-ray powder diffraction data of clinoenstatite-type $MgGeO_3$

h	k	l	$d_{obs.}$	$d_{calc.}$	Intensity
1	1	0	6.4839	6.4828	m
2	0	0	4.7148	4.7118	s
0	2	0	4.4644	4.4661	w
-1	1	1	4.2720	4.2729	vw
0	2	1	3.3488	3.3495	m
2	2	0	3.2412	3.2414	vs
3	1	0	2.9630	2.9633	vs
-2	2	1	2.9093	2.9095	w
-3	1	1	2.7864	2.7862	w
2	2	1	2.5804	2.5801	s
-1	3	1	2.5387	2.5397	m
0	0	2	2.5310	2.5319	w
-1	1	2	2.4710	2.4713	vw
-2	0	2	2.4323	2.4329	vw
1	3	1	2.4190	2.4177	vw
3	1	1	2.3770	2.3773	vw
0	4	0	2.2331	2.2331	w
-3	1	2	2.1226	2.1236	vw
-4	2	1	2.0533	2.0532	vw
0	4	1	2.0434	2.0432	w
2	4	0	2.0181	2.0179	m
-2	4	1	1.9280	1.9297	vw
3	3	1	1.8991	1.8991	vw
5	1	0	1.8438	1.8441	m
2	4	1	1.8224	1.8239	w
4	2	1	1.8224	1.8215	w
3	1	2	1.7730	1.7733	vw
-5	1	2	1.6446	1.6444	vw
1	5	1	1.6400	1.6404	vw
5	1	1	1.6373	1.6370	vw
4	4	0	1.6199	1.6207	vw
-3	1	3	1.5944	1.5958	m
-5	3	1	1.5944	1.5947	m
5	3	0	1.5914	1.5925	vw
4	0	2	1.5807	1.5805	vw
6	0	0	1.5702	1.5706	vw
3	5	0	1.5529	1.5529	w
-1	3	3	1.4887	1.4891	m
0	6	0	1.4887	1.4887	m
-6	0	2	1.4664	1.4663	vw
5	3	1	1.4532	1.4534	m
-4	2	3	1.4352	1.4359	vw
-3	3	3	1.4201	1.4243	w
2	2	3	1.4201	1.4224	w
2	6	0	1.4201	1.4195	w
1	5	2	1.4201	1.4190	w
-3	5	2	1.3834	1.3834	vw
5	1	2	1.3722	1.3733	vw
7	1	0	1.3306	1.3312	w
5	5	0	1.2965	1.2966	w
0	6	2	1.2831	1.2833	vw

monoclinic *C2/c*
a = 9.6010(8) Å, b = 8.9323(6) Å, c = 5.1592(5) Å,
β = 101.034(9)°, V = 434.27(6) $Å^3$, Z = 8,
$\rho_{calc.}$ = 4.431 g/cm^3

The monoclinic $MgGeO_3$ crystals grown below 810°C (type A) were found to have unit cell dimensions of a = 9.6010(8), b = 8.9323(6), c = 5.1592(5)Å, β = 101.034(9)°. X-ray diffraction data taken for powdered type A monoclinic $MgGeO_3$ are shown in Table 4 with the calculated d-spacings based on the refined unit cell dimensions determined for a single crystal using high 2θ angle reflections and a four-circle diffractometer. These d-spacings are close to those by Robbins and Levin (1959) except for their three unindexed lines mentioned below. In Table 5, the present crystal data for monoclinic $MgGeO_3$ are compared to those of Robbins and Levin (1959) and Kirfel and Neuhaus (1974). The space group of this phase is $C2/c$ which is the same as that for "high-clinoenstatite" (Smith, 1969) and diopside. The present result is different from that of Kirfel and Neuhaus (1974) who deduced $P2_1/m$ or $P2_1$ on the basis of the diffraction data for polycrystalline powder by Robbins and Levin (1959). Furthermore, our value of the unit cell dimension, a, is about half of that given by them. As has been noted in the JCPDS-card No. 11-504 by L. G. Berry, three strong reflections reported by Robbins and Levin (1959) could not be indexed on the basis of the unit cell dimensons a = 9.60, b = 8.92, c = 5.16Å, β = 100.49°. In order to index these three lines, Kirfel and Neuhaus (1974) had to double the a-value. Consequently, they were forced to conclude the space group was P not C.

As shown in the crystal growth experiments, both monoclinic and orthorhombic phases have grown, and furthermore the "clino-from proto" phase was also obtained below 955°C. We also found that single crystals of proto-type $MgGeO_3$ inverted both to clinoenstatite- and orthoenstatite-type $MgGeO_3$ during the cooling process to room temperature. These experimental results strongly imply that the sample (polycrystalline powder) prepared by Roth (1955) ("Ge-enstatite"), Robbins and Levin (1959) ("enstatite form" and "clinoenstatite form"), and by Kirfel and Neuhaus (1974) ("ortho-$MgGeO_3$" and "klino-$MgGeO_3$") might not have been a single phase. In the case of $MgGeO_3$, as well as $MgSiO_3$, phase transitions at atmospheric pressure among orthorhombic, monoclinic and proto-type orthorhombic phases do not induce a drastic change in the crystal structure. Therefore, for a powder sample of $MgGeO_3$, it would be very difficult to determine whether the sample is really single phase or composed of both the orthoenstatite-type and the clinoenstatite-type. The three unindexed lines in Robbins and Levin (1959) imply that their "clinoenstatite form" sample contained considerable amounts of an extra phase. Actually, these three lines can be successfully indexed for an orthoenstatite-type. In particular, these three lines ((1) d = 4.74, I/I_o = 35, (2) d = 3.35, I/I_o = 70, (3) d = 3.25, I/I_o = 14) could be regarded as the (400), (121), and (420) reflections, respectively. Another possibility is as follows: As will be seen in Table 2 and 4, since d_{200} of the clinoenstatite-type is slightly larger than d_{400} of the orthoenstatite-type, the d = 4.74 line would be d_{200} of clinoenstatite-type, and d = 4.70 line previously indexed as d_{200} of clinoenstatite-type might correspond to d_{400} of orthoenstatite-type. These interpretations seem to be reasonable, since Robbins and Levin (1959) prepared their sample "clinoenstatite form" $MgGeO_3$ above 1555°C, and on cooling, the orthoensatite-type can be expected to appear. Their "clinoenstatite form" $MgGeO_3$ sample should be assigned to our type B monoclinic phase, "clino-from proto" $MgGeO_3$, and should be distinguished from the type A (primary) monoclinic $MgGeO_3$.

Table 5. Crystal data of clinoenstatite-type $MgGeO_3$

	Robbins & Levin(1959)	Kirfel & Neuhaus(1974)	This study
a /Å	9.60	19.246(17)	9.6010(8)
b /Å	8.92	8.960(5)	8.9323(6)
c /Å	5.16	5.196(3)	5.1592(5)
β	100°49'	100°52'(3')	101.034(9)°
V /Å^3	434.01	880.0(9)	434.27(6)
Space Group	Cc or $C2/c$	$P2_1$ or $P2_1/m$	$C2/c$

Both "clino-from proto" and "clino-from ortho" $MgGeO_3$ crystals with very fine twinning structure (Fig. 1(iii), (iv)) were also confirmed to be crystallographically identical to the type A monoclinic $MgGeO_3$ grown at temperatures below 810°C (Fig. 1 (i), (ii)). No clinoenstatite-type $MgGeO_3$ crystals with P lattice type were found in this study. Detailed structure analyses of both orthoenstatite-type and clinoenstatite-type $MgGeO_3$ will be reported elsewhere.

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