An unquenchable perovskite phase of MgGeO₃ and comparison with MgSiO₃ perovskite

KURT LEINENWEBER, YANBIN WANG

CHiPR and Mineral Physics Institute, SUNY, Stony Brook, New York 11794-2100, U.S.A.

TAKEHIKO YAGI, HITOSHI YUSA

Institute for Solid State Physics, Roppongi, Minato-ku, Tokyo 106, Japan

ABSTRACT

An unquenchable polymorph of $MgGeO_3$, having a perovskite structure, has been observed using in situ X-ray diffraction in a diamond-anvil cell. The perovskite polymorph formed at room temperature and 12–14 GPa by pressure-induced phase transition from the lithium niobate phase of $MgGeO_3$. It is indexed on an orthorhombic lattice, with unit-cell parameters $a = 4.832(11)$, $b = 5.031(13)$, $c = 7.022(16)$ Å, and $V = 170.7(5)$ Å³ at 17.9 GPa. The transition is fully reversed during decompression.

Like $MgSiO_3$ perovskite, $MgGeO_3$ perovskite only becomes thermodynamically stable at very high pressures (over 23 GPa). Unlike $MgSiO_3$, it also becomes unstable relative to the lithium niobate phase during pressure release. The latter property accounts for the lack of observation of the perovskite phase in previous studies of $MgGeO_3$ as an analogue material.

INTRODUCTION

The $MgGeO_3$ composition has been used in the geosciences as an analogue of $MgSiO_3$ at low and intermediate pressures. The principle that germanates act as low-pressure analogues to silicates is based on the larger size of the Ge cation, which can allow pressure-induced transitions to higher coordination or denser topologies to occur more readily. This concept works very well in many germanates (cf. Ross and Navrotsky, 1988).

$MgGeO_3$ was surprising in that a perovskite polymorph, well known in $MgSiO_3$, was not observed. Ito and Matsui (1979) found a rhombohedral phase of $MgGeO_3$, only 1.8% denser than the ilmenite phase, in experimental products from 1000 °C and above 23 GPa. By comparison, the perovskite phase of $MgSiO_3$ is 7.0% denser than is $MgSiO_3$ ilmenite. The germanate was recently assigned the lithium niobate structure, space group $R3c$, from powder X-ray refinement (Taegyung Ko, personal communication).

The significance of the lithium niobate phase is that it points toward the possible existence of a perovskite polymorph of $MgGeO_3$. Megaw (1968) described a topological relationship between the lithium niobate structure and the perovskite structure, based on octahedral rotations, which provides an easy reaction pathway between the two phases. Pressure-induced phase transitions to perovskite occur at room temperature in compounds with the lithium niobate structure such as $MnTiO_3$ and $FeTiO_3$ (Ross et al., 1989; Leinenweber et al., 1991). On the basis of these systematics, the present study was undertaken to search for a perovskite polymorph of $MgGeO_3$, by recompression and in situ study of the lithium niobate phase.

EXPERIMENTAL

The starting material for these experiments was a powder sample of $MgGeO_3$ clinopyroxene, formed by reacting MgO and GeO_2 in a welded Pt capsule for 3 d at 1300 °C. The $MgGeO_3$ clinopyroxene product was identified by powder X-ray diffraction.

A sample of $MgGeO_3$ in the lithium niobate structure was synthesized from the pyroxene starting material in the uniaxial split-sphere apparatus (USSA 2000) at Stony Brook. The high-pressure synthesis conditions were 26 GPa and 1300 °C. The high-pressure assembly is described in detail by Wang et al. (1992). An X-ray powder pattern of the recovered sample matched the original data of Ito and Matsui (1979) for the lithium niobate form of $MgGeO_3$.

A small chip of the recovered sample was polished to make a standard 30-μm thin section. Thin foil was prepared by conventional Ar ion milling. TEM observations were carried out using a JEOL 200CX transmission electron microscope operating at 200 kV.

The $MgGeO_3$ sample was recompressed in a gasketed diamond-anvil pressure cell at the Institute for Solid State Physics, University of Tokyo. A 4:1 mixture of methanol to ethanol was used as a pressure medium, and pressure was measured using the ruby fluorescence technique. High-pressure powder diffraction data were taken using the film technique with a molybdenum rotating-anode X-ray source. Further details are given by Yagi et al. (1985).

RESULTS

TEM observations

The sample of $MgGeO_3$ with the lithium niobate structure recovered from high pressure and temperature exhibited pervasive twinning (Fig. 1A). Figure 1B is a selected-area electron diffraction pattern showing that the majority of the twins are characterized by reflection operations across the rhombohedral $(110)_{rhomb}$ plane. The contact planes of the twin domains are nearly parallel to the rhombohedral $(110)_{rhomb}$ planes; microtwins with a
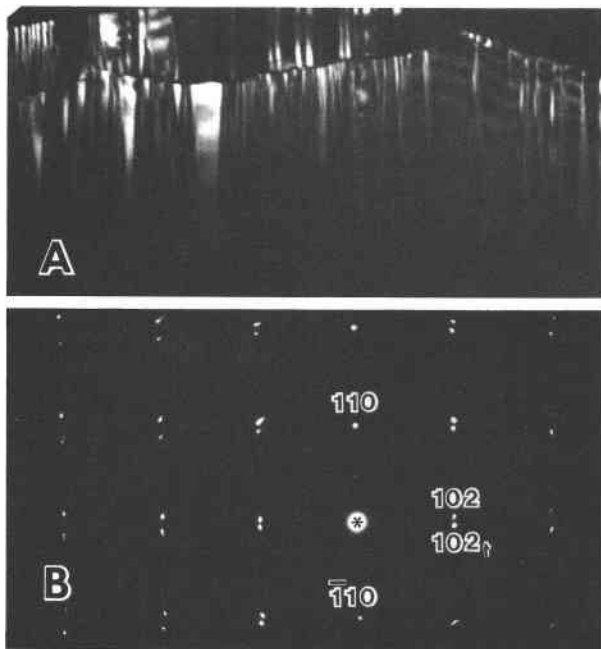
Fig. 1.　(A) TEM image down the pseudocubic axis [011] of MgGeO₃ in the lithium niobate structure, showing twin lamellae parallel to (110). (B) Selected-area electron diffraction pattern, viewed down [011]. The main splitting results from reflection twinning across (110).

TABLE 1. X-ray data for MgGeO₃ perovskite at 17.9 GPa

hkl	d_{obs}	d_{calc}	$I/I_{0\ est}$
002	3.516(17)	3.511	70
110		3.485	
020	2.533(9)	2.516	20
112	2.476(9)	2.473	100
200	2.412(8)	2.416	30
004	1.755(4)	1.756	50
220		1.742	
024	1.441(3)	1.440	40
132		1.444	
312	1.404(3)	1.406	30

Note: a = 4.832(11), *b* = 5.031(13), *c* = 7.022(16) Å, *V* = 170.7(5) Å³ (*Z* = 4).

domain width below 0.1 μm are commonly observed (Fig. 1A). The twin angle measured from this image is 5.0°. The microstructure observed in this sample resembles that in the rhombohedral LaGaO₃ perovskite after the *Pbnm-R$\bar{3}$c* transition above 150 °C (Wang et al., 1991), but with a larger twin angle.

Compression experiment

Five powder patterns of the MgGeO₃ lithium niobate polymorph were taken between 0 and 10 GPa, prior to the perovskite transformation. No change in structure was observed in this pressure range. A zero-pressure bulk modulus K_0 = 213(10) Mbar and zero-pressure volume V_0 = 47.0(1) Å³ pfu are obtained from a second-order Birch-Murnaghan fit to the data.

A change in the optical appearance of the sample in transmitted light was observed during continued compression. The sample had a finely divided appearance up to 12.2 GPa, resulting from the pervasive twinning in each grain. At 12.2 GPa, a few large grains were observed to become clear. The optical change began in the bulk of the sample at 12.9 GPa. By 13.3 GPa, about half of the sample appeared more transparent than before, and by 14.0 GPa the sample consisted entirely of transparent grains, with an average grain size of 10 μm. The transparency is presumed to result from a loss of the (110) twin boundaries during a pressure-induced phase transition, which results in higher transmittance of light.

An X-ray pattern taken at 18 GPa revealed a clearly different crystal structure. The new structure was indexed as orthorhombic GdFeO₃-type perovskite. The indexing and

cell parameters are shown in Table 1. The measured volume decrease for the transformation from lithium niobate to perovskite at high pressure is about 3%. This gives a volume change for the ilmenite to perovskite transition of about 6%, similar to the 7.0% volume difference between MgSiO₃ ilmenite and perovskite at ambient pressure.

In optical observations made during decompression from the perovskite phase, the finely divided appearance of the lithium niobate phase reappeared. The onset of the reversal was first noticed at 12.9 GPa, and most of the sample had reverted to the low-pressure phase by 10.7 GPa. An X-ray pattern of the fully unloaded sample showed that the sample had the lithium niobate structure, with no significant change in the zero-pressure cell parameters compared with the sample before compression. The transition was therefore fully reversed at room temperature.

DISCUSSION

TEM observations

The twin-domain structure observed in the MgGeO₃ crystals with the lithium niobate structure converted from perovskite may be explained as analogous to LaGaO₃ perovskite, which transforms from the orthorhombic to the rhombohedral phase during heating (Wang et al., 1991). Both structures observed in this study, the *R3c* lithium niobate and the *Pbnm* perovskite, may be obtained from the ideal cubic perovskite structure by displacive motions. These motions may be described to a first approximation as rigid rotations of cation-anion octahedra (Burns and Glazer, 1990). For MgGeO₃, it is assumed that the Ge octahedron is rigid and the Mg polyhedron is fully deformable. Adopting Glazer's notation for cation octahedral rotation in perovskite, the *Pbnm* perovskite structure may be described by two out-of-phase rotations of octahedra about the cubic [100] and [010] axes, and one in-phase rotation about [001]. On the other hand, both *R$\bar{3}$c* perovskite and *R3c* lithium niobate are a result of simultaneous out-of-phase rotations about the three cubic axes of the perovskite structure. Thus, both transitions are characterized by switching from out-of-phase rotation to in-phase rotations about the cubic [001] axis.

During the transition from orthorhombic perovskite to lithium niobate, all three mirror planes in the perovskite are lost. However, for only one of these, the orthorhom-

bic (001) mirror, the disappearance of the mirror plane is accompanied by a change in the sense of octahedral rotation from the ideal perovskite geometry. It is the disappearance of this mirror plane that results in twinning, with a large twin angle across planes parallel to the rhombohedral (110) planes. This twinning is visible in the selected-area electron diffraction pattern in Figure 1, which is a view of the pseudocubic axes [110]* and [101]*, viewed approximately down the third pseudocubic axis [011].* Other twin planes, though theoretically present as a result of the loss of the other two mirror planes, are not obvious in the TEM images because of their small twin angles.

The twin angle measured from the diffraction pattern in Figure 1 is 5.0°. This is in good agreement with the theoretical twin angle, obtained from the angle between the reciprocal lattice vectors [110]* and [101]* in the rhombohedral basis. This angle is 92.6°, which gives a twin half-angle of 2.6°, or a twin angle of 5.2°.

Systematics and comparison with $MgSiO_3$

Based on these results, it is apparent that $MgGeO_3$ is a perovskite-forming compound, like $MgSiO_3$, and so the difference between the two compounds is not as great as previously thought. However, it is also evident that the large size of Ge compared with Si does not enhance the thermodynamic stability of the perovskite phase; the perovskite is thermodynamically stable only at over 23 GPa in both materials. In addition, the presence of Ge causes the perovskite to become unstable relative to the kinetically accessible lithium niobate phase at ambient conditions.

A systematic comparison can be made with other oxides where high-pressure perovskite is destabilized relative to lithium niobate at ambient conditions. This behavior is seen in oxides with cations similar in size to Mg and Ge ($MnTiO_3$: Ross et al., 1989; and $MnSnO_3$ and $FeTiO_3$: Leinenweber et al., 1991). The condition that leads to this behavior is the presence of a large tetravalent cation (e.g., Ge^{4+} with $r = 0.540$ Å: Shannon and Prewitt, 1969) in the octahedral site, with a small divalent cation (e.g., Mg^{2+} with $r = 0.89$ Å) in the large site. During the octahedral rotations leading from the perovskite structure to the lithium niobate structure described by Megaw (1968), the large perovskite site is split into two edge-sharing octahedra, one vacant and one occupied, of the lithium niobate structure. The latter structure is more appropriate for the relative ionic sizes when there is no confining pressure.

For $MgSiO_3$, the relative sizes of the cations are such that a perovskite structure can be maintained at room pressure, albeit with a large amount of orthorhombic dis-

tortion to accommodate the relatively small Mg cation; similar arguments hold for $MnGeO_3$, $CdGeO_3$, $CaGeO_3$, $CdTiO_3$, and others.

The difference between the two groups of perovskite can be systematized in terms of the Goldschmidt tolerance factor for perovskite, $t = (A-O)/\sqrt{2}(B-O)$, where A-O and B-O are the cation to O distances. We use the sixfold B and eightfold A ionic radii of Shannon and Prewitt (1969), with $r(O^{2-}) = 1.40$ Å. The high-pressure perovskite phases that transform to lithium niobates at low pressure all have tolerance factors below about 0.84, whereas stable perovskite phases have tolerance factors above 0.84.

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