An unquenchable perovskite phase of MgGeO$_3$ and comparison with MgSiO$_3$ perovskite

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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 $V = 170.76(5)$ Å$^3$ 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 germainate 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 re-compression 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)$_{\text{rhom}}$ plane. The contact planes of the twin domains are nearly parallel to the rhombohedral (110)$_{\text{rhom}}$ 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).

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-R3c 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 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. A few large grains were observed to become clear. The optical change began in the bulk of the sample 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 displaceable 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].

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.

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

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

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 [10]* and [01]* 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 MgSiO₃

Based on these results, it is apparent that MgGeO₃ is a perovskite-forming compound, like MgSiO₃, 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 (MnTiO₃; Ross et al., 1989; and MnSnO₃ and FeTiO₃; Leinenweber et al., 1991). The condition that leads to this behavior is the presence of a large tetravalent cation (e.g., Ge⁴⁺ with r = 0.540 Å; Shannon and Prewitt, 1969) in the octahedral site, with a small divalent cation (e.g., Mg²⁺ 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 MgSiO₃, 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 distortion to accommodate the relatively small Mg cation; similar arguments hold for MnGeO₃, CdGeO₃, CaGeO₃, CdTiO₃, 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)/√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(O²⁻) = 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.

Acknowledgments

The authors wish to thank C.T. Prewitt for valuable discussions and H. Nekvasil for preparation of the MgGeO₃ clinopyroxene starting material. Thorough reviews were provided by Dion Heinz and an anonymous reviewer. Synthesis of high-pressure MgGeO₃ was funded by NSF grant EAR-8917563. Travel to Japan was funded by a fellowship from JISTEC.

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