Complete Fe-Mg solid solution in lithium niobate and perovskite structures in titanates at high pressures and temperatures

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ABSTRACT

A new high-pressure $MgTiO_3$ phase with the lithium niobate structure ($R3c$) has been recovered from experiments at 21 GPa and 1200 °C. Phases with the lithium niobate structure were also synthesized for intermediate compositions between $FeTiO_3$ and $MgTiO_3$ and their lattice parameters determined. Previous thermodynamic calculations indicated the stable $FeTiO_3$ phase at high pressure has the perovskite structure while the lithium niobate polymorph is a metastable quench phase. This suggests that these magnesium-iron titanates with lithium niobate structures may also be metastable quench phases from perovskite. This example of a complete solid solution between Fe and Mg in the lithium niobate structure probably reveals a case of complete solid solution between Fe and Mg in the A sites of the perovskite structure.

INTRODUCTION

Ilmenite occurs as a common accessory mineral in many igneous and metamorphic rocks where ilmenite-geikielite solid-solution minerals, in conjunction with other minerals such as hematite and olivine, can be used as indicators of the state (T, P, f_{O_2}) of crystallization (e.g., Frost et al. 1988). Phase relations between ilmenite ($FeTiO_3$) and geikielite ($MgTiO_3$) at high pressures are of interest both because of the presence of these minerals in ultra-high-pressure rocks such as the Alpe Arami peridotite, where ilmenite grains with unique structures were found as inclusions in olivine (Dobrzhinetskaya et al. 1996), and because of the importance of the silicate ilmenite and perovskite phases in the Earth's mantle. At mantle pressures the complete solid solution of Mg and Fe, so common in crustal minerals, sometimes breaks down, as in the limited substitution of Fe in $(Mg,Fe)SiO_3$ ilmenite and perovskite. Examining Mg-Fe solid solution in a system with Fe-rich perovskite might help to clarify the behavior of Fe in the mantle.

Under ambient conditions both $FeTiO_3$ and $MgTiO_3$ are stable in the ilmenite structure ($R\bar{3}$), and complete solid solution occurs (e.g., Wood et al. 1991). Syono et al. (1980) described a phase transition at high pressures (20 GPa and 1000 °C) of $FeTiO_3$ between the ilmenite structure and a hexagonal structure, later determined to be the lithium niobate structure (Leinenweber et al. 1995). Leinenweber et al. (1991) observed the transformation in situ at 16 GPa and room temperature of $FeTiO_3$ in the lithium niobate structure to an orthorhombic perovskite polymorph. During quenching this $FeTiO_3$ perovskite reverted to the lithium niobate structure (Leinenweber et al. 1991).

In situ Raman spectroscopy detected no phase transitions in $MgTiO_3$ up to 27 GPa at room temperature and no phase change or order-disorder transition up to 1547 °C at 1 bar (Reynard and Guyot 1994). Ito and Matsui (1979) observed $MgTiO_3$ to decompose to MgO and a dense form of TiO_2 at 1000 °C and 20–25 GPa. This apparent difference in behavior of $FeTiO_3$ and $MgTiO_3$ suggested the possibility of more complicated phase relations between the two minerals at high pressures. Liu (1975) reported an ilmenite-perovskite transition at 14 GPa and 1400–1800 °C in an experiment using a natural ilmenite with approximately 40 mol% $MgTiO_3$, but his results are difficult to interpret because of the presence of up to 12 mol% Fe_2O_3 and other minor impurities.

The purpose of the present study is to examine further the effect of high pressure (21 GPa) and high temperature (1200 °C) on $MgTiO_3$ and to begin to examine $FeTiO_3$-$MgTiO_3$ phase relations at high pressures (15–21 GPa) and high temperatures (1200–1400 °C).

EXPERIMENTAL METHODS

Sample synthesis

Geikielite ($MgTiO_3$) was synthesized from stoichiometric quantities of MgO and TiO_2. The mixture was first heated at 1200 °C for 48 h and then reground and heated for 24 h at 1450 °C. X-ray diffraction patterns of the product show only geikielite peaks, with no MgO, TiO_2, or other magnesium titanates.

$MgTiO_3$-$FeTiO_3$ ilmenite samples were synthesized from mixtures of predried Fe_2O_3 and TiO_2 plus $MgTiO_3$. The mixture was ground in an agate mortar for 1 h and then heated in a platinum crucible at 1200 °C. The oxygen fugacity was controlled at about $10^{-10.77}$ by flowing CO and CO_2. To control Fe loss to the platinum for each

TABLE 1. Unit-cell and refinement parameters for lithium niobate structures

	MgTiO$_3$	(Mg$_{0.8}$Fe$_{0.2}$)TiO$_3$	(Mg$_{0.5}$Fe$_{0.5}$)TiO$_3$	(Mg$_{0.2}$Fe$_{0.8}$)TiO$_3$	FeTiO$_3$*
a (Å)	5.07580(24)	5.08516(46)	5.10126(39)	5.11470(26)	5.12334(5)
c (Å)	13.71325(90)	13.72435(171)	13.73818(156)	13.75560(107)	13.76020(17)
V (Å^3)	305.970(34)	307.349(62)	309.610(61)	311.638(43)	312.796
R_{wp}	0.1263	0.1429	0.1223	0.1163	
R_p	0.0945	0.1108	0.0867	0.0845	
χ^2	1.346	1.393	1.827	1.888	

* FeTiO$_3$ unit-cell parameters are from Leinenweber et al. (1995).

composition two lots were reacted in the same crucible and the first was thrown away. The purity of the products was confirmed by XRD and microprobe. The molar Fe^{3+}/ Fe$_{tot}$, determined through Mössbauer spectroscopy (details of Mössbauer technique given in Fei et al. 1994), was < 0.05 both before and after the high-pressure synthesis.

High-pressure experiments

Experiments were performed in a multi-anvil press at the Geophysical Laboratory. Two types of assemblies were used; preliminary experiments used a 4 mm long rhenium foil combination sample capsule and furnace with a thermal gradient of > 200 °C. Temperature was measured in the middle of the capsule (the hot zone) with a W5%Re-W26%Re thermocouple. In subsequent experiments pure MgTiO$_3$ samples were run in platinum capsules, whereas samples containing Fe were run in gold or molybdenum capsules. The capsules (0.5–1 mm in diameter by 1–2 mm in length) for this assembly were separated by a MgO sleeve from a rhenium foil heater and have a thermal gradient of < 50 °C. Temperature was measured with W5%Re-W26%Re (type C) thermocouples. Both sample assemblies were set in pressure media of MgO octahedra with 8 or 10 mm edge lengths (smaller assemblies were used for higher pressure runs). Eight tungsten carbide cubes with a corner truncation of 3 or 5 mm applied pressure on the cell. Samples were fully pressurized at a rate of 2–2.5 GPa/h and then heated at 20 °C/min. At the end of the experiment, samples were thermally quenched by cutting off power to the furnace, then slowly depressurized. The pressure calibration at high temperature (e.g., 1200 °C) was established by determining the phase relations in the Mg-Si-O system. Details of the pressure calibration and determination of the thermal gradient of the cell are given by Bertka and Fei (1996).

Analysis of products

After the experiments the samples and capsules were embedded in epoxy and polished to examine the length of the capsule. Major-element mineral analyses were acquired using a JEOL JXM 8900 microprobe. An acceleration voltage of 15 kV and a beam current 20 nA were used. The locations for analysis and imaging were obtained in back-scattered electron mode.

X-ray patterns were obtained on a Scintag XDS-2000 powder diffractometer using Cu$K\alpha$ radiation with a solid-state Ge detector. Data for lattice parameter calculations were collected from 3 to 120° 2θ for MgTiO$_3$ and 10 to 70° 2θ for the intermediate compositions. Data collection was in step-scan mode with a 0.02° step size and a 6 s count time. Because of the small volume of the sample (3–4 mg) the Soller slits were adjusted to minimize the area irradiated and to maximize intensity.

RESULTS

Pure geikielite starting material, after being held for 3 h at 21 GPa and 1200 °C in the large thermal gradient assembly, changed color from white to gray in the hot zone of the sample capsule. Microprobe analysis detected no contamination of the sample and showed a stoichiometric MgTiO$_3$ composition throughout the sample capsule. However, a very small amount of reduction of Ti^{4+} to Ti^{3+} (<0.5%) could account for the gray color and would not be otherwise detectable in our work.

The gray crystals from the middle of the sample were analyzed using powder X-ray diffraction. Disappearance of $h0l$ peaks with l = odd from the starting material pattern indicated the presence of a c glide. We used FeTiO$_3$ in the lithium niobate structure (Leinenweber et al. 1995) as a starting model and refined the structure of the high-pressure MgTiO$_3$ using the Rietveld refinement program GSAS (Larson and Von Dreele 1988). Displacement parameters were set at reasonable values and not refined. A fit to the lithium niobate structure ($R3c$) was achieved with R_{wp} = 0.1278 (Table 1). The volume of the new phase (305.97 Å^3) is 0.5% smaller than MgTiO$_3$ in the ilmenite structure, which has lattice parameters: a = 5.05478(26), c = 13.8992(7) Å (Wechsler and Von Dreele 1989). Mg is on site $6a$ with z = 0.2854(7), Ti is also on site $6a$ with z = −0.0022(7), and O is on site $18b$ with x = 0.0556(14), y = 0.3560(40), and z = 0.0718(14).

Three lithium niobate phases with compositions intermediate between FeTiO$_3$ and MgTiO$_3$, 20, 50, and 80 mol% geikielite starting material, were synthesized at 15, 16, and 21 GPa, respectively, and 1250–1350 °C. Although microprobe analyses of the products found them to be fairly homogeneous (Mg$_{0.19(2)}$Fe$_{0.81(2)}$Ti$_{1.000(9)}$O$_3$, Mg$_{0.51(4)}$Fe$_{0.49(3)}$Ti$_{1.00(1)}$O$_3$, and Mg$_{0.81(3)}$Fe$_{0.19(1)}$Ti$_{1.00(1)}$O$_3$), the 50 and 80 mol% geikielite samples contained some ilmenite polymorph. This indicates either that K_D is close to one for Mg and Fe between the low- and high-pressures phases or that the ilmenite could have formed during the quench, without compositional re-equilibration. The ilmenite content was refined to 11 wt% in the 50
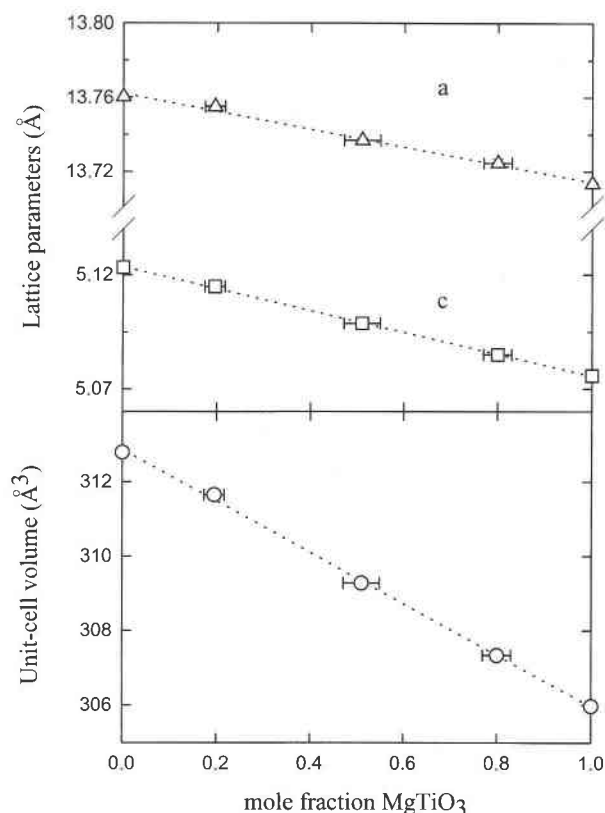
FIGURE 1. Unit-cell parameters vs. composition for $FeTiO_3$-$MgTiO_3$ lithium niobate solid solution. Horizontal error bars reflect the compositional variability within each sample charge. Vertical error bars are the same size or smaller than the symbols. $FeTiO_3$ data are from Leinenweber et al. (1995).

mol% sample and 36 wt% in the 80 mol% sample. The lattice parameters refined for the lithium niobate phases indicate no significant volume of mixing in the lithium niobate phase solid-solution series (Fig. 1).

DISCUSSION

$MgTiO_3$ is one of several ABO_3 compounds, including $FeTiO_3$, $MnTiO_3$, $MnSnO_3$, and $MgGeO_3$ that form lithium niobate structures at high pressures (Leinenweber et al. 1991; Ko and Prewitt 1988; Ito and Matsui 1979). Three of these compounds, $FeTiO_3$, $MnSnO_3$ (Leinenweber et al. 1991), and $MnTiO_3$ (Ross et al. 1989), have been observed in situ to transform from the lithium niobate structure to a perovskite structure at high pressure and room temperature; upon decompression the perovskite converts spontaneously back to the lithium niobate form. The instability of the perovskite polymorphs possibly results from the comparatively small difference in radius of the A and B cations when compared to more stable perovskite compounds such as $CaTiO_3$ (Leinenweber et al. 1991). The synthesis of $MgTiO_3$-$FeTiO_3$ lithium niobate polymorphs at intermediate compositions indicates the existence of a high-pressure solid solution between the Fe and Mg end-member compositions and

suggests that $MgTiO_3$ and $FeTiO_3$ have isostructural high-pressure forms.

$FeTiO_3$ in the lithium niobate structure has previously been described as a quench phase from a perovskite structure (Mehta et al. 1994; Leinenweber et al. 1991). Mehta et al. (1994) used calorimetry to determine the enthalpy of transformation from lithium niobate to ilmenite. The phase diagram predicted using this enthalpy of transformation and the change in volume between the ilmenite and lithium niobate structures disagreed with the experimentally determined phase diagram of Syono et al. (1980). Mehta et al. (1994) found that the phase diagram of Syono et al. could be more realistically explained as the boundary between ilmenite and the orthorhombic perovskite polymorph of $FeTiO_3$ described by Leinenweber et al. (1991). If this is correct the $MgTiO_3$ with the lithium niobate structure may also be a perovskite at high pressure and temperature, as may the $(Mg,Fe)TiO_3$ lithium niobate solid solutions. This would be the first case of a complete solid solution between Fe and Mg, presumably on the A site, in the perovskite structure.

The 50 mol% $FeTiO_3$ lithium niobate polymorph was synthesized at 17 GPa and 1200 °C. Our preliminary estimates of the phase diagram of the $MgTiO_3$-$FeTiO_3$ join indicate that the phase transition from ilmenite for this composition might occur at a pressure as low as 15 GPa. This is particularly interesting because, in a typical kimberlitic ilmenite, geikielite contents range from 25–60% (Haggerty 1991). Several authors (e.g., Haggerty and Sautter 1990; Ringwood et al. 1992) have suggested that some kimberlites might originate at such high pressures. Examining the crystal structure and textures of ilmenites from these kimberlites might verify their high-pressure origin. Dobrzhinetskaya et al. (1996) found topotaxially oriented $(Fe,Mg)TiO_3$ rod-shaped precipitates with orthorhombic crystal structures in olivine, which they proposed as being metastable decomposition structures from perovskite. Because our study shows that the pressure for the transition of the ilmenite to perovskite (or lithium niobate) structure increases with Mg content, these precipitates, if formed from $(Fe,Mg)TiO_3$ perovskite, would indicate even greater depths of origin for the Alpe Arami peridotite.

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