

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 MgTiO₃ 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 FeTiO₃ and MgTiO₃ and their lattice parameters determined. Previous thermodynamic calculations indicated the stable FeTiO₃ 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*_{O₂}) of crystallization (e.g., Frost et al. 1988). Phase relations between ilmenite (FeTiO₃) and geikielite (MgTiO₃) 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)SiO₃ 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 FeTiO₃ and MgTiO₃ are stable in the ilmenite structure (*R3̄*), 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 FeTiO₃ 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 FeTiO₃ in the lithium niobate structure to an orthorhombic perovskite polymorph. During quenching this FeTiO₃ perovskite reverted to the lithium niobate structure (Leinenweber et al. 1991).

In situ Raman spectroscopy detected no phase transi-

tions in MgTiO₃ 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 MgTiO₃ to decompose to MgO and a dense form of TiO₂ at 1000 °C and 20–25 GPa. This apparent difference in behavior of FeTiO₃ and MgTiO₃ 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% MgTiO₃, but his results are difficult to interpret because of the presence of up to 12 mol% Fe₂O₃ 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 MgTiO₃ and to begin to examine FeTiO₃-MgTiO₃ phase relations at high pressures (15–21 GPa) and high temperatures (1200–1400 °C).

EXPERIMENTAL METHODS

Sample synthesis

Geikielite (MgTiO₃) was synthesized from stoichiometric quantities of MgO and TiO₂. 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, TiO₂, or other magnesium titanates.

MgTiO₃-FeTiO₃ ilmenite samples were synthesized from mixtures of predried Fe₂O₃ and TiO₂ plus MgTiO₃. 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 CO₂. 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 *
<i>a</i> (Å)	5.07580(24)	5.08516(46)	5.10126(39)	5.11470(26)	5.12334(5)
<i>c</i> (Å)	13.71325(90)	13.72435(171)	13.73818(156)	13.75560(107)	13.76020(17)
<i>V</i> (Å ³)	305.970(34)	307.349(62)	309.610(61)	311.638(43)	312.796
<i>R</i> _{wp}	0.1263	0.1429	0.1223	0.1163	
<i>R</i> _p	0.0945	0.1108	0.0867	0.0845	
χ ²	1.346	1.393	1.827	1.888	

* FeTiO₃ 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 Fe³⁺/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 MgTiO₃ 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 CuKα radiation with a solid-state Ge detector. Data for lattice parameter calculations

were collected from 3 to 120° 2θ for MgTiO₃ 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 MgTiO₃ composition throughout the sample capsule. However, a very small amount of reduction of Ti⁴⁺ to Ti³⁺ (<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 FeTiO₃ in the lithium niobate structure (Leinenweber et al. 1995) as a starting model and refined the structure of the high-pressure MgTiO₃ 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 Å³) is 0.5% smaller than MgTiO₃ 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 6*a* with *z* = 0.2854(7), Ti is also on site 6*a* with *z* = -0.0022(7), and O is on site 18*b* with *x* = 0.0556(14), *y* = 0.3560(40), and *z* = 0.0718(14).

Three lithium niobate phases with compositions intermediate between FeTiO₃ and MgTiO₃, 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)}O₃, Mg_{0.51(4)}Fe_{0.49(3)}Ti_{1.00(1)}O₃, and Mg_{0.81(3)}Fe_{0.19(1)}Ti_{1.00(1)}O₃), 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

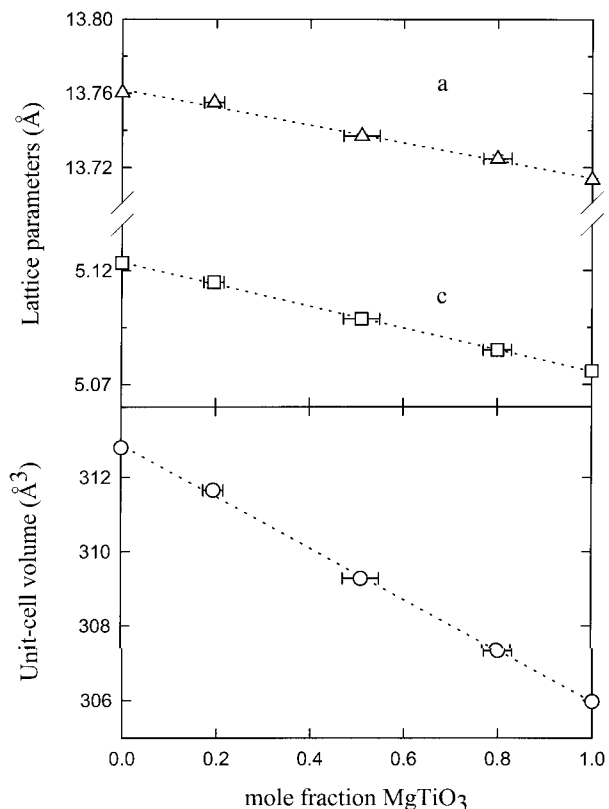


FIGURE 1. Unit-cell parameters vs. composition for FeTiO₃-MgTiO₃ lithium niobate solid solution. Horizontal error bars reflect the compositional variability within each sample charge. Vertical error bars are the same size or smaller than the symbols. FeTiO₃ data are from Leinenweber et al. (1995).

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

MgTiO₃ is one of several ABO₃ compounds, including FeTiO₃, MnTiO₃, MnSnO₃, and MgGeO₃ that form lithium niobate structures at high pressures (Leinenweber et al. 1991; Ko and Prewitt 1988; Ito and Matsui 1979). Three of these compounds, FeTiO₃, MnSnO₃ (Leinenweber et al. 1991), and MnTiO₃ (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 CaTiO₃ (Leinenweber et al. 1991). The synthesis of MgTiO₃-FeTiO₃ 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 MgTiO₃ and FeTiO₃ have isostructural high-pressure forms.

FeTiO₃ 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 FeTiO₃ described by Leinenweber et al. (1991). If this is correct the MgTiO₃ with the lithium niobate structure may also be a perovskite at high pressure and temperature, as may the (Mg,Fe)TiO₃ 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% FeTiO₃ lithium niobate polymorph was synthesized at 17 GPa and 1200 °C. Our preliminary estimates of the phase diagram of the MgTiO₃-FeTiO₃ 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 kimberlite 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)TiO₃ 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)TiO₃ perovskite, would indicate even greater depths of origin for the Alpe Arami peridotite.

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REFERENCES CITED

- Bertka, C.M. and Fei, Y. (1996) Constraints on the mineralogy of an iron-rich Martian mantle from high-pressure experiments. *Planetary and Space Science*, 44, 1269–1276.
- Dobrzhinetskaya, L., Green H.W., and Wang S. (1996) Alpe Arami: a peridotite massif from depths of more than 300 kilometers. *Science*, 271, 1841–1845.
- Fei Y., Virgo D., and Mysen B.O. (1994) Temperature-dependent electron delocalization in (Mg,Fe)SiO₃ perovskite. *American Mineralogist*, 79, 826–837.

- Frost, B.R., Lindsley, D.H., and Andersen, D.J. (1988) Fe-Ti oxide-silicate equilibria: Assemblages with fayalitic olivine. *American Mineralogist*, 73, 727–740.
- Haggerty, S.E. (1991) Oxide mineralogy of the upper mantle. In *Mineralogical Society of America Reviews in Mineralogy*, 25, 355–416.
- Haggerty, S.E. and Sautter, V. (1990) Ultradeep (greater than 300 kilometers), ultramafic upper mantle xenoliths. *Science*, 248, 993–996.
- Ito, E. and Matsui, Y. (1979) High-pressure transformations in silicates, germanates and titanates with ABO_3 stoichiometry. *Physics and Chemistry of Minerals*, 4, 265–273.
- Ko, J. and Prewitt, C.T. (1988) High-pressure phase transition in $MnTiO_3$ from the ilmenite to the $LiNbO_3$ structure. *Physics and Chemistry of Minerals*, 15, 355–362.
- Larson, A.C. and Von Dreele, R.B. (1988) GSAS Generalized structure analysis system. LAUR 86-748. Los Alamos National Laboratory, Los Alamos, NM 87545.
- Leinenweber, K., Utsumi, W., Tsuchida, Y., Yagi, T., and Kurita, K. (1991) Unquenchable high-pressure perovskite polymorphs of $MnSnO_3$ and $FeTiO_3$. *Physics and Chemistry of Minerals* 18, 244–250.
- Leinenweber K., Linton J., Navrotsky A., Fei Y., and Parise J.B. (1995) High-pressure perovskites on the join $CaTiO_3$ - $FeTiO_3$. *Physics and Chemistry of Minerals*, 22, 251–258.
- Liu, L.G. (1975) High-pressure phase transformations and compressions of ilmenite and rutile, I. experimental results. *Physics of the Earth and Planetary Int.*, 10, 167–176.
- Mehta, A., Leinenweber, K., and Navrotsky, A. (1994) Calorimetric study of high pressure polymorphism in $FeTiO_3$: the stability of the perovskite phase. *Physics and Chemistry of Minerals*, 21, 207–212.
- Reynard B. and Guyot F. (1994) High-temperature properties of geikielite ($MgTiO_3$ -ilmenite) from high temperature high-pressure Raman Spectroscopy—some implications for $MgSiO_3$ -ilmenite. *Physics and Chemistry of Minerals*, 21, 441–450.
- Ringwood, A.E., Kesson, S.E., Hibberson, W., and Ware, N. (1992) Origin of kimberlites and related magmas. *Earth and planetary Science Letters*, 113, 521–538.
- Ross, N.L., Ko, J., and Prewitt, C.T. (1989) A new phase transition in $MnTiO_3$: $LiNbO_3$ -perovskite structure. *Physics and Chemistry of Minerals*, 16, 621–629.
- Syono, Y., Yamauchi, H., Ito, A., Someya, Y., Ito, E., Matsui, Y., Akaogi, M., and Akimoto, S. (1980) Magnetic properties of the disordered ilmenite $FeTiO_3$ II synthesized at very high pressure. In H. Watanabe, S. Iida, and Sugimoto, Eds., *Ferrites: Proceedings of the International Conference*, p. 192–195. Tokyo, Japan.
- Wechsler, B. and Von Dreele, R.B. (1989) Structure refinements of Mg_2TiO_4 , $MgTiO_3$ and $MgTi_2O_5$ by time-of-flight neutron powder diffraction. *Acta Crystallographica*, B45, 542–549.
- Wood, B.J., Nell, J., and Woodland, A.B. (1991) Macroscopic and microscopic thermodynamic properties of oxides. In *Mineralogical Society of America Reviews in Mineralogy*, 25, 265–299.

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