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In situ X-ray diffraction study of phase transitions of $FeTiO_3$ at high pressures and temperatures using a large-volume press and synchrotron radiation

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ABSTRACT

The phase transformation from ilmenite to perovskite in $FeTiO_3$ was directly observed using synchrotron-based X-ray diffraction and a large-volume press. The perovskite phase is temperature quenchable at 20 GPa and converts into the $LiNbO_3$ phase at pressures below 15 GPa at room temperature. The $LiNbO_3$ phase transforms into the ilmenite phase at 10 GPa and 673 K. However, the back-transformation from the ilmenite to the $LiNbO_3$ phase was not observed, thus strongly suggesting that the $LiNbO_3$ phase is not thermodynamically stable but rather a retrogressive phase formed from perovskite during decompression at room temperature.

By cycling the pressure up and down at temperatures between 773 and 1023 K, the perovskite-ilmenite transformation could be observed in both directions, thus confirming that perovskite is the true high-pressure phase with respect to the ilmenite phase at lower pressures. The phase boundary of the perovskite-ilmenite transformation thus determined in this study is represented by P (GPa) = 16.0 (±1.4) – 0.0012 (±0.0014) T (K), which is inconsistent with $P = 25.2 - 0.01\ T$ (K) reported previously (Syono et al. 1980). The discrepancy could be attributed to the different experimental methods (i.e., in situ vs. quench) used in the two studies. The ilmenite-perovskite phase boundary with such a small slope would potentially serve as a useful geobarometer for ilmenite-bearing rocks derived from the deep mantle or for those shocked in meteor craters.

Keywords: Ilmenite, perovskite, $LiNbO_3$, phase transformation, X-ray diffraction, high pressure

INTRODUCTION

Among the ABO_3 compounds, ilmenite ($FeTiO_3$) represents an important structural type in which the oxygen anions form a hexagonal closest-packing array with both A and B cations orderly occupying two thirds of the octahedral sites and leaving one third of the octahedral sites vacant. Because enstatite ($MgSiO_3$), the second most abundant mineral in the upper mantle, adopts the ilmenite structure at high pressure (21–23 GPa) and high temperature (1473–1873 K), $MgSiO_3$-ilmenite (known as akimotoite) is believed to be one of the phases present in the lower part of the transition zone (e.g., Ito and Yamada 1982; Sawamoto 1987). Knowledge of the phase transformations of ilmenite ($FeTiO_3$) under high pressures and temperatures would provide valuable information regarding high-pressure phases of $MgSiO_3$ at much higher pressure conditions. Ilmenite is also an important accessory mineral in igneous and metamorphic rocks, commonly present as $(Mg,Fe)TiO_3$ solid solution in kimberlites, with $MgSiO_3$ ranging from 25 to 60 mol% (Haggerty 1991). It is generally believed that most of the kimberlites originate at depths between 150 and 250 km, based on the presence of diamond and coesite and the absence of stishovite (Mitchell 1986; Wyatt and Lawless 1984; Schultze 1984). There are, however, indications that some kimberlites may come from depths greater than 300 km (Haggerty and Sautter 1990; Ringwood et al. 1992). Information on high-pressure phase transformations in ilmenite would potentially serve as a useful geobarometer for ilmenite-bearing rocks either shocked by a meteorite or being uplifted from the deep mantle (Mehta et al. 1994; Dobrzhinetskaya et al. 1996; Linton et al. 1999). The phase transformations of ilmenite and its structural analogs at high pressures and temperatures have, therefore, received continual attention in the past 30 years.

In a study with the laser-heated diamond-anvil cell, Liu (1975) first reported that a natural ilmenite $(Fe,Mg)TiO_3$ with ~40 mol% $MgTiO_3$ transformed into the perovskite structure and then disproportionated into oxides, (Mg,Fe)O + a cubic phase of TiO_2, at pressures of 14 and 25 GPa, respectively, and temperatures of 1673–2073 K. Ito and Matsui (1979) found that a synthetic ilmenite ($FeTiO_3$) first transformed into the corundum phase at 15 GPa, which in turn broke down into a mixture of FeO and TiO_2 (with α-PbO_2 structure) at higher pressures around 1273 K. Syono et al. (1980) determined the phase boundary between ilmenite and the high-pressure phase as P (GPa) = $25.2 - 0.01\ T$ (K) and also concluded that the high-pressure phase is disordered with the corundum structure. Single-crystal study of $MnTiO_3$ (with the ilmenite structure) revealed a high-pressure polymorph, $MnTiO_3$ II, which possesses the $LiNbO_3$ structure and which transforms into $MnTiO_3$ with the perovskite structure at higher pressures (Ko and Prewitt 1988; Ross et al. 1989). Because $MnTiO_3$ (ilmenite str.) is a structural analog to $FeTiO_3$ (ilmenite),

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it was suggested that similar transformations would take place in $FeTiO_3$. Such predictions were subsequently confirmed when the quenchable lithium niobate phase was obtained from $FeTiO_3$-ilmenite at 18 GPa and 1473 K and was then found to transform into the perovskite phase at pressures above 16 GPa at room temperature (Leinenweber et al. 1991). The ilmenite-corundum phase boundary was revised accordingly, with $LiNbO_3$ being the high-pressure phase (see Fig. 1 in Mehta et al. 1994). However, based on calorimetric measurements of the ilmenite and lithium niobate polymorphs of $FeTiO_3$, Mehta et al. (1994) obtained an enthalpy change (ΔH = 13.5 kJ/mol) for the ilmenite-$LiNbO_3$ transformation, which yielded an intercept of the *P-T* phase boundary at 0 K at 40 GPa. This value is difficult to reconcile with that at 25 GPa derived from the phase boundary of Syono et al. (1980). Thermodynamic calculations also indicate that Syono's phase boundary is more consistent with the ilmenite-perovskite phase transformation than with the ilmenite-$LiNbO_3$ phase transformation (Mehta et al. 1994). Accordingly, the previously reported phase boundary for $FeTiO_3$ was once again interpreted as the ilmenite-perovskite phase boundary (Mehta et al. 1994; Navrotsky 1998). Moreover, Linton et al. (1999) demonstrated that a complete $(Fe,Mg)TiO_3$ solid solution with the lithium niobate structure was recovered from pressures between 15 and 21 GPa at a temperature of 1573 K and that $(Mg_{0.5}Fe_{0.5})TiO_3$ with the $LiNbO_3$ structure transformed into a perovskite phase at 21 GPa and 1075 K. It was therefore suggested that a complete $(Fe,Mg)TiO_3$ solid solution in the perovskite phase is present at high pressure and temperature (Linton et al., 1999).

In this study we present for the first time experimental evidence confirming that perovskite is indeed a stable phase at high pressure and temperature with respect to the ilmenite phase at low pressure and low temperature and that the $LiNbO_3$ phase is a metastable phase, a retrogressive product that results from the perovskite phase during decompression at room temperature. In addition, we have re-determined the phase boundary between the ilmenite and the perovskite phases under in situ high-pressure and high-temperature conditions and present the new results.

EXPERIMENTAL METHODS

The two natural samples of ilmenite ($FeTiO_3$) used in this study are from the Bookcheon and Okjong areas, Hadong, South Korea. The ilmenite was collected from a Precambrian anorthosite massif where it occurs as disseminated, lenticular, or massive ores in association with plagioclase and some hornblende (Chung et al. 1989). The ilmenite-bearing anorthosite, when weathered, consists of a very complex mineralogy with orthopyroxene, biotite, zircon, apatite, and allanite in addition to plagioclase and hornblende.

The ilmenite ores were first crushed and pure ilmenite grains were carefully selected under a binocular microscope and ground into fine powder. X-ray diffraction showed that all the peaks belonged to the ilmenite phase. Table 1 shows the lattice parameters thus obtained by least-squares fitting of all the peaks to a hexagonal unit cell, which are comparable with those previously reported. Table 2 shows the chemical composition of ilmenite samples A and B as determined by microprobe analysis. Sample B is relatively pure while sample A contains 7 wt% Fe_2O_3.

Powdered samples of ilmenite were studied in a large-volume press with a T-CUP apparatus to 19.6 GPa and 1150 K. Detailed descriptions of the sample assembly and the 250-ton press were given previously by Uchida et al. (2001) and Wang et al. (1998), respectively. In situ X-ray diffraction measurements were carried out using the energy dispersive method at the GSECARS beamline 13-BMD, at Advanced Photon Source (APS), Argonne National Laboratory (ANL). The incident X-ray beam was collimated by two pairs of tungsten carbide slits—a front slit of 150 × 150 μm before entering the sample and a back slit with dimensions 100 × 300 μm on the detector side. The diffracted X-rays were detected with a Ge solid state detector with preset 2θ angles of 5.556°, 5.386°, and 5.944°, respectively, for the three separate experiments. Data were stored in a 2K multi-channel analyzer. The 2θ angle was calibrated using seven diffraction peaks of the Al_2O_3 standard, and the photon energy for each channel was calibrated using seven radiation sources ranging from 22 to 132 keV. The acquisition time for each spectrum was 300 s.

By driving the beam-collimating slits away from the beam path, the transmitted X-rays were converted to visible light by a YAG crystal and the light was directed to a CCD camera so that a radiograph could be seen and recorded. The imaging setup helped us locate the sample assembly so that we could X-ray the sample and the pressure calibrant (NaCl or Mg + Au) separately and accurately for each pressure and temperature. The sample temperature was monitored by means of a $W_{0.94}Re_{0.06}$-$W_{0.75}Re_{0.25}$ thermocouple and maintained within 2 K. The effect of pressure on the thermocouple emf was ignored. The sample pressure at various temperatures was calculated from the diffraction peaks of the pressure standard such as NaCl, MgO, or Au using their respective equations of state (Decker 1971; Anderson et al. 1982; Jamieson et al. 1982). In the case of NaCl, diffraction peaks (200), (220), (222), (400), and (420) were used for the pressure determination. For Au and MgO, (111), (200), and (220) were used for the calculations. The pressures thus calculated from the different diffraction peaks of NaCl or MgO +Au were consistent within 1% and an average pressure is reported here. Corrections for thermal pressure at high temperatures were made using 0.0028 GPa/K for NaCl, 0.0063 GPa/K for MgO, and 0.0071 GPa/K for Au (Anderson et al. 1982, 1989). Three separate experiments were performed in this study; sample A was used in experiment 1 and sample B in experiments 2 and 3. For the internal pressure calibrant, NaCl was used in experiments 1 and 2, and a mixture of MgO and 1wt% Au was used in experiment 3.

RESULTS AND DISCUSSIONS

Selected X-ray diffraction patterns at high pressure and high temperature are given in Figure 1, showing that the ilmenite phase persists to 19.3 GPa at room temperature (see pattern a). As temperature was increased from 298 to 873 K at a constant load, the sample pressure increased slightly from 19.3 to 20.1 GPa, mainly due to the contribution from the thermal pressure. The ilmenite phase remained as the only phase present at 873 K at 20.1 GPa (see pattern b). When temperature was raised to 973

TABLE 1. Lattice parameters of ilmenite and $LiNbO_3$ phases of $FeTiO_3$

Phase	*a*, Å	*c*, Å	*c/a*	Reference
ilm	5.0791(88)	14.187(36)	2.7932	sample A (This study)
ilm	5.0900(23)	14.056(8)	2.7614	sample B (This study)
ilm	5.079	14.135	2.7830	JCPDS no. 3-078
ilm	5.0865(4)	14.084(2)	2.7690	from synthetic single crystal (Syono et al. 1980)
ilm	5.0884(1)	14.0855(4)	2.7682	synthetic single crystal (Wechsler and Prewitt 1984)
ilm	5.075(2)	13.972(5)	2.753	natural sample (Liu 1975)*
$LiNbO_3$	5.1288(3)	13.756(2)	2.6821	synthetic powder sample (Leinenweber et al. 1991)

* A natural ilmenite specimen containing 40.7 mol% $MgTiO_3$ and 12.8 mol% Fe_2O_3.

TABLE 2. Microprobe analyses of the natural ilmenite samples used in this study

Oxide (wt%)	Sample A	Sample B
SiO_2	0.02	0.018
TiO_2	49.56	51.83
Cr_2O_3	0.01	0.05
Fe_2O_3*	6.91	1.18
FeO	43.77	46.57
MnO	0.66	0.05
MgO	0.01	0.03
Total	100.94	99.59

* The Fe_2O_3 content was calculated using SAM-X software. Initially it assumes Fe as FeO (valence state of 2+) with the Fe^{+2} being bonded with Ti and Si. Other divalent cations are also used to balance Ti and Si (and any other 4+ cations that were measured). The Fe left over after making the ilmenite component is assumed to be in the trivalent state and is used to make the hematite component. Then Fe^{+3} is calculated assuming charge balance and a stoichiometry of 2 cations per 3 O atoms.

K, the pressure dropped very slightly to 20.0 GPa, and new peaks appeared, indicating that a transformation was starting to take place (pattern c). After about 20 minutes the ilmenite diffraction pattern was completely replaced by a new set of peaks, indicating that the phase transformation was completed (see pattern d). X-ray diffraction data obtained from the new phase at 20.0 GPa and 973 K are tabulated in Table 3 and can be interpreted by an orthorhombic unit cell with lattice parameters a = 4.9755(34), b = 5.1961(24), and c = 7.2604(24) Å, with a unit-cell volume V = 187.71 Å^3. These parameters are in good agreement with those for a perovskite phase transformed from the $LiNbO_3$ phase of $FeTiO_3$ at 16 GPa and room temperature (i.e., a = 5.026, b = 5.174, and c = 7.245 Å, V = 188.41 Å^3, Leinenweber et al. 1991) and those for $(Mg_{0.5}Fe_{0.5})TiO_3$-perovskite formed at 21 GPa and 1075 K (i.e., a = 4.9852, b = 5.2104, and c = 7.2305 Å, V = 188.41 Å^3, Linton et al. 1999). Our observation of the perovskite phase at high pressure and high temperature, demonstrates experimentally for the first time that the ilmenite phase was directly transformed into the perovskite phase rather than into the $LiNbO_3$ phase, and thus confirms the predictions made previously (Navrotsky 1998; Leinenweber et al. 1991; Mehta et al. 1994; Linton et al. 1997).

When the perovskite phase at 20.0 GPa and 973 K was quenched to room temperature by turning off the electrical power, X-ray diffraction showed only the perovskite phase, indicating that the perovskite phase is temperature quenchable at this pressure (see pattern e in Fig. 1). Based on the P-T phase boundary for the ilmenite phase determined earlier as P (GPa) = 25.2 – 0.01 T (K) (Syono et al. 1980), we expected that at 20.0 GPa the perovskite phase would only be stable at temperatures above 520 K, below which it would convert back to the ilmenite phase. However, we observed that when the temperature was gradually raised from room temperature to 973 K again at 20 GPa the perovskite phase remained stable and did not convert back to the ilmenite phase. It is evident that the perovskite phase at 20 GPa is within its own stability field regardless of the temperature and, therefore, has a much wider P-T stability field than previously reported (Syono et al. 1980). The phase boundary between the perovskite phase at high pressure and the ilmenite phase at low pressure was, therefore, re-determined and will be described in detail below.

When pressure was gradually decreased at room temperature, the perovskite phase remained the only phase present until 14.5 GPa, where a new peak appeared, indicating a phase transformation had taken place. With the pressure being further decreased to 10.5 GPa the new phase grew rapidly at the expense of the perovskite phase (Fig. 2). Table 4 lists X-ray diffraction data for the new phase at 10.5 GPa, which could be interpreted by a hexagonal unit cell with a = 5.0734(19) and c = 13.425(13) Å, in excellent agreement with the $LiNbO_3$ phase at similar conditions (Leinenweber et al. 1991). Our results are in accord with the forward transition of $LiNbO_3 \rightarrow$ perovskite observed at 16 GPa at room temperature (Leinenweber et al. 1991). Results from both forward and backward transformations suggest that the perovskite phase is stable only at pressures above 15 GPa at room temperature. These results are also consistent with previous quench experiments, where, instead of the ilmenite phase, it

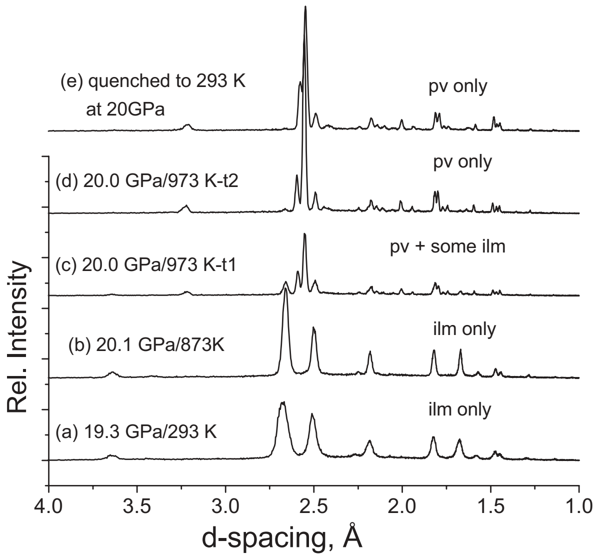

FIGURE 1. Some selected X-ray diffraction patterns of $FeTiO_3$ at high pressure and high temperature show that direct phase transformation of the ilmenite phase into the perovskite phase has taken place at 20.0 GPa and 973 K (see patterns **c**, **d**), and that the perovskite phase persists at high pressure after the temperature was quenched to room temperature at 20 GPa (see pattern **e**). Pattern (**d**) at t2 was collected 20 minutes later than the pattern (**c**) at t1.

TABLE 3. In situ X-ray diffraction data for $FeTiO_3$ (perovskite phase) at 20.0 GPa and 973 K

I/I_0	d_{obs} (Å)	(hkl)	d^*_{calc} (Å)	d_{diff} (Å)
w	3.2203	(111)	3.2208	–0.0005
ms	2.5985	(020)	2.5981	0.0004
vs	2.5540	(112)	2.5539	0.0001
m	2.4869	(200)	2.4878	–0.0009
w	2.1774	(103)	2.1764	0.0010
w	2.1449	(211)	2.1438	0.0011
w	2.1123	(022)	2.1128	–0.0005
wm	2.0107	(113)	2.0074	0.0033
w	1.9433	(122)	1.9447	–0.0014
m	1.8165	(004)	1.8151	0.0014
m	1.7933	(220)	1.7969	–0.0036
w	1.7700	(023)	1.7709	–0.0009
w	1.7438	(221)	1.7442	–0.0004
w	1.6364	(130)	1.6358	0.0006
wm	1.5960	(131)	1.5958	0.0002
wm	1.4887	(024)	1.4880	0.0007
w	1.4665	(204)	1.4663	0.0002
w	1.4504	(005)	1.4521	–0.0017
w	1.2774	(224)	1.2770	0.0004

* Based on an orthorhombic unit cell: a = 4.9755(34), b = 5.1961(24), and c = 7.2604(24) Å, V = 187.71(11) Å^3, Z = 4, V = 28.263 (16) cm^3/mol.

TABLE 4. In situ X-ray diffraction data for the $LiNbO_3$ phase obtained at 10.5 GPa and at room temperature

I/I_0 Å	d_{obs} (Å)	(hkl)	d^*_{cal} (Å)	d_{diff} (Å)
w	3.683	(012)	3.689	–0.006
vs	2.676	(104)	2.679	–0.003
s	2.540	(110)	2.543	–0.003
m	2.212	(113)	2.214	–0.002
ms	1.847	(024)	1.844	0.003
m	1.684	(116)	1.685	–0.001
w	1.576	(018)	1.576	0.000
m	1.495	(214)	1.493	0.002
m	1.467	(300)	1.468	–0.001

* Calculated on the basis of a hexagonal unit cell with a = 5.0859(27) and c = 13.502(11) Å, c/a = 2.655, Z = 6, V = 30.364(33) cm^3/mol.

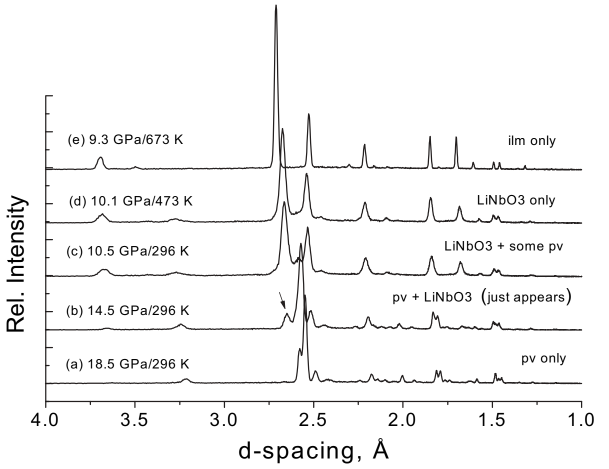

FIGURE 2. Selected X-ray diffraction patterns obtained during decompression of the $FeTiO_3$ (perovskite structure) from 18.5 GPa and room temperature (**a**), showing that perovskite transforms to the $LiNbO_3$ phase at 14.5 GPa as indicated by the arrow showing the appearance of a new peak (104) belonging to the $LiNbO_3$ phase (**b**). The figure also shows that $FeTiO_3$ ($LiNbO_3$ structure) transforms to the $FeTiO_3$ (ilmenite structure) on heating to 673 K at 10.5 GPa (see patterns **c**, **d**, and **e**).

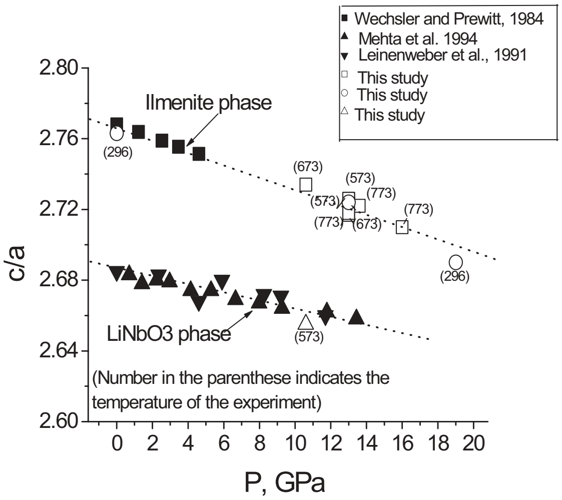

FIGURE 3. Effect of pressure on *c*/*a* for the ilmenite and the $LiNbO_3$ phases in $FeTiO_3$ both at room temperature and high temperature.

was the $LiNbO_3$ phase that was recovered at ambient conditions from high *P*-*T* experiments.

The $LiNbO_3$-perovskite phase transformation occurred both with increasing and decreasing pressure at room temperature. Does this mean that the $LiNbO_3$ phase is a thermodynamically stable phase sitting between the perovskite phase at high pressure and the ilmenite phase at low pressure? Is it simply kinetic hindrance that prevents the ilmenite phase from transforming into the $LiNbO_3$ phase during compression at room temperature? To answer these questions unambiguously, it was necessary to show that the $LiNbO_3$-ilmenite transition occurs both in forward and backward directions with pressure at high temperatures. Our in situ diffraction data show that the $LiNbO_3$ phase transforms completely into ilmenite phase at 673 K and 9.3 GPa. However, the back transformation was not observed—the ilmenite phase, once formed, does not convert back to the $LiNbO_3$ phase but persists all the way to ambient conditions. It is therefore concluded that $LiNbO_3$ is most likely a metastable phase with no stability field in the *P*-*T* space. These results are in line with results based on high-temperature calorimetry (Mehta et al. 1994).

The powder X-ray diffraction pattern of the $LiNbO_3$ phase is very similar to that of the ilmenite phase. This is because both are similar to α-Al_2O_3 (corundum structure), a hexagonal close-packed structure in the oxygen array with two thirds of the octahedral sites occupied and one third of the octahedral sites vacant. And yet, in contrast with α-Al_2O_3, which is fully disordered, both ilmenite and the $LiNbO_3$ phases are fully ordered with only the cations arranged differently between the two phases such that Fe-Ti-V-Ti-Fe-V... for the ilmenite phase and Fe-Ti-V-Fe-Ti-V... for the $LiNbO_3$ phase, where the symbol V represents the vacant site (Ko and Prewitt 1988; Ross et al. 1989). As a result, the *a* and *c* lattice parameters between the two phases are distinctly different. Figure 3 shows a plot of *c*/*a* ratio as a function of pressure for ilmenite and $LiNbO_3$ phases obtained from this study and previous studies over a wide *P*-*T* range, depicting clearly that *c*/*a* for $LiNbO_3$ is consistently smaller than for ilmenite and therefore can serve as a reliable parameter to distinguish one phase from the other (Wechsler and Prewitt 1984; Mehta et al. 1994; Leinenweber et al. 1991).

We have demonstrated that only the ilmenite-perovskite transformation was observed under in situ high *P*-*T* conditions with the perovskite phase being stable at pressures above 16 GPa. When quenched rapidly and decompressed at room temperature, the perovskite phase will bypass the ilmenite field and convert to the $LiNbO_3$ phase, which persists as a metastable phase to ambient conditions. We also found that once the perovskite phase transforms into the ilmenite phase during decompression at some high temperature, the ilmenite phase remains as the stable phase all the way to ambient conditions. A similar behavior was observed for $(Mg_{0.5}Fe_{0.5})TiO_3$ in a large-volume press and in a resistively heated diamond-anvil cell (Linton et al. 1999). In contrast, an experiment using a natural ilmenite sample (with 40.7 mol% $MgTiO_3$ and 12.8 mol% Fe_2O_3) and laser-heating in a diamond cell showed that the ilmenite phase transforms into the perovskite phase at 14 GPa and 1673–2073 K, which could be quenched and recovered at ambient conditions (Liu 1975). The transformation pressure obtained by Liu (1975) is about 2 GPa lower than that of Linton et al. (1999), with a similar chemical composition, and is probably due to the different pressure calibration used in each experiment. The perovskite phase recovered by Liu (1975) at ambient conditions is most interesting, indicating that different experimental methods (e.g., laser-heating vs. resistive heating, and gasketed sample vs. ungasketed sample, fast decompression in the DAC vs. very slow decompression in the LVP) may result in a very different final product.

Figures 4 and 5 show the forward (i.e., ilm → pv) and backward (pv → ilm) transformations, respectively. The ilmenite phase is clearly the dominating phase at 13.5 GPa and 773 K (Fig. 4, pattern a) with some tiny residue of the perovskite phase as indicated by the weak peak (112) between the first two strong peaks (104) and (110) of the ilmenite phase. When the pressure is increased to 16 GPa at 773 K, the (112) diffraction peak of the perovskite phase grows at the expense of the ilmenite phase, indicating that the sample is within the stability field of the perovskite phase (Fig. 4, patterns b, c, and d). By decompressing to 13.6 GPa at 773 K, the perovskite phase decreases drastically and disappears completely in a short period of time indicating that the sample is now back in the stability field of the ilmenite phase (Fig. 5, patterns b and c). By cycling the pressure up and down at four different temperatures (i.e., 773, 873, 1000, and 1023 K), the equilibrium pressure of the perovskite-ilmenite transformation can be bracketed at each given temperature. Regardless of the Fe_2O_3 content of the sample used in the first experiment at 775 K being 7% higher than the second one at higher temperatures, the phase boundary can be best represented by P (GPa) = 16.0 (±1.4) – 0.0012 (±0.0014) T (K) (see Fig. 6). Therefore, the effect of the Fe_2O_3 content on the phase boundary seems to be small. The slope of 0.0012 GPa/K determined in this study is an order of magnitude smaller than the 0.01 GPa/K reported previously (Syono et al. 1980). This discrepancy could be attributed to the different methods used in the two studies; in situ type in this study vs. the quenched type in previous work (e.g., Akimoto et al. 1977; Zhang et al. 1996). Such a discrepancy is expected because the sample pressure in the quench type experiments was not obtained directly from internal pressure(s) as in the in situ experiment but rather indirectly from a calibration curve based only on the standard fixed points of Bi (I-II at 2.54 GPa), Bi (III-V at 8.8 GPa), Fe ($\alpha \rightarrow \varepsilon$ at 13.3 GPa), and Pb (I-II at 16.1 GPa) at room temperature (e.g., Kawai and Endo 1970).

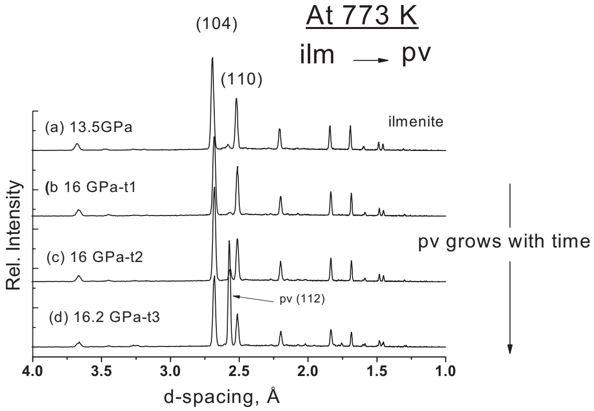

FIGURE 4. In situ X-ray diffraction patterns of the ilmenite → perovskite transformation in $FeTiO_3$ at 773 K, where the ilmenite phase is stable at 13.5 GPa and then starts to change into the perovskite phase at 16 GPa. Patterns labeled as t2 and t3 were collected 5 and 10 minutes later than t1, respectively. Accordingly, the phase boundary lies between 13.5 and 16 GPa at this temperature.

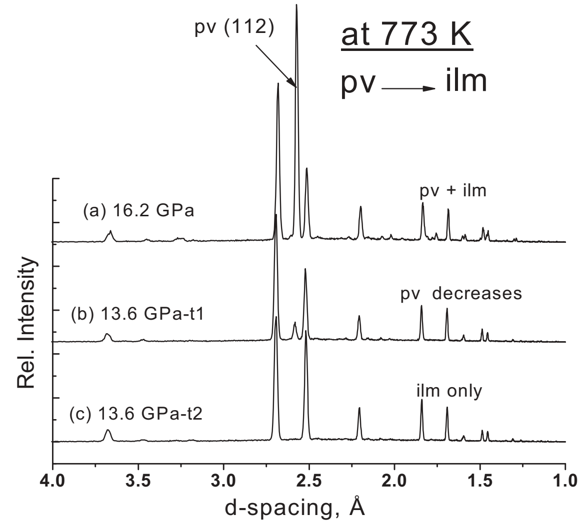

FIGURE 5. In situ X-ray diffraction patterns of the reverse transformation of perovskite → ilmenite at 773 K, where t2 was collected at the same P/T conditions as t1 but 5 minutes later.

The very small negative slope obtained in this study is in reasonably good agreement with the –0.0057 GPa/K calculated from calorimetric data (Linton et al. 1999) and with other ilmenite-perovskite transformations as in $CdGeO_3$ (–0.0017 GPa/K, Akaogi and Navrotsky 1987), $MgTiO_3$ (–0.0025 GPa/K, Linton et al. 1999), and $MgSiO_3$ (–0.0023 GPa/K, Hirose et al. 2001). The negative slope suggests that the entropy of the high-pressure phase is larger than that of the low-pressure counterpart. This is not unusual for high-pressure phase transformations involving coordination changes (Navrotsky 1980). In the ilmenite-perovskite transformation of ABO_3 compounds, the large entropy in perovskite could be attributed to the greater distortion in the A-cation polyhedron (Reznitskii 1978) and the longer metal-oxygen (A-O) bond length in the perovskite phase with respect to the low-pressure ilmenite phase (Navrotsky 1980). Using the Clausius-Clapeyron equation ($dP/dT = \Delta S/\Delta V \sim \Delta S_0/\Delta V_0$) along with the slope determined in this study and the estimated values of ΔV_0 from different sources given in Table 5, we obtained values of ΔS_0 ranging from 1.20 to 1.88 J/mol-degree for the ilmenite-perovskite phase transformation. The extremely small slope of the ilmenite-perovskite phase boundary shows the transition pressure is essentially temperature-independent, and as a result, the ilm-pv transition could be used as a reliable pressure standard for pressure calibration at high temperature in a large-volume press. A phase transformation with such a small slope would potentially have geological/geophysical applications as well.

Recently, abundant ilmenite precipitates were found in olivine of the Alpe Arami peridotite massif in Switzerland. It was suggested that these precipitates are new metastable phases converted from the perovskite phase during the ascending process (Dobrzhinetskaya et al. 1996). Using the ilmenite-perovskite phase boundary reported earlier (Syono et al. 1980), the minimum depth for the Arami peridotite was placed at 300 km at a

TABLE 5. Thermodynamic data for the ilm-pv phase transformation in $FeTiO_3$

$\Delta P/\Delta S$, GPa/K	ΔV_0, cm^3/mol	ΔS_0, cal/mol·K
0.0012*	–1.55†	1.88‡
0.0012*	–1.05§	1.26‡
0.0012*	–1.0#	1.20‡

* Experimental value, this study.
† Linton et al. 1999.
‡ Calculated values, this study.
§ Leinenweber et al. 1991.
\# Mehta et al. 1994.

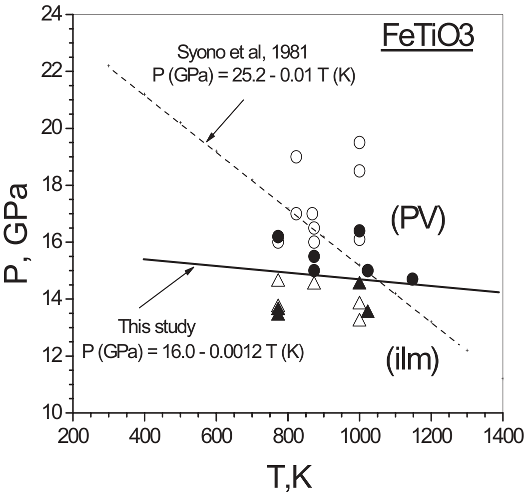

FIGURE 6. The phase boundary of the ilmenite-perovskite transformation determined in this study. Open and solid symbols show decompression and compression cycles, respectively. Circles and triangles represent the perovskite and ilmenite phases, respectively.

temperature around 1600 K (see Fig. 4 of Dobrzhinetskaya et al. 1996). If our scenario is proved to be true, the results obtained from this study will place the peridotite to a depth greater than 480 km, which is well within the transition zone. The new metastable phase was found to be of orthorhombic structure and has not yet been observed experimentally. It would be of great interest to carry out a systematic study on $FeTiO_3$ using both in situ and quench methods over a much wider *P-T* range.

In the meteor crater in Ries, Germany, ilmenite-bearing rocks were shocked to high pressures and high temperatures. Based on the finding of baddeleyite-type TiO_2 in the crater, a peak shock pressure in the shocked rocks was suggested to lie between 16 and 20 GPa (El Goresy et al. 2001). The ilmenite-perovskite phase transformation, if preserved in these rocks, would serve as a valuable geobarometer, providing an additional constraint for the *P-T* conditions under which the rocks were formed. Evidence of the ilm-pv transformation, in addition to the presence of the perovskite phase itself, could include the presence of metastable phases such as the $LiNbO_3$ structure (Syono et al. 1980; Leinenweber et al. 1991; Linton et al. 1999; and this study), or orthorhombic structure (Dobrzhinetskaya et al. 1996), or the Fe-enriched/Mg-enriched areas in $(Mg,Fe)TiO_3$ ilmenite (Linton et al. 1999), or the presence of twins in the $LiNbO_3$ phase (Leinenweber et al. 1994).

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