

## Phase Transition Study on Ilmenite under High Pressure and Temperature

고온 - 고압하에서 티탄철석에 대한 상변이 연구

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**ABSTRACT** : Several phase transition studies have been previously reported on ilmenite ( $\text{FeTiO}_3$ ) at high pressure and temperature conditions. However, those results are not consistent with one another, and phase boundary between ilmenite and perovskite phases determined only from the quenching method may be not so reliable at all. Therefore, *in-situ* high pressure-temperature (hP-T) X-ray diffraction measurements were performed up to 19 GPa and 700°C in a large volume press apparatus using synchrotron radiation. Experimental results show that perovskite phase is stable at pressures above 16 GPa, and transforms back to  $\text{LiNbO}_3$  phase near 15 GPa at room temperature, and that the perovskite-ilmenite transition is back and forth near 15 GPa at 500°C.  $\text{LiNbO}_3$  phase transforms to ilmenite at 13 GPa and 300°C and at 10.8 GPa and 400°C, respectively. These data indicate that  $\text{LiNbO}_3$  phase may have a stability region in the hP-T phase diagram and that the perovskite-ilmenite phase boundary would be quite different from that previously reported.

**Key words** : phase transition, ilmenite, perovskite,  $\text{LiNbO}_3$  phase, synchrotron radiation

요약 : 고온-고압 상태에서 티탄철석 ( $\text{FeTiO}_3$ )의 상변이에 대한 연구가 있었으나, 그 결과는 서로 일치하지 않고 있다. 특히, 티탄철석상과 페롭스카이트상의 상변이 경계는 담금방법에 의해 결정된 것으로 신뢰도에 의문이 제기되고 있다. 이러한 문제를 해결하기 위해, 고온-고압 현장상태에서 라지 볼륨 기기와 방사광을 이용하여 19 GPa와 700°C의 범위에서 X선 회절실험을 시행하였다. 이러한 실험결과, 페롭스카이트상은 상온에서 16 GPa 이상의 압력에서 안정하며, 15 GPa 근처에서  $\text{LiNbO}_3$ 상으로 변이한다. 또한 이 두 고온-고압상은 500°C에서는 순간적인 상변이를 하고 있다.  $\text{LiNbO}_3$ 상은 각각 13 GPa 및 300°C와 10.8 GPa 및 400°C에서 티탄철석상으로 상변이 한다. 따라서 본 실험결과는  $\text{LiNbO}_3$ 상은 고온-고압하에서 안정 영역을 확보하고 있으며, 페롭스카이트-티탄철석 상경계는 이전에 발표된 결과와는 매우 다르다는 것을 지시해주고 있다.

주요어 : 상변이, 티탄철석, 페롭스카이트,  $\text{LiNbO}_3$ 상, 방사광

## Introduction

Ilmenite ( $\text{FeTiO}_3$ ) is one of the common accessory minerals embedded in the igneous and metamorphic rocks. It usually forms a solid solution with hematite ( $\text{Fe}_2\text{O}_3$ ) and geikilite ( $\text{MgTiO}_3$ ). The ilmenite that occurs as intergrowth with pyroxene in the xenoliths from South Africa kimberlite has been interpreted as an exsolution from a homogenous garnet phase below 10 GPa, or at a depth about 300 km (Ringwood and Lovering, 1970). Recently, abundant ilmenite precipitates were found in olivine crystals of the Alpe Arami peridotite massif, Switzerland, leading to a suggestion that the peridotite massif has been brought to the surface from the depths of 400~660 km in the transition zone of the Earth interior (Dobrzhinetskaya *et al.*, 1996).

Limitation of its magnetic susceptibility (i.e., less than  $10^{-4}$  emu/g) is the major divide to identify the two series of the granotoids between magnetite- and ilmenite- series (Ishihara, 1977). Furthermore, with other iron-bearing minerals such as magnetite, ulvospinel, and olivine, it has been served as useful geothermometers and geobarometers, which indicate the temperature and the oxygen fugacity conditions where rock was formed (Frost *et al.*, 1988). It is evident that more information on the phase transformations of ilmenite and its solid solutions under high pressure and temperature simultaneously would help constrain the depth of formation of the host kimberlites and peridotite.

There are several previous studies on ilmenite for its phase transformations. Phase transformations on ilmenite ( $\text{FeTiO}_3$ ) at high pressures and temperatures have been studied by several investigators. However, the results are not consistent with one another. Based on an experiment in the laser-heated diamond anvil cell, it was reported that a natural ilmenite ( $\text{Fe, MgTiO}_3$ ) transforms to the perovskite structure and then disproportionates into its oxides, ( $\text{Mg, Fe})\text{O} + \text{a cubic phase of TiO}_2$  at pressures of 14 and 25 GPa, and at temperatures of 1400 and

1800°C, respectively (Liu, 1975).

After this work, it was found that at 1000°C a synthetic  $\text{FeTiO}_3$  transforms into the corundum phase at 15 GPa, which changes into a mixture of constituent oxides such that  $\text{FeO} + \text{TiO}_2$  ( $\alpha$ - $\text{PbO}_2$  structure) at approximately 27 GPa (Ito and Matsui, 1979). Based on the shock wave experiments, the phase boundary between the ilmenite  $\text{FeTiO}_3$  (I) and the high pressure phase  $\text{FeTiO}_3$  (II) was reported as  $P$  (GPa) =  $25.2 - 0.01 T$  (K) (Syono *et al.*, 1980). Subsequently, a quenchable lithium niobate ( $\text{LiNbO}_3$ ) phase was synthesized from the ilmenite at 18 GPa and 1200°C, and the lithium niobate phase transforms further into the perovskite phase at pressure above 16 GPa and at room temperature (Leinenweber *et al.*, 1991). Based on the calorimetric measurement on the ilmenite and lithium niobate polymorphs of  $\text{FeTiO}_3$ , it was indicated that the ilmenite-lithium niobate phase boundary is metastable with respect to an ilmenite-perovskite phase boundary, and the stable phase at high pressure is probably the perovskite phase (Mehta *et al.*, 1994). A complete ( $\text{Fe, MgTiO}_3$ ) solid solution in lithium niobate structure was synthesized at 21 GPa and at 1200°C, thus suggesting a complete solid solution that may be present in the perovskite phase at higher pressures (Linton *et al.*, 1997).

However, several interesting questions that still remain are: (1) Is the lithium niobate phase indeed a metastable phase with respect to the perovskite phase? (2) Is the different result between Frost *et al.*, (1988) and Liu (1975) due to the difference in composition of the starting materials? (3) Is there an ilmenite-perovskite transition at room temperature? Moreover, three unknown structures were identified in the  $\text{FeTiO}_3$  precipitates indicating that the phase relationship in  $\text{FeTiO}_3$  is probably much more complicated than previously thought.

In order to clarify these questions, high pressure and high temperature experiments were performed on a natural ilmenite for its phase transformations up to 19 GPa and 700°C in a

large volume press on the beamline 13-BM-D at the Advanced Photon Source (APS) of the University of Chicago. This beamline has been equipped with the 250-ton large-volume press (LVP) and Ge-solid state detector (SSD). Energy dispersive X-ray diffraction (EDXRD) technique was employed in collaboration with white radiation from synchrotron source.

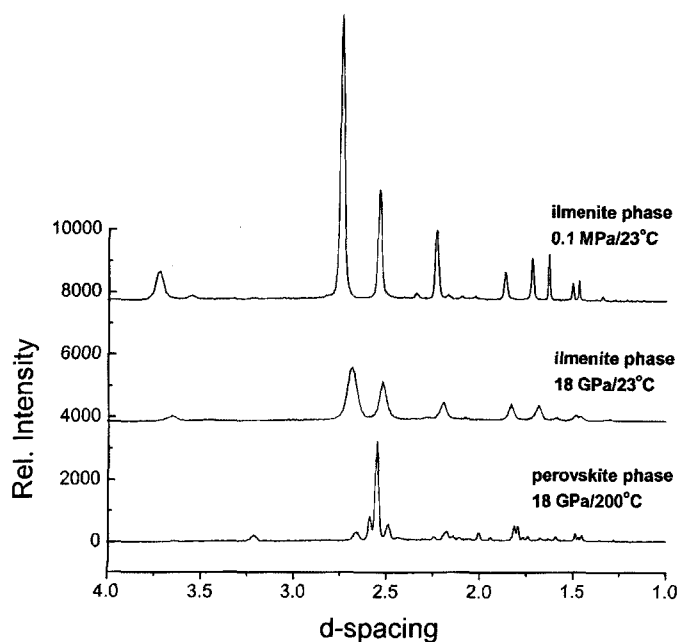
### Experiment Result and Discussions

When pressure was increased from atmospheric pressure (i.e., 0.1 MPa) up to 18 GPa at room temperature, starting ilmenite phase still sustains, but ilmenite converts to perovskite structure at the same pressure when temperature increased to 200°C, (Fig. 1). However, in the independent run as shown in Fig. 2, perovskite phase was observed at 17.3 GPa and room temperature. Without any change in temperature, pressure was unloaded to 14.2 GPa, then lithium niobate (LiNbO<sub>3</sub>) phase starts to appear. At this pressure of 14.2 GPa when heated up to 300°C, lithium niobate phase transforms back to ilmenite phase. When heated more up to 500°C, this phase reverts back to ilmenite phase

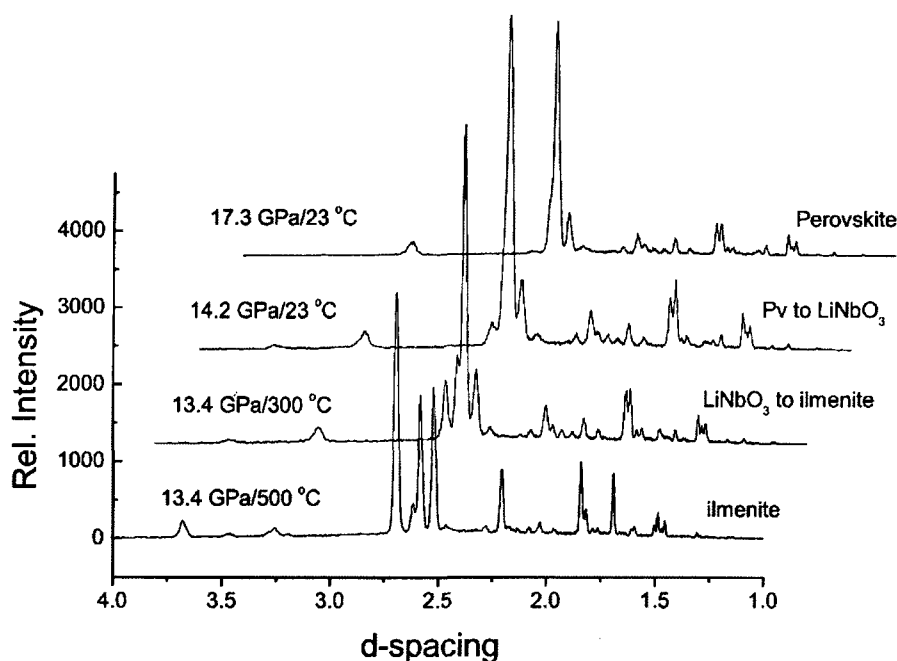
completely.

Phase transformation sequence is shown in Fig. 3 at the constant temperature of 500°C with increasing pressure. At 13.5 GPa and 500°C, only ilmenite phase exists. However, when pressure increases to 16 GPa, it starts perovskite phase to grow. More perovskite phase grows with time elapse at the fixed pressure and temperature conditions. Spectrum at the bottom shows the increased pressure value from 16.0 to 16.2 GPa, and this variation might be due to the thermal energy effect in the sample chamber. In Fig. 4, spectra series shows the subsequent process after Fig. 3. Spectrum at the top in Fig. 4 is the same as that at the bottom in Fig. 3. At 500°C, when decreased pressure down to 13.6 GPa, relative amount of ilmenite phase increases again. Decreasing temperature to 500°C at this pressure, all phase reverts back to the starting ilmenite phase only.

Figure 5 shows a series of spectra showing backward phase transformation sequence from perovskite to lithium niobate and then finally to ilmenite phase. Only perovskite phase exists at 19.6 GPa and room temperature conditions. When pressure only releases to 14.6 GPa at



**Fig. 1.** X-ray diffraction spectra showing phase transition sequence from ilmenite to perovskite phase. At 18 GPa and room temperature conditions, ilmenite phase still sustains, but at same pressure when temperature increased to 200°C, ilmenite phase changes to perovskite structure. The unit of d-spacings is Å.



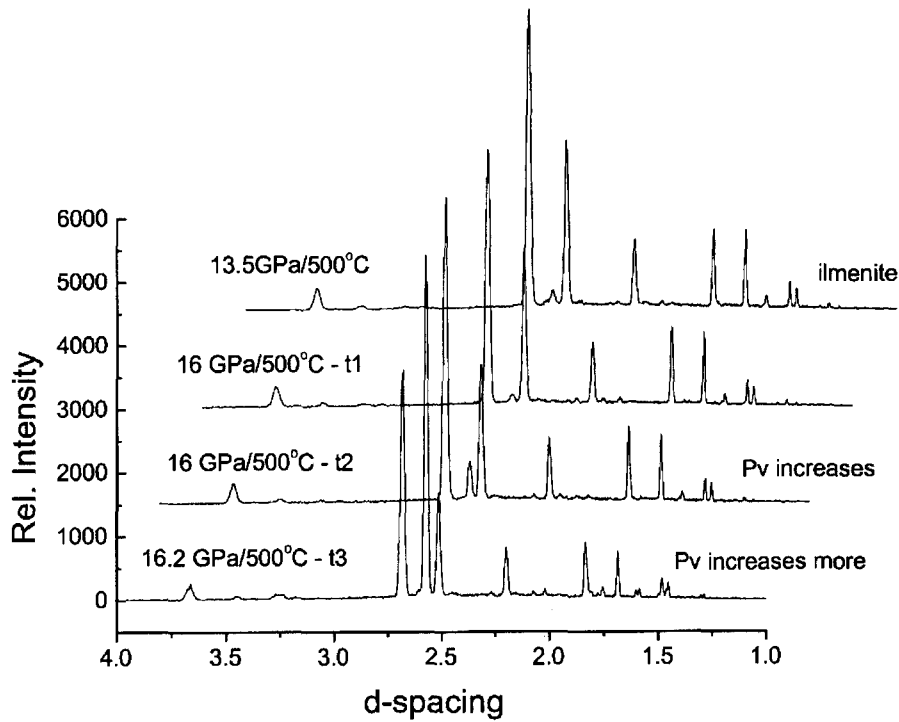
**Fig. 2.** A series of spectra showing the backward phase transition sequence. From perovskite to lithium niobate ( $\text{LiNbO}_3$ ) phase, then to ilmenite structure at room temperature with decreasing pressure from 17.3 GPa to 14.2 GPa. At this pressure of 14.2 GPa when heated up to 300°C, lithium niobate phase transforms back to ilmenite phase. Decrease of pressure from 14.2 GPa to 13.4 GPa is due to the heating, which might influence the sample chamber environment. When heated more up to 500°C, it reverts back to ilmenite phase completely. The unit of d-spacings is Å.

room temperature, XRD peaks belong to lithium niobate phase starts to appear. At approximately 10 GPa after decreasing pressure, both perovskite and lithium niobate phases exist at the equal amount. When temperature increased to 200°C at this pressure, perovskite phase disappears, and only lithium niobate phase exists.

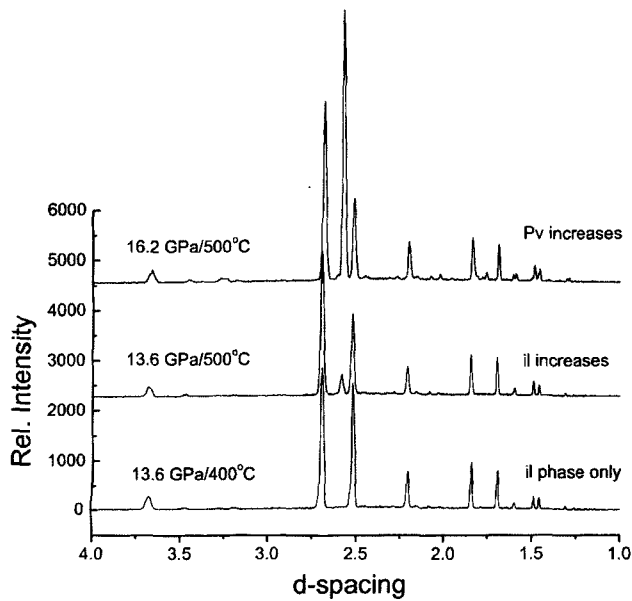
Fig. 6 shows the axial ratio  $c/a$  variations with respect to the pressure in ilmenite phase and  $\text{LiNbO}_3$ . Data from the previous studies (those in solid symbols from Leinenweber *et al.*, (1991), Mehta *et al.*, (1994) and Wechsler and Prewitt (1984)) and this study (shown in open symbols) are shown together. Numbers in the parentheses indicate the temperature of the experiments conducted in this study.

Experimental data show that perovskite is the stable phase at pressures above 16 GPa, and transforms back to  $\text{LiNbO}_3$  phase near 15 GPa

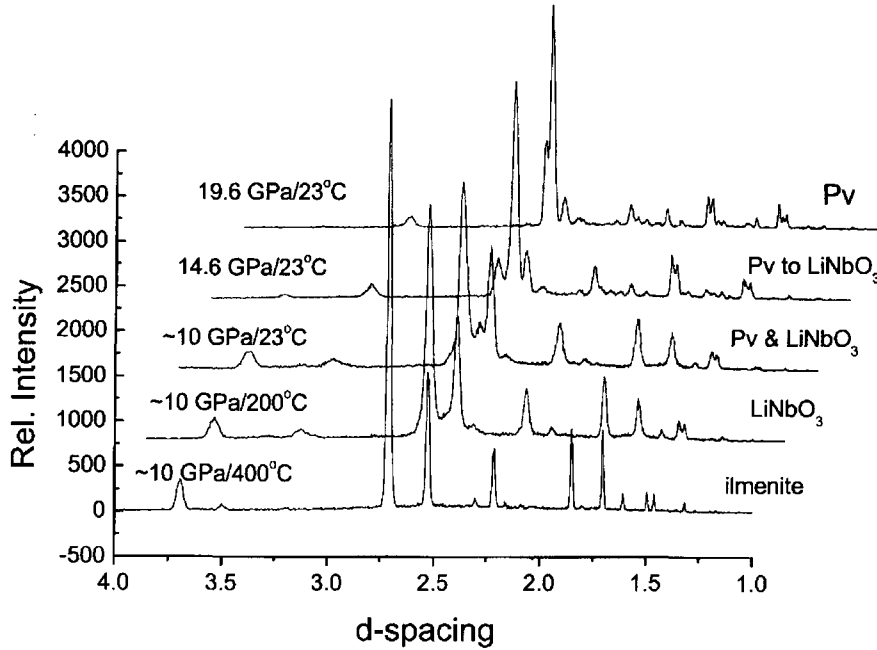
at room temperature, and that the perovskite-ilmenite transition is back and forth near 15 GPa at 500°C. Based on these results, it was proposed a tentative P-T phase diagram in Fig. 7 for  $\text{FeTiO}_3$ , indicating that the  $\text{LiNbO}_3$  phase may have a stability field and that the perovskite-ilmenite phase boundary would be quite different from that reported previously. Solid line is from Syono *et al.*, (1980), which shows the steeper negative gradient compared with the present one. Phase boundary between  $\text{LiNbO}_3$  and ilmenite is positive. That of ilmenite and perovskite is the same, but it is slightly ambiguous between  $\text{LiNbO}_3$  and perovskite phases. Furthermore, in order to clarify the phase boundary between lithium niobate phase and ilmenite phase, one experimental run was carried out independently and results are shown in Tables 1 and 2.



**Fig. 3.** Phase transition sequence at the constant temperature of 500°C with increasing pressure. At 13.5 GPa and high temperature, only ilmenite phase exists. But, when pressure increases to 16 GPa, perovskite phase starts to grow. Perovskite phase grows more with time elapse which is designated t1, t2 and t3 at the fixed pressure and the given temperature conditions. Spectrum at the bottom shows the increased pressure value from 16.0 to 16.2 GPa, and this variation might be due to the thermal energy effect in the sample chamber. The unit of d-spacings is Å.



**Fig. 4.** This spectra series shows the subsequent process after Figure 3. Spectrum at the top is the same as that at the bottom in Figure 3. At 500°C, when decreased pressure down to 13.6 GPa, ilmenite phase increases again. At this pressure when temperature decreases to 400°C, all phase reverts back to the starting ilmenite phase only. The unit of d-spacings is Å.



**Fig. 5.** A series of spectra showing backward phase transition sequence from perovskite to lithium niobate and then finally to ilmenite phase. Only perovskite phase exists at 19.6 GPa and room temperature conditions. When pressure only releases to 14.6 GPa at room temperature, XRD peaks belong to lithium niobate phase starts to appear. At approximately 10 GPa after decreasing pressure, both perovskite and lithium niobate phases exist at the equal amount. When temperature increased to 200 °C at this pressure, perovskite phase disappears, and only lithium niobate phase exists. The unit of d-spacings is Å.

**Table 1.** *In-situ* X-ray diffraction data of FeTiO<sub>3</sub> at 10.6 GPa and 200 °C (in LiNbO<sub>3</sub> phase)

$I/I_0$	$d_{(obs.)}$	(hkl)	$d^*_{(calc.)}$	$d_{(diff.)}$
w	3.683	(012)	3.689	-0.006
vs	2.676	(104)	2.679	-0.003
vs	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	-
m	1.495	(214)	1.493	0.002
m	1.467	(300)	1.468	-0.001

\*  $a=5.086(3)$  Å,  $c=13.50(1)$  Å,  $c/a=2.655$ ,  $Z=6$ ,  $V=30.36(3)$  cm<sup>3</sup>/mole

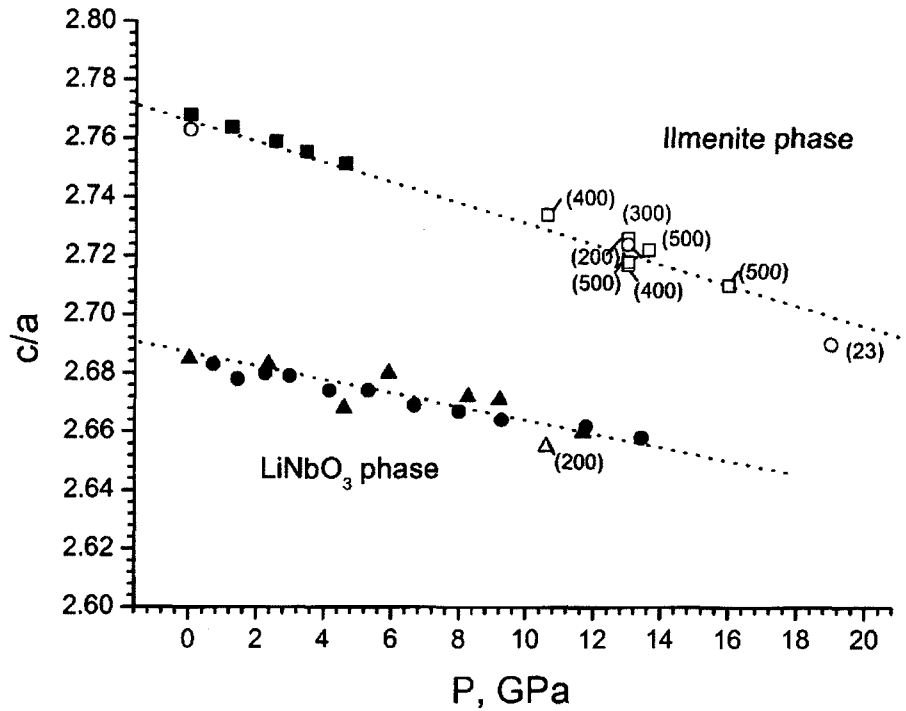
*In-situ* XRD data at 10.6 GPa and 200 °C in lithium niobate phase is listed in Table 1. Lattice parameters of this phase was determined as  $a=5.086(3)$  Å,  $c=13.50(1)$  Å,  $c/a=2.655$ ,  $Z=6$ ,  $V=30.36(3)$  cm<sup>3</sup>/mole. On the other hand,

**Table 2.** *In-situ* X-ray diffraction data of FeTiO<sub>3</sub> at 10.6 GPa and 400 °C (in ilmenite phase)

$I/I_0$	$d_{(obs.)}$	(hkl)	$d^*_{(calc.)}$	$d_{(diff.)}$
w	3.695	(012)	3.699	-0.004
vs	2.711	(104)	2.713	-0.002
vs	2.529	(110)	2.528	-0.001
m	2.214	(113)	2.217	-0.003
ms	1.848	(024)	1.850	-0.002
m	1.703	(116)	1.703	.000
w	1.608	(018)	1.608	.000
m	1.493	(214)	1.493	.000
m	1.460	(300)	1.460	.000

\*  $a=5.0563(1)$  Å,  $c=13.826(6)$  Å,  $c/a=2.734$ ,  $Z=6$ ,  $V=30.73(2)$  cm<sup>3</sup>/mole

XRD data in ilmenite phase at the same pressure but at 400 °C is given in Table 2. Lattice parameters of this phase were determined as follows :  $a=5.0563(1)$  Å,  $c=13.826(6)$  Å,  $c/a=2.734$ ,  $Z=6$ ,  $V=30.73(2)$  cm<sup>3</sup>/mole. To



**Fig. 6.** Axial ratio of  $c/a$  versus pressure in ilmenite phase and  $\text{LiNbO}_3$  phase. Data from the previous studies (solid square from Leinenweber *et al.*, (1991), solid circle from Mehta *et al.*, (1994) and solid triangle from Wechsler and Prewitt (1984)) and this study (square, circle and triangle in open symbols from three independent runs) are shown together. Numbers in the parentheses indicate the temperature of the experiments conducted in this study.

**Table 3.** *In-situ* X-ray diffraction data of  $\text{FeTiO}_3$  at 19 GPa and 700°C (in perovskite phase)

$I/I_0$	$d_{(obs.)}$	(hkl)	$d_{(calc.)}^*$	$d_{(diff.)}$
w	3.221	(111)	3.220	0.001
ms	2.596	(020)	2.591	0.005
vs	2.555	(112)	2.547	0.008
m	2.493	(200)	2.500	-0.007
w	2.178	(103)	2.167	0.011
wm	2.011	(113)	1.999	0.012
w	1.944	(122)	1.940	0.004
m	1.816	(004)	1.803	0.013
m	1.800	(220)	1.799	0.001
w	1.772	(023)	1.763	0.009
w	1.744	(221)	1.745	-0.001
wm	1.596	(131)	1.593	0.003
wm	1.489	(132)	1.487	0.002
w	1.468	(024)	1.480	-0.012
w	1.451	(312)	1.452	-0.001

\*  $a=5.00(2)\text{Å}$ ,  $b=5.18(2)\text{Å}$ ,  $c=7.21(2)\text{Å}$ ,  $Z=4$ ,  $V=28.14\text{ cm}^3/\text{mole}$

compare these phases with the perovskite phase, one XRD data from 19 GPa and 700°C is given in Table 3. Perovskite phase peaks exist more than any other two phases do. Table 4 shows the comparison of ilmenite structure with  $\text{LiNbO}_3$  phase in  $\text{FeTiO}_3$ . Two phases are belonged to different space group, and show similar lattice parameters. Peculiar one is the ratio of  $c$  and  $a$  axes (i.e.,  $c/a$ ). This difference might be due to the alternative sequence of the cations as shown at the bottom of the Table 4. Ti and Fe sequence is different in two phases.

There are still unclear questions remained as follows : Firstly, is the lithium niobate phase indeed a metastable phase with respect to the perovskite phase as suggested, based on the calorimetric measurement on the ilmenite and lithium niobate polymorphs of  $\text{FeTiO}_3$  (Mehta *et*

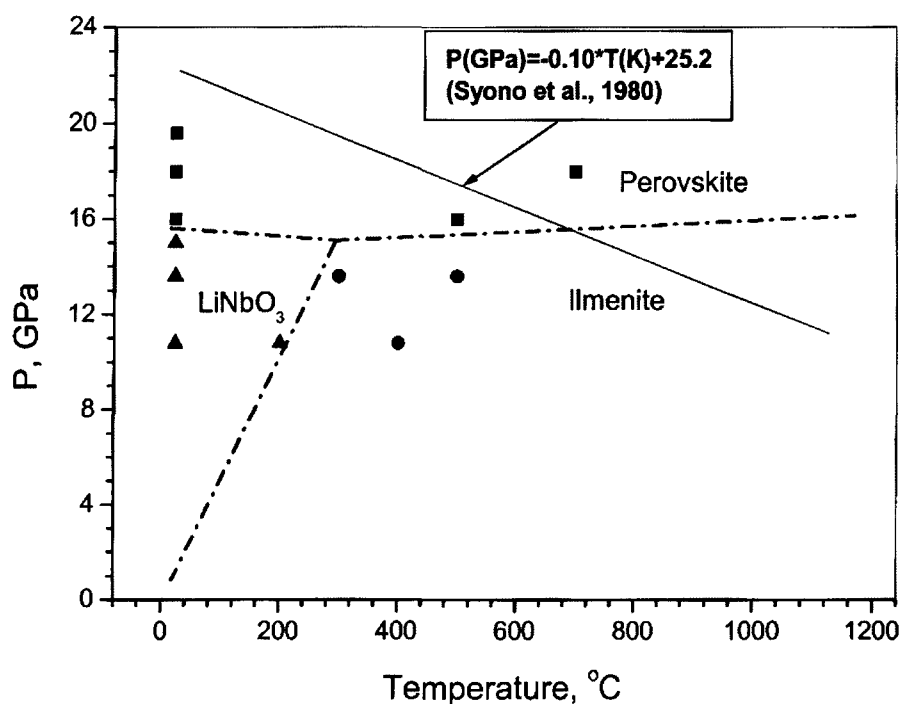


Fig. 7. Tentative phase diagram of ilmenite under high pressure and temperature. Solid line is from Syono *et al.*, (1980), which shows the steeper negative gradient compared with the present result. Phase boundary between  $\text{LiNbO}_3$  and ilmenite is positive. Further, that of ilmenite and perovskite is the same, but it is slightly ambiguous between  $\text{LiNbO}_3$  and perovskite phases.

Table 4. Comparison of ilmenite versus  $\text{LiNbO}_3$  phases in  $\text{FeTiO}_3$

	ilmenite	$\text{LiNbO}_3$
Space group	$R3$	$R3c$
$a$ (Å)	5.0875	5.1228
$c$ (Å)	14.0827	13.756
$c/a$	2.761	2.685
$V$ ( $\text{cm}^3/\text{mole}$ )	31.689	31.383
Cation seq. (// c-axis)	$\text{FeTi}\square\text{TiFe}\square\text{FeTi}\dots$	$\text{FeTi}\square\text{FeTi}\square\text{FeTi}\square\dots$

*al.*, 1994)? Secondly, is the different result between Liu (1975) and Ito and Matsui (1979) due to the difference in composition of the starting materials? Thirdly, how reliable is the ilmenite-perovskite phase boundary previously determined (Syono *et al.*, 1980)? Finally, what are the structure of the three unknown phases of the  $\text{FeTiO}_3$  precipitates found in olivines of the Alpe Arami peridotite massif (Dobrzhinetskaya *et al.*, 1996)?

It is, therefore, needed to clarify the situa-

tions so as to solidify systematically the phase transformations on ilmenite under high pressure and temperature in light of the proposed high pressure-temperature phase diagram (Fig. 7). There are two focused aspects as the followings:

1. Additional data at higher temperatures to define the slope of the perovskite-ilmenite phase boundary. This requires a series of isothermal compression/decompression cycles, as the perovskite-ilmenite boundary is subparallel to the



temperature axis.

2. The  $\text{LiNbO}_3$  - ilmenite boundary is still in question. Is the  $\text{LiNbO}_3$  phase thermodynamically stable? If this boundary is close to what is drawn, then a few isobaric heating/cooling cycles below 15 GPa can be determined its slope.

Once the two boundaries are determined, the triple point should be determined without much more difficulty.

### Conclusion

*In-situ* high pressure and high temperature X-ray diffraction studies on the natural polycrystalline ilmenite up to 19 GPa and 700°C in a large volume press using synchrotron radiation source were performed and those results are as follows :

1) The ilmenite-perovskite transition in  $\text{FeTiO}_3$  was observed directly at 500°C, with the forward transition at 16 GPa and the backward at 15.5 GPa.

2) Whereas the forward transition ( $\text{LiNbO}_3 \rightarrow$  perovskite) was reported at 16 GPa and at 23°C (Leinenweber et al., (1991), the backward transition (perovskite  $\rightarrow$   $\text{LiNbO}_3$ ) transition was observed in this study at 15.5 GPa and 23°C.

3) The  $\text{LiNbO}_3 \rightarrow$  ilmenite transition was observed at 13.5 GPa and 300°C and also at 10.8 GPa and 400°C, respectively. The  $\text{LiNbO}_3$  phase could be distinguished from the ilmenite phases based on the *c/a* ratio.

4) These results indicate that the  $\text{LiNbO}_3$  phase may have a stability field in the P-T phase diagram and that the perovskite-ilmenite phase boundary would be quite different from that previously reported.

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