BRIEF REPORTS

*Brief Reports are accounts of completed research which, while meeting the usual **Physical Review B** standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

High-pressure phase above 40 GPa in ferroelectric KNbO$_3$

Y. Kobayashi and S. Endo

Research Center for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan

T. Ashida

Department of Chemistry and Environmental Technology, Kinki University, Higashihiroshima, Hiroshima 729-2115, Japan

L. C. Ming

Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa, Honolulu, Hawaii 96822

T. Kikegawa

Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan

A ferroelectric KNbO$_3$ of the barium titanate family has been investigated to 69 GPa at room temperature by angle-dispersive powder diffraction using synchrotron radiation and an imaging plate. A phase transition was observed to take place at around 40 GPa, and the Rietveld analysis showed that the high-pressure phase has GdFeO$_3$-type orthorhombic structure, which is also one of the distorted perovskite structures.

I. INTRODUCTION

Potassium niobate KNbO$_3$ belonging to the perovskite-type ferroelectrics of the barium titanate family exhibits the following three structural transitions with decreasing temperature at ambient pressure: from cubic to tetragonal at 691 K, then to orthorhombic at 498 K, and finally to rhombohedral at 263 K. The highest-temperature cubic phase is paraelectric, and the other three phases are all ferroelectric. These successive structural and dielectrical transitions are completely the same as BaTiO$_3$. On the behavior of KNbO$_3$ under high pressure at room temperature, two Raman spectroscopic experiments were performed. However, their results did not agree with each other. On the one hand, Gourdian *et al.*[1] found by Raman spectroscopy and optical observation that the ferroelectric orthorhombic phase transforms to the paraelectric cubic phase around 9–10 GPa at room temperature. On the other hand, Shen *et al.*[2] reported that as the pressure increases, there are three crystalline phases appearing at 2.0, 6.0, and 9.0 GPa, respectively, and finally an amorphous phase appears at a pressure of around

15 GPa, but none of these high-pressure phases is the paraelectric cubic phase. Moya *et al.*[3] tried to confirm the transition to the cubic phase at high pressure by a powder x-ray diffraction, but no structural transition from the orthorhombic phase was observed up to 12 GPa. Frenkel *et al.*[4,5] investigated the local structure of KNbO$_3$ at 77 and 300 K under high pressure up to 15.8 GPa using the x-ray-absorption fine-structure (XAFS) technique, and found that the local-structure symmetry of the initial rhombohedral phase does not change over these temperature and pressure ranges. The main purpose of the present study is the search for a pressure-induced transition which may appear at pressures much higher than those of previous studies.

II. EXPERIMENT

In situ x-ray-diffraction experiments for a powder sample of KNbO$_3$ were performed in a diamond anvil cell up to 69 GPa at room temperature. The sample used in this experiment was purchased from Johnson & Matthey, with a purity of 99.999% in metal basis (CAS#12030-85-2) and was con-
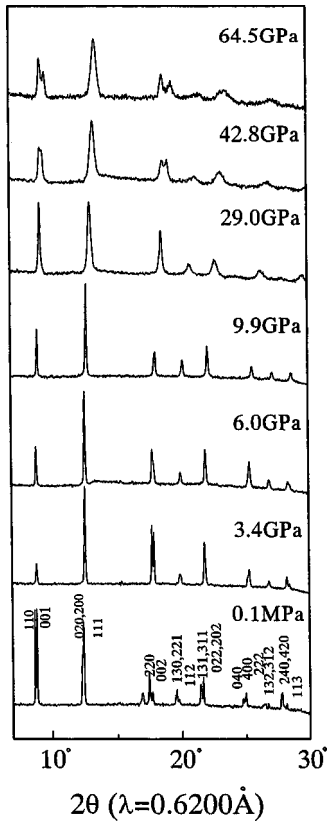
BRIEF REPORTS

FIG. 1. X-ray-diffraction patterns of KNbO$_3$ at several pressures at room temperature.
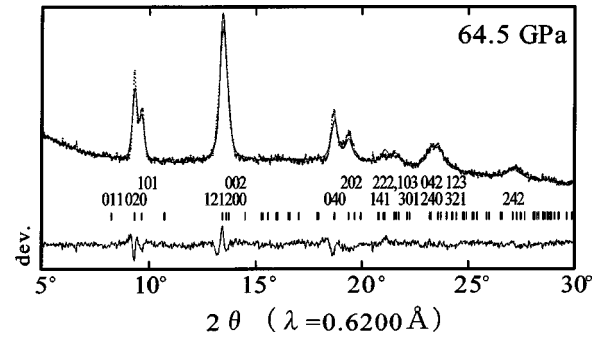

FIG. 2. Rietveld refinement for the pattern of KNbO$_3$ at 64.5 GPa. Some of the main diffraction lines are indexed.

III. RESULTS AND DISCUSSION

Several x-ray-diffraction patterns obtained under a compression process at room temperature are shown in Fig. 1. It seems that all the doublets and triplets in the orthorhombic structure at 0.1 MPa gradually become a single peak up to ~10 GPa, and then the diffraction patterns seem unchanged from 10 to 40 GPa. X-ray-diffraction data at 18.4 GPa are listed in Table I and are explained very well by a cubic unit cell. Similar results were also observed independently by Kim and Ming[6] in their recent x-ray diffraction at the National Synchrotron Light Source (NSLS) and Stanford Synchrotron Radiation Laboratory (SSRL). The critical transition pressure to the cubic phase and the related problem of whether there is a tetragonal phase before the cubic phase are not possible to determine due to the low spatial resolution in the present experiment. In our recent dielectric constant measurements under high pressure, we have also observed a clear change at around 10.5 GPa at room temperature, which is characteristic of the transition to the cubic paraelectric phase.[7]

At pressure above 40 GPa, each of the two peaks at around $2\theta = 9.3°$ and $18.6°$, respectively, splits into two peaks, indicating clearly that another structural transition has taken place at ~40 GPa. The observed pattern of the high-pressure phase above 40 GPa can be explained by an orthorhombic unit cell. For structural determination, several ortho-

firmed to be a single orthorhombic phase. Diamond anvils with a culet face of 0.3 mm and a gasket (T301, full-hardened, 10 mil thick) with a 50 μm hole serving as a sample chamber were used with 4:1 methanol-ethanol as the pressue medium. The pressure was determined by the ruby fluorescence method. Angle-dispersive diffractometry was adopted using a monochromatized synchrotron radiation ($\lambda = 0.6200$ Å) and an imaging plate detector at the Photon Factory of Institute of Materials Structure Science. The sample-to-plate distance in this study was 220.54 mm. With the storage ring operating at 2.5 GeV and 360 mA and a collimated beam of 40 μm diameter, each spectrum was collected for 40 min.

TABLE I. *In situ* x-ray-diffraction data of KNbO$_3$ at 18.4 GPa and room temperature.

d_{obs}	(hkl)	d_{cal}[a]
3.989	(100)	3.899
2.759	(110)	2.757
1.947	(200)	1.950
1.745	(210)	1.744
1.592	(211)	1.592
1.379	(220)	1.379
1.232	(310)	1.233
1.125	(222)	1.126
1.043	(321)	1.042

[a]Calculated values on the basis of a cubic unit cell with $a = 3.8994(10)$ Å.

TABLE II. Values of optimized parameters in the Rietveld calculation.

Crystal structure: GdFeO$_3$ type. S. G.:   *Pnma*.
Criteria of fitness: Rwp 4.59%, Rp 3.53%.
Lattice parameters: $a = 5.205(3)$ Å, $b = 7.627(1)$ Å, $c = 5.212(3)$ Å, and $Z = 4$.
Preferred orientation (March-Dollase):   0.73.
Overall thermal parameter: 1.5.
Atomic coordinates:

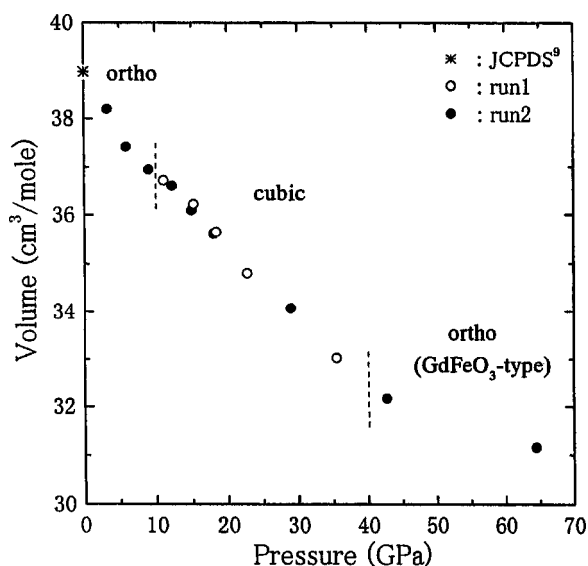|	x	y	z	Isothermal thermal parameter B
K	0.03(1)	0.25[a]	0.01(2)	4.3[a]
Nb	0[a]	0[a]	0.5[a]	2.3[a]
O(1)	0.51(4)	0.25[a]	0.00(4)	6.4[a]
O(2)	0.26(5)	0.05(2)	0.75(6)	6.4[a]

[a]Fixed in the calculation.

FIG. 3. Volume change for the orthorhombic, cubic, and GdFeO$_3$-type orthorhombic phases of KNbO$_3$ as a function of pressure.

rhombic perovskite-type structures were applied to the diffraction pattern of the high-pressure phase at 64.5 GPa. In the analysis, we employed the FAT-RIETAN97 program developed by Izumi.[8] The parameters optimized in the Rietveld calculation were the atomic coordinates, the lattice parameters, the preferred orientation parameter, the overall thermal parameters, and several peak profile parameters. The zero-point shift parameters were not included in the calculation because the zero point was reliably determined in our experiment using an imaging plate.

The best fit shown in Fig. 2 is obtained from the GdFeO$_3$-type structure (space group *Pnma*),[9] with the values of parameters given in Table II. It was difficult to determine the atomic coordinate y of O(2) together with all other parameters by Rietveld calculation. Then the coordinate y of O(2) was optimized after other atomic coordinates of K and O(1) converged. The coordinate z of O(1) was obtained to be as small as 0.00(4) by fitting. Although we searched for a structure with higher symmetry in which the coordinate z of O(1) is fixed to 0, no suitable candidates were found. Gadolinium iron oxide, GdFeO$_3$, has an orthorhombic distorted perovskite-type structure, which is different from the orthorhombic one (space group *Bmm*2) of KNbO$_3$ at ambient conditions. Some broad peaks in Fig. 2 are probably due to the overlap of plural peaks with slightly different d values. In this pressure-induced phase transition, atomic coordinates in the high-pressure phase do not seem to change so dramati-

cally from those of the primitive cubic perovskite structure. This indicates that the pressure-induced phase transition is driven by atomic displacement rather than atomic rearrangement, similar to the temperature-induced phase transitions at ambient pressure. It is worth noting that the value of the preferred orientation is 0.73. This value was evaluated using the March-Dollase function in the Rietveld calculation and is much lower than the value of 1.01 for those of no-preferred orientation. It may be ascribed partly to the quasihydrostatic condition in which the solid-to-solid phase transition occurs and partly to the polarization of synchrotron radiation light.

It is interesting to know that both KMnF$_3$ (Ref. 10) and NaMnF$_3$ (Ref. 11) have a cubic perovskite-type structure and transform to the orthorhombic (GdFeO$_3$-type) structure when the temperature decreases. Results obtained from this study on KNbO$_3$ demonstrate that the high-temperature–low-temperature transition in KMnF$_3$ (Ref. 10) and NaMnF$_3$ (Ref. 11) can be realized by the pressure at room temperature. The molar volumes for the orthorhombic, cubic, and GdFeO$_3$-type orthorhombic phases of KNbO$_3$ are plotted in Fig. 3, where the value at ambient pressure is taken from JCPDS (Ref. 12) and those values up to 10 GPa are obtained by tentatively assuming the phase to be orthorhombic because the transition to the tetragonal phase is not yet clarified.[1–5] The rate of the volume change with pressure up to about 10 GPa almost agrees with previous experimental results.[3,5] As can be seen, the volume change from the cubic to the orthorhombic perovskite is probably insignificantly small at the transition pressure ($\sim$40 GPa). This is in accordance with the closely packed nature in the perovskite structure.

In summary, we observed the successive transitions of orthorhombic-(tetragonal?)-cubic-orthorhombic (GaFeO$_3$-type) phases taking place in KNbO$_3$ with increasing pressure at room temperature. The transition to the cubic phase at $\sim$10 GPa is consistent with previous observation based on high-pressure Raman spectroscopy.[1] However, the amorphous phase suggested to appear at $\sim$15 GPa (Ref. 2) is not confirmed in this study. Three interesting problems remain to be answered: (i) does the tetragonal phase really exist under pressure at room temperature? (ii) what is the dielectric property of the high-pressure phase with the GdFeO$_3$-type structure? and (iii) is it still possible to change the GdFeO$_3$-type structure further into a different structure under much higher pressures?

ACKNOWLEDGMENT

[1] D. Gourdain, E. Moya, J. C. Chervin, B. Canny, and Ph. Pruzan, Phys. Rev. B **52**, 3108 (1995).

[2] Z. X. Shen, Z. P. Hu, T. C. Chong, C. Y. Beh, S. H. Tang, and M. H. Kuok, Phys. Rev. B **52**, 3976 (1995).

[3] E. Moya, T. Tinoco, A. Polian, and J. P. Itie, Ferroelectr. Lett. Sect. **22**, 59 (1997).

[4] A. I. Frenkel, F. M. Wang, S. Kelly, R. Ingalls, D. Haskel, E. A. Stern, and Y. Yacoby, Phys. Rev. B **56**, 10 869 (1997).

[5] A. I. Frenkel, E. A. Stern, and Y. Yacoby, in *First-Principles Calculations for Ferroelectrics*, edited by R. E. Cohen, AIP Conf. Proc. No. **436** (AIP, Woodbury, NY, 1998), p. 238.

[6] Y. H. Kim and L. C. Ming (unpublished).

[7] Y. Kobayashi, S. Endo, K. Deguchi, L. C. Ming, and G. Zou (unpublished).

[8] F. Izumi, in *The Rietveld Method*, edited by R. A. Young (Oxford University Press, Oxford, 1995), p. 236.

[9] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Krieger, Malabar, FL, 1986), Vol. 2, p. 407.

[10] See R. W. G. Wyckoff, *Crystal Structures* (Ref. 9), Vol. 2, p. 411.

[11] Y. Zhao, D. J. Weidner, J. Ko, K. Leinenweber, X. Liu, B. Li, Y. Meng, R. E. G. Pacalo, M. T. Vaughan, Y. Wang, and A. Yaganeh-Haeri, J. Geophys. Res. B **99**, 2871 (1994).

[12] *Powder Diffraction File* (JCPDS International Center for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081), Inorganic 9-156.