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Compression of $KNbO_3$ up to 30 GPa: Transition sequence orthorhombic→tetragonal→cubic

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From neutron diffraction and x-ray diffraction of compressed $KNbO_3$ up to 11 and 30 GPa, respectively, firm conclusions were obtained on the occurrences and on the transition pressures of the structural transformations, orthorhombic to tetragonal and tetragonal to cubic, along the room-temperature isotherm.

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INTRODUCTION

Ferroelectric perovskites of the $BaTiO_3$ family play an important role in fundamental and applied physics. This kind of material, as well as other perovskites, such as the ferrodistorsive $SrTiO_3$, $KTaO_3$, and mixed compounds, have given rise to a tremendous amount of scientific work. One of the main problems is the nature of the various solid phases, which can be obtained either by temperature or pressure change or by chemical substitution. As a rule investigations involved dynamical and structural properties. This work concerns structural investigations of the pressure-induced transitions in $KNbO_3$ at room temperature.

$BaTiO_3$ and $KNbO_3$ are isostructural and undergo the same sequence of phase transitions with increasing temperature, at ambient pressure, from a rhombohedral $R3m$ ($C_{3\nu}^{5}$), fully ordered solid, to partly disordered orthorhombic $Amm2$ ($C_{2\nu}^{14}$) and tetragonal $P4mm$ ($C_{4\nu}^{1}$) and to a disordered cubic $Pm3m$ (O_h^1) solid. The cubic phase is paraelectric, whereas the ordered and partially ordered phases are ferroelectric (FE). In these materials pressure plays a role similar to temperature: the ferroelectric ordering eventually vanishes under compression, and all the various FE-FE transition temperatures decrease upon compression. These features were first revealed some 30 years ago in $BaTiO_3$ (Ref. 1) and more thoroughly investigated more recently for the compounds $BaTiO_3$ (Refs. 2–4) and $KNbO_3$ (Refs. 5–12) using a variety of techniques: dielectric measurement, Raman light scattering, and x-ray diffraction. Specifically it was shown that for $KNbO_3$ at 10–11 GPa, the ferroelectric Curie temperature, which is around 703 K at room pressure, shifts down to 295 K (i.e., ambient temperature).[5,7–9,11] This is shown in Fig. 1, where the phase diagram determined from preliminary Raman scattering experiments is given.[11] Data on the locations of the various transformations were also obtained by another group from dielectric measurements.[8] Despite the results obtained, the existence of the cubic solid was in doubt until recently. This feature seems now to be admitted, however, there is still controversy about the transition pressure that is either 8 or 10 GPa.[9,10] The orthorhombic-tetragonal (OT) transition, which occurs at ~491 K at room pressure, and expected below 10 GPa at 295 K, was difficult to detect. However, lately with Raman scattering, clear evidence of the transformation was obtained in our group.[11] The somewhat sluggish transition was found to take place over the pressure interval 5–7 GPa, while another team observed a mode

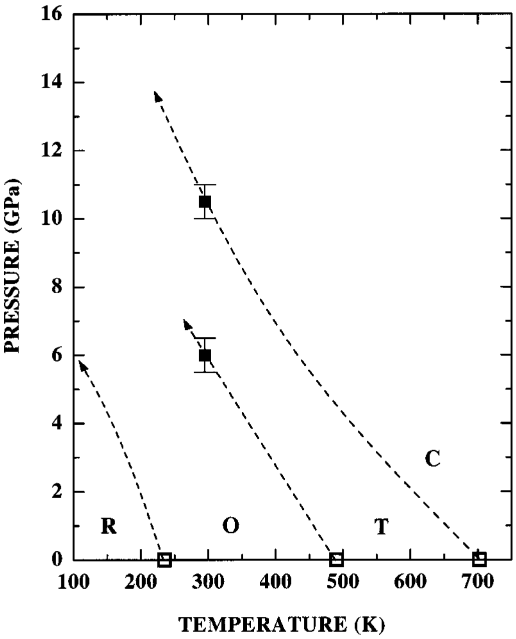

FIG. 1. Phase diagram of $KNbO_3$. Dashed lines: from Raman scattering experiments (Ref. 11). Open symbols: cubic (*C*)-tetragonal (*T*), tetragonal-orthorhombic (*O*), orthorhombic-rhombohedral (*R*) transition temperatures (high temperature from Ref. 20 and at low temperature our result with Raman scattering). Close symbols: neutron and x-ray diffraction (present work). Error bars: pressure range of the transitions.

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width discontinuity at 7 GPa.[12]

One of the goals of this work was to determine, using diffraction methods, the room temperature OT transition pressure and to check the location of the cubic phase. In the present work results obtained from neutron and x-ray diffraction experiments are reported. We found, in agreement with our Raman investigations, that the OT and the tetragonal-cubic (TC) transitions take place in the 5–7 and 10–11 GPa ranges, respectively.

EXPERIMENT

X-ray diffraction

The high-pressure diffraction experiment was performed using a membrane diamond anvil cell[13] (MDAC) with full x-ray aperture around 56°.[14] This cell was equipped with tungsten carbide seats, the diamonds were *Ia* stones whose culet diameters were 0.5-mm. Gaskets were 301 stainless steel with 150-μm hole diameters. The $KNbO_3$ samples, synthesized in the laboratoire de Physique des Solides, Orsay, were finely ground and placed in the gasket hole with small ruby spheres for *in-situ* pressure measurements using the power-five pressure calibration law of the $R1$ ruby line.[15] The pressure transmitting medium was either silicon oil, or nitrogen. In the latter case the cell was filled with the liquefied gas at 77 K. High-pressure powder-diffraction experiments were performed in the angle-dispersive mode at the ESRF (Grenoble, France) on station ID9 using a large area ($340\times400\,\mathrm{mm}^2$) image plate and the MDAC on an X-Y-Z-Θ micropositioner. The monochromatic x-ray beam was collimated down to $50\times50\,\mu\mathrm{m}^2$ and ‘‘cleaned up’’ close to the cell using fine slits to avoid contamination by gasket scattering. During exposure times, the DAC was rocked through ± 3° in order to improve the crystallite averaging. A silicon powder standard was used to determine the wavelength and sample-to-plate distance.

Neutron diffraction

The neutron-diffraction experiment was performed using the PEARL beamline High-Pressure Facility, HiPr, of the ISIS neutron spallation source located at the Rutherford Appleton laboratory (Didcot, Chilton, UK). PEARL/HiPr is an intermediate resolution ($\Delta d/d=0.8\%$ at $2\theta=90°$), high-flux neutron time-of-flight diffractometer, the scattering geometries of which are optimised around the capabilities of the Paris-Edinburgh pressure cell.[16,17] The cell was equipped with a null-scattering TiZr toroidal gasket. The sample volume, initially around 80 mm^3, was filled with $KNbO_3$ powder and Fluorinert as pressure transmitting medium. In order to investigate the phase diagram at low temperature, the cell was placed in a liquid nitrogen cooled cryostat. Using the standard transverse scattering geometry of PEARL/HiPr ($83°<2\theta<97°$), diffraction data were collected for a total of 23 pressure-temperature points following isobaric and isothermal paths in the range 0–11 GPa and from 150 to 290 K. The sample pressure was calculated using the refined unit-cell volume and the $KNbO_3$ equation of state as determined by the x-ray diffraction investigations described elsewhere[7] and in the present work. The temperature was determined using two thermocouples attached onto the anvils of the cell. The typical data-collection time for each neutron-diffraction pattern was ~30 min. The intensity vs *d*-spacings spectra, corrected for the attenuation for the in and out going beams were analyzed by the Rietveld refinements procedures using the GSAS package.[18]

RESULTS AND DISCUSSION

X-ray diffraction

X-ray diffraction data were collected on image plates for exposure times of just a few minutes. The two-dimensional powder rings were integrated into a conventional profile through the program FIT2D.[19] Simulations of the intensities were performed with the program CARINE. The main features expected at the OT transition are strong relative intensity variations of the components of doublets and multiplets, leading to intensity inversions or significant changes of the reflection profiles. This should be particularly the case for the doublets 011,100 and 022,200. At the TC transition the lines become single lines. It is worth recalling that, as for $BaTiO_3$, the various structures of $KNbO_3$ are very similar, e.g., at ambient pressure the lattice parameters of the pseudocubic description of the orthorhombic phase are close to 3.973, 4.0270, 4.0454 Å, respectively,[20,21] so that relatively small changes of the cell parameter values are expected at the phase transitions. At low pressure the diffraction patterns obtained in the 2θ range from 6 to 26° were consistent with the orthorhombic structure. On compression and in the 5–7 GPa pressure range, modifications of the patterns were observed. Actually the compression causes a strong overlapping of the close reflections that prevented the visual observation of doublet intensity inversions; on the other hand these inversions, specifically on the doublets 001,100 and 022,200, were observed at lower pressure and higher temperature.[22] Accordingly profile modifications and intensity inversions were either observed directly on the patterns, intensity vs 2θ, as shown in Fig. 2 for the multiplets 013 +031+122, 211 and 024+042, 311, or using the decomposition for doublets and other multiplets. Furthermore in the same pressure range slight decrease of the slopes in the 2θ vs p plots were observed. These features can be assigned to the OT transition that according to the present observations occurred over a pressure range estimated around 2 GPa centered at ~6 GPa. On further compression and between 10–11 GPa, the doublets and multiplets transformed to singlets. Actually the various multiple reflections became symmetric and exhibited width minima around 11 GPa showing a coalescence of the components of the multiplets. These last features were assigned to the TC transition. Using the program U-FIT (Ref. 23) the cell parameters of the orthorhombic, tetragonal, and cubic structures were refined. In the next section the pressure variations of the cell parameters obtained from x-ray and neutron diffractions are compared.

Neutron diffraction

The features expected at the OT transition are similar to those given above: i.e., modifications of the profiles of dou-

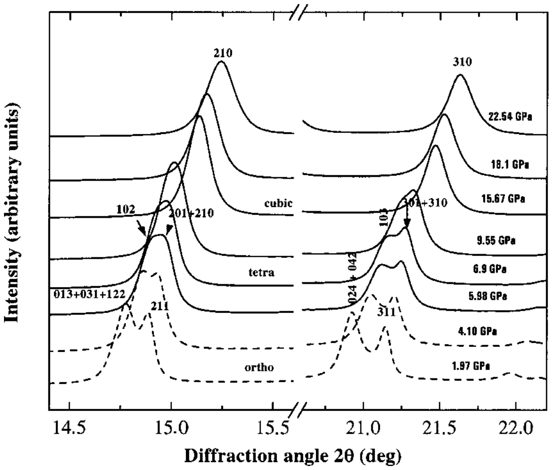

FIG. 2. Evolution of the x-ray diffraction patterns of $KNbO_3$ at 295 K at various pressures for the reflections $013+031+122$, 211 and $024+042$, 311 showing the intensity inversions at ~6 GPa that indicate the onset of the OT transition.

blets and multiplets. Close to ambient pressure the diffraction pattern exhibited the expected doublets and multiplets of the orthorhombic structure ($Amm2$). On compression the doublets became progressively less well resolved; in Fig. 3 the diffraction pattern shown at 4.4 GPa still exhibits the doublet 200,022, the corresponding profile refinement illustrates the quality of the fit. Beyond ~6 GPa there was no visual indication of the presence of separate reflections. Accordingly the OT transition could not be located by straightforward observation of the reflection profiles, so that the intensity inversions of the doublets expected at the transition were not observed. On the other hand the results obtained from the profile Rietveld refinements allowed us to extract precise structural parameters as a function of pressure. The analysis up to 6 GPa was made in orthorhombic space group $Amm2$ similar to previous neutron powder data by Hewat.[21] The refinements included the three lattice parameters, four fractional atomic co-ordinates $z(\mathrm{K})$, $z(\mathrm{O3})$ and $z(\mathrm{O4})$ and $y(\mathrm{O4})$ and four isotropic thermal parameters U for all atoms. At 0 GPa they are, within error, identical with ambient pressure values from Ref. 21.[24] Among these structural parameters, only the lattice parameters, shown in Fig. 4, showed a significant change with pressure. The orthorhombic splitting between the b and c is seen to reduce by 50% up to 6 GPa. At higher pressures the orthorhombic structure model gave lattice parameters that exhibited a marked change of slope at 6 GPa. Given the additional evidence from the x-ray (as discussed above) and Raman measurements, these changes were hence assigned to the onset of the OT transition. The analysis between 6.6 and 10 GPa was, therefore, based on the tetragonal $P4mm$ structure, refining two lattice parameters, three fractional atomic coordinates $z(\mathrm{K})$, $z(\mathrm{O3})$, and $z(\mathrm{O4})$, and four isotropic thermal parameters. The validity of this assumption was checked *a posteriori* in that apparently well-behaved cell parameter vs pressure behavior was obtained after refinement of the data beyond 6 GPa using the expected tetragonal structure. Again, the fractional coordinates in the $P4mm$ structure are found to be identical with 0 GPa values from Hewat and only the lattice parameters

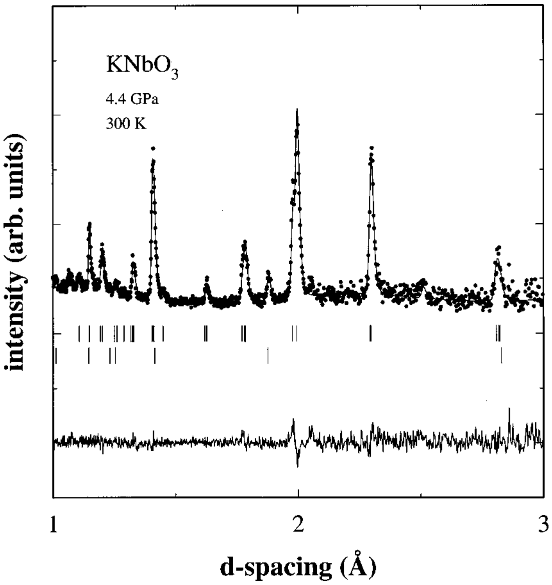

FIG. 3. A neutron diffraction spectrum collected from $KNbO_3$ at 4.4 GPa in the 1 to 3 Å d-spacing range. The dots are measured data. Solid line is the result of a Rietveld profile refinement of the data, at the bottom: residuals. Upper ticks: $KNbO_3$ reflections; lower ticks: tungsten carbide reflections from the anvils. The doublet 200,022 is still observed around $d=2$ Å.

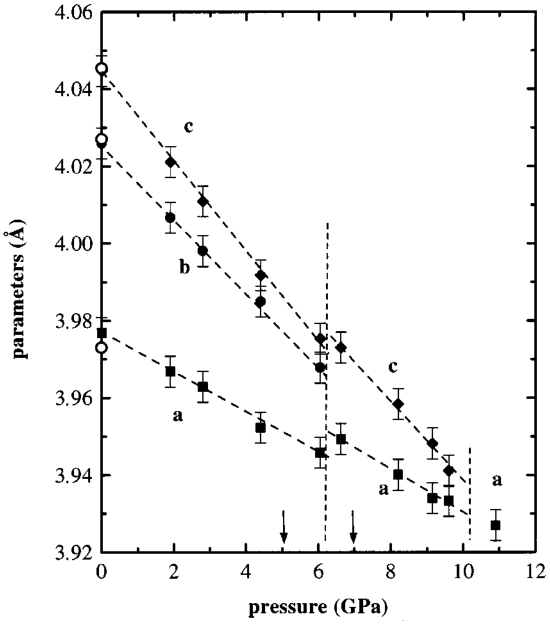

FIG. 4. Lattice parameters of $KNbO_3$ determined by neutron diffraction at 295 K as a function of pressure. Dark symbols: this work, open circles: Hewat (Ref. 21). Dashed lines: guides for the eyes. The orthorhombic-tetragonal (OT) and the tetragonal-cubic (TC) transitions are located at ~6 GPa and 10–11 GPa, respectively (vertical dashed lines). The error on the cell parameters is estimated around 0.004 Å. Arrows: pressure range where the OT transition takes place according to x-ray diffraction and Raman scattering techniques; in our neutron data analysis the Rietveld refinement was based on the orthorhombic structure up to 6 GPa and to the tetragonal structure above.

showed significant changes under pressure.[25] Based on this analysis we find that the change of the cell dimensions at the OT transition is consistent with the behavior found at room pressure under variable temperature for $BaTiO_3$ or $KNbO_3$.[26] The *c* parameter increases slightly, actually the *c* direction is related to the ferroelectric axis; the *b* parameter decreases that correlates with a slight discontinuity of the *a* parameter. On further compression the pressure dependencies of the *a* and *c* parameters suggest that these two parameters merge around 11 GPa. Actually around this pressure it was found that the Rietveld refinement provided a slightly better fit for the cubic structure than for the tetragonal structure. Five isobars were investigated from room temperature down to 150 K. At approximately ambient pressure the diffraction pattern of the rhombohedral solid was obtained below ∼200 K and at ∼2.8 GPa the orthorhombic-rhombohedral transition was located between 198 and 160 K. At higher pressure and up to ∼11 GPa, the upper pressure of this investigation, we were not able to observe any difference between the patterns. The number of p,T points investigated were not sufficient to perform a treatment as the one described above for the room-temperature isotherm.

Excellent agreement was obtained between the x-ray and neutron-derived lattice parameters for the orthorhombic phase: the maximum discrepancy is $\sim 3\times10^{-3}$ Å at 5 GPa for the *c* parameter. The agreement is less good for the case of the tetragonal phase, for which the discrepancy reaches a maximum value of ∼0.01 Å for the *c* parameter at 9.5 GPa. For the cubic phase the agreement between the lattice parameter values was better than 2×10^{-3} Å. From our neutron and x-ray diffraction measurements the estimated volume change of the pseudocubic cell, ΔV, at the OT transition was around -0.08 Å^3. From ambient pressure x-ray experiments, reliable ΔV values are difficult to obtain. From Shirane Newnham, and Pepinsky[20] the jump may be estimated less than -0.1 Å^3. The same authors measured the latent heat of transformation to be 85 cal/mole. From our recent high-temperature–high-pressure investigations, with x-ray diffraction and Raman scattering, we found a line slope, dp/dT, for the transition OT, close to -0.03 GPa K^{-1};[22] this provides, with the Clapeyron relationship, a volume change $\Delta V \sim -0.04$ Å^3, which is significantly smaller than the one observed at 6 GPa. It is very likely that our values for ΔV under pressure are overestimated as it is known that the first-order character of the transition weakens with increasing pressure (see Ref. 5, and references therein). In the same way, from our x-ray data, ΔV at the TC transition was estimated to be ~ -0.2 Å^3, whereas the results of Shirane Newnham, and Pepinsky[20] suggest a volume change of ~ -0.15 Å^3.

The x-ray diffraction measurements were performed for pressures up to 29.5 GPa. A plot of the pseudocubic cell volume vs pressure exhibited a regular variation with small changes at the OT and TC transition points. Accordingly the equation of state least-squares fit to our unit-cell volume data was performed using the same analytical form for all phases. Sufficient accuracy was obtained with the Murnaghan equation of state,

$$V = V_0\left[1+\frac{B_0'}{B_0}p\right]^{-1/B_0'},$$

where V_0 is the unit-cell volume, B_0 the bulk modulus $[B = -V(\partial p/\partial V)_T]$ and B' the first derivative of B, all evaluated at ambient pressure. The parameter V_0 was found very close to the literature cell volume data and accordingly was set to 64.732 Å^3.[20] The resulting fit to our volume data provided values of B_0 and B_0' close to 146 GPa and 5, respectively, with a mean relative error in V of less than 10^{-4} and a maximum relative error of $\sim 2\times10^{-3}$. The bulk modulus B_0 may also be computed from the elastic constant values, although data are scarce concerning $KNbO_3$. From the compliances obtained from Brillouin scattering experiments[27] we found B_0 close to 172 GPa. This discrepancy with the B_0 value of Eq. (1) is very likely due to the uncertainties on the elastic constants, which may reach 10 to 30 %.

CONCLUSION

Clear evidence of the pressure-induced orthorhombic to tetragonal and tetragonal to cubic transformations has been observed in $KNbO_3$ using the angle-dispersive x-ray and neutron time-of-flight diffraction techniques at room temperature (295 K). From x-ray diffraction and Raman scattering techniques the OT and TC transitions have been observed to occur over the finite pressure ranges 5-7 GPa and 10–11 GPa, respectively.

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[24] Our results, ∼0 GPa/300 K: $z(\mathrm{K})=0.008(3)$, $z(\mathrm{O3})=0.537(2)$, $z(\mathrm{O4})=0.282(1)$, $y(\mathrm{O4})=0.249(1)$; thermal parameters (all in 10^{-2} Å^2): $U(\mathrm{K})=0.4(1)$, $U(\mathrm{Nb})=0.4(1)$, $U(\mathrm{O3})=0.7(2)$, $U(\mathrm{O4})=0.7(1)$; Ref. 21, 0 GPa/295 K: $z(\mathrm{K})=0.013(2)$, $z(\mathrm{O3})=0.538(1)$, $z(\mathrm{O4})=0.2836(5)$, $y(\mathrm{O4})=0.2489(5)$; $U(\mathrm{K})=0.77(7)$, $U(\mathrm{Nb})=0.38(4)$, $U(\mathrm{O3})=0.42(8)$, $U(4)=0.71(5)$.

[25] Our results, 6.6 GPa/300 K: $z(\mathrm{K})=0.505(6)$, $z(\mathrm{O3})=0.542(3)$, $z(\mathrm{O4})=0.041(2)$; thermal parameters (all in 10^{-2} Å^2): $U(\mathrm{K})=0.4(2)$, $U(\mathrm{Nb})=0.3(1)$, $U(\mathrm{O3})=0.5(4)$, $U(\mathrm{O4})=0.4(2)$; Ref. 21, 0 GPa/543 K: $z(\mathrm{K})=0.518(3)$, $z(\mathrm{O3})=0.540(3)$, $z(\mathrm{O4})=0.542(3)$; thermal parameters (all in 10^{-2} Å^2): $U(\mathrm{K})=1.5$; $U(\mathrm{Nb})=0.70(4)$, $U(\mathrm{O3})=1.6(1)$, $U(\mathrm{O4})=0.92(5)$.

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