Pressure-induced phase transitions of KNbO$_3$

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Abstract
We studied crystal structures of potassium niobate (KNbO$_3$) at high pressure
by means of first-principles self-consistent total-energy calculations within the
local density approximation using the full-potential linear muffin-tin orbital
method. For the first time, we have calculated the atomic equilibrium volume,
bulk modulus, total energy, and transition pressures for KNbO$_3$, covering the
full pressure range for which the above-mentioned experiments have been done.
Two pressure-induced transitions are derived theoretically, namely one from
orthorhombic (I) to cubic structure at around 13.2 GPa and a second from cubic
to orthorhombic (II) structure at a pressure of 39.7 GPa. This fully confirms
the recent experiments by Kobayashi *et al* (Kobayashi Y, Endo S, Ashida T,
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(Some figures in this article are in colour only in the electronic version)

1. Introduction

Potassium niobate (KNbO$_3$) belongs to the group of perovskite-type ferroelectrics of the
barium titanate family. It has outstanding electro-optical, nonlinear optical, and photo-
refractive properties and has found widespread application in nonlinear optics and electro-
optics. Furthermore, its successive phase transitions induced by pressure provide a typical
example for studies of the paraelectric-to-ferroelectric transition. During the last decade,
KNbO$_3$ has been one of the most intensively studied materials.

The properties of KNbO$_3$ are similar to those of barium titanate. It exhibits 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. The polarization
direction changes at each phase transition. But whether the mechanisms of these transitions
are displacements characterized by soft modes or disorders characterized by central peaks [2]
is still a matter of dispute.

As regards the behaviour of $KNbO_3$ under high pressure at room temperature, two Raman scattering experiments have been done. Gourdain *et al* [3] used optical observation and Raman scattering techniques to investigate the stability range at room temperature of the orthorhombic phase of $KNbO_3$. The ferroelectric orthorhombic solid was observed to be stable up to 9–10 GPa and then it transformed to a paraelectric cubic solid through a weak first-order transformation. Meanwhile, Shen *et al* [4] used a similar method to study single-crystal samples up to 20 GPa. But their results were strikingly different from those of Gourdian *et al*. They reported that there are three new crystalline phases appearing at 2.0, 6.0, and 9.0 GPa, and finally an amorphous phase appears at around 15 GPa. Among the transitions, those at 2.0 and 6.0 GPa are thought to be of displacive types. No paraelectric cubic phase was found in this experiment. Chervin *et al* [5] investigated the phase diagram of the perovskite $KNbO_3$ up to 19 GPa by the energy-dispersive x-ray diffraction technique. They reported an orthorhombic–tetragonal transition, in the 4–5 GPa pressure range, prior to the occurrence of the cubic phase. Although they did not find complete agreement with Gourdian *et al*, their results provided a confirmation of the orthorhombic–cubic transition at ~9 GPa.

Recently another phase transition at around 40 GPa, a much higher pressure, has been reported. Kobayashi *et al* [1] investigated the ferroelectric $KNbO_3$ up to 69 GPa at room temperature by means of angle-dispersive powder diffraction using synchrotron radiation and an imaging plate. The x-ray diffraction data obtained at 18.4 GPa are explained quite well by a cubic unit cell. In their paper they write: 'a clear change at around 10.5 GPa was observed at room temperature, which is characteristic of the transition to the cubic paraelectric phase'.

This result provides second confirmation of the orthorhombic–cubic phase change at around 10 GPa. But due to experimental limitations, it is hard to decide the on phase before the cubic phase. Together with the x-ray diffraction patterns obtained in the experiment, the splitting of the two peaks at around $2\theta = 9.3°$ and $18.6°$ at a pressure of 40 GPa indicates that another structural transition takes place at 40 GPa. Rietveld analysis indicates the high-pressure phase to have the $GdFeO_3$-type orthorhombic structure, which is also one of the distorted perovskite structures.

The success of recent experimental work motivated us to undertake a thorough theoretical investigation of $KNbO_3$ at high compression. Utilizing full-potential linear muffin-tin orbital (FPLMTO) calculations based on the local density approximation (LDA), we calculated the atomic equilibrium volume, bulk modulus, total energy, and transition pressure for $KNbO_3$, covering the full pressure range for which the above-mentioned experiments were done. The results also address differences between experiment and theory, which provide us with a better understanding of the pressure behaviour of $KNbO_3$.

2. Details of the calculation

To study the electronic structure of $KNbO_3$, a FPLMTO method was used. The calculations were based on the LDA with the exchange and correlation term provided by the Hedin–Lundqvist parametrization [6]. The FPLMTO calculations were all-electron, fully relativistic, and without shape approximation of the charge density. To reduce the core leakage at the sphere boundary, a double basis with a total of four different κ^2-values was used. For K, the semicore states 3s, 3p and valence states 4s, 4p, and 3d, were used. For Nb, 4p was chosen as a semicore state and 5s, 5p, and 4d were the valence states. Only the valence band 2s, 2p, and 3d were selected for O. The resulting basis formed a single, fully hybridizing basis set. This approach has been proven to give a well-converged basis [7, 8]. For sampling the irreducible wedge of the Brillouin zone, we used a special-k-point method [9]. In order to speed up the convergence, a Gaussian broadening of width 20 mRyd was associated with
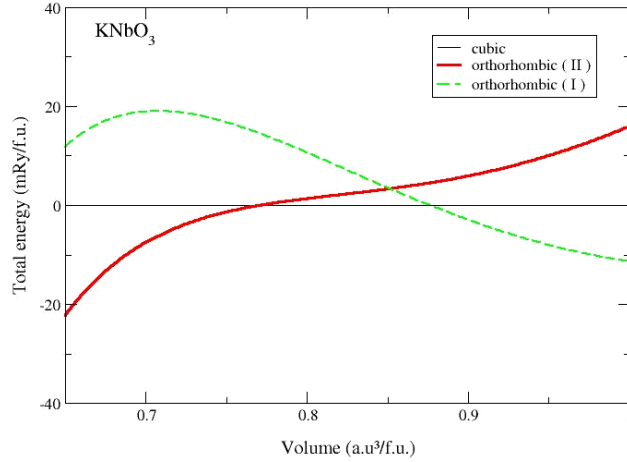
Figure 1. The total-energy differences as a function of volume for three different crystal structures of KNbO₃: orthorhombic (I), cubic, and orthorhombic (II). The total energy of the cubic phase is defined as the reference state.

Table 1. Comparison between theory and experiment. V_0 (Å³) is the equilibrium pseudo-cubic cell volume, B_0 (GPa) is the bulk modulus at ambient pressure, and B'_0 is the first pressure derivative of the bulk modulus.

	Theory			Experiment		
	V_0	B_0	B'_0	V_0	B_0	B'_0
Orthorhombic I	63.6	190.4	3.3	64.8	165	4
Cubic	62.7	177.3	4.1			
Orthorhombic II	61.7	198.7	3.6			

each calculated eigenvalue. Since there were many internal free (positional) parameters in the two orthorhombic crystal structures, we also took relaxation into consideration for these two structures. We found that our calculation results were in good agreement with the experimental data.

In figure 1, we show the calculated total energy of KNbO₃ as a function of volume, where the cubic structure is chosen as the zero-energy reference level for the three different structures. Notice that: from $V/V_0 = 1$ to 0.88, the orthorhombic (I) phase is the most stable; from $V/V_0 = 0.88$ to 0.77, the cubic phase is lowest in energy; and from $V/V_0 = 0.77$ to 0.65, the orthorhombic (II) structure prevails.

When we fitted the whole volume data set to the Murnaghan equation of state (EOS), we got the parameters in table 1. Figure 2 shows the Murnaghan EOS for KNbO₃ based on our theoretical results together with the experimental data of Kobayashi *et al*.

3. Crystal structure

Under ambient pressure and temperature, KNbO₃ has an orthorhombic crystal structure with space group *Amm*2. We took the simple orthorhombic structure as the primitive unit cell; the experimental lattice parameters are $a = 3.971$ Å, $b = 5.694$ Å, and $c = 5.720$ Å [10]. In the structure, K is on the 2a sites with $x = 0$, $y = 0$, and $z = 0$; Nb is on the 2b positions with
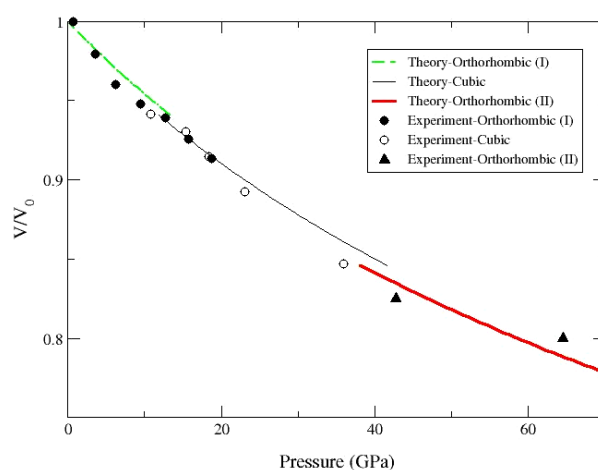
Figure 2. The EOS for KNbO$_3$. The experimental data are from [1]. The theoretical data were fitted by the Murnaghan EOS.

Table 2. Comparison between the experimental and theoretical atomic positions for the orthorhombic (I) structure.

	Theory	Experiment
K(2a) z	−0.001	0.000
Nb(2b) z	0.532	0.510
O(2a) z	0.488	0.490
O(4a) y	0.245	0.253
O(4e) z	0.244	0.237

$x = 1/2$, $y = 0.0$, and $z = 0.51$; two atoms of O are on the 2a positions with $x = 0$, $y = 0$, and $z = 0.49$; the other four atoms of O are on the 4e positions with $x = 1/2$, $y = 0.253$, and $z = 0.237$. There are all together ten atoms in the primitive unit cell. We also compare the experimental and theoretical internal atomic positions for the orthorhombic (I) structure between theory and experiment in table 2. We note that there is a very good agreement, demonstrating the accuracy of state-of-the-art electronic structure calculations.

In our calculation, the transition from the orthorhombic to the cubic phase takes place at 13.2 GPa. The cubic structure belongs to the space group $Pm3m$. There are five atoms of three types, in the cubic unit cell. K is in the 1a position (0, 0, 0); Nb is located at the central position (0.5, 0.5, 0.5); and O takes the 3c positions: (0, 1/2, 1/2), (1/2, 0, 1/2), and (1/2, 1/2, 0).

The second transition in KNbO$_3$, from cubic to orthorhombic, takes place according to theory at the pressure 39.7 GPa. The orthorhombic structure belongs to the space group $Pnma$. We choose a simple orthorhombic structure as a primitive unit cell. Experimentally K is on 4c sites with $x = 0.03(1)$, $y = 1/4$, and $z = 0.01(2)$; Nb is on 4b sites with $x = 0$, $y = 0$, and $z = 1/2$; O divides into two types—one type in 4c positions with $x = 0.51(4)$, $y = 1/4$, and $z = 0.00(4)$, the other taking the 8d positions with $x = 0.26(5)$, $y = 0.05(2)$, and $z = 0.75(6)$. There are 20 atoms in this primitive cell. The comparison between theory and experiment for the atomic positions for the orthorhombic (II) structure is shown in table 3. Our calculated atom positions agree quite well with the experimental data.

Table 3. Comparison between the experimental and theoretical atomic positions for the orthorhombic (II) structure.

	Theory	Experiment
K(4c) x	0.017	0.03(1)
K(4c) z	0.000	0.01(1)
O(4c) x	0.505	0.51(4)
O(4c) z	0.037	0.00(4)
O(8d) x	0.256	0.26(5)
O(8d) y	0.023	0.05(2)
O(8d) z	0.744	0.75(6)

Table 4. Transition pressures (GPa) in theory and experiment.

Orthorhombic (I) → cubic	13.2	10
Cubic → orthorhombic (II)	39.7	40

4. Conclusions

We studied the crystallographic phase transitions in KNbO₃ using the FPLMTO method. Two pressure-induced transitions were found theoretically: from orthorhombic to cubic at around 13.2 GPa; and from cubic to orthorhombic at a pressure of 39.7 GPa. As regards the transition pressure, the comparison between theory and experiment is given in table 4.

A large number of experiments have been made during the last decade; the recent ones carried out by Kobayashi *et al* were fully confirmed by our calculations. Relaxation plays an important role when calculating the transition pressure. Upon relaxations of the atoms in the orthorhombic structures, the total energy is lowered by about 0.6 mRyd/atom for the orthorhombic (I) structure and 6 mRyd/atom for the orthorhombic (II) structure. The equilibrium volume and bulk modulus for the orthorhombic (I) phase were well reproduced by our calculation. No experimental results are available for the cubic and orthorhombic (II) structures of zero pressure. We hope our work will stimulate further experimental study of the high-pressure behaviour of KNbO₃.

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