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Report:

AIM OF THE EXPERIMENT

The present work concerned powder x-rays investigations of $KNbO_3$ in the diamond anvil cell (DAC) up to 30 GPa and between 100 to 500 K. $KNbO_3$ is a ferroelectric perovskite of the $BaTiO_3$ family. In these compounds the ferroelectricity vanishes under pressure.[1] The present investigation aimed at obtaining, first the stability range of the ferroelectric domains,[2] and secondly the equation of state v(p,T) in a large temperature range.

EXPERIMENTAL

The high-pressure devices used were membrane diamond anvil cells (DAC) designed in our laboratory.[3] The diamond culet diameters were around 500 μm and the full (4θ) x-ray aperture was 56 °. A preindented stainless-steel gasket confined the sample ($KNbO_3$ powder + pressure transmitting medium) into a 150 μm diameter hole. Various pressure transmitting medium were used : silicone oil at room and high temperature, nitrogen or argon at low temperature. Small ruby pellets were placed into the hole for *in situ* pressure measurement according to the shift of the ruby luminescence R1 line. Samarium doped strontium borate was also used as a pressure sensor and for *in situ* temperature measurement above room temperature.[4] Depending on the temperature, the cell was placed either in a cryostat or a thermostat. Powder diffraction was performed in an angle-dispersive method on station ID09 with image plate detector. The monochromatic x-ray beam ($\lambda \sim 0.4$ A), parallel to the symmetry axis of the DAC, was collimated down to 50x50 μm^2 and cleaned up close to the cell to avoid gasket signal. During exposure times, the cell 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.

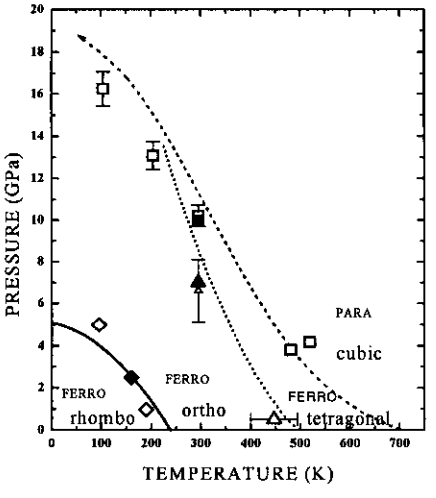
RESULTS

We investigated four isotherms close to 100, 200, 300 and 500 K up to ~ 30 GPa respectively and the isobar 1 GPa from 100 to 500 K. We performed several checks along the various investigated isotherms using the different pressure transmitting medium quoted above. The locations of the transitions (cubic-tetragonal, tetragonal-orthorhombic, orthorhombic-rhombohedral) (C-T, T-O, O-R), determined during the present work and the transition lines determined by Raman scattering[5] are given in Fig.1.The main results of the present study are summarized below.[6]

i) In the various stability ranges the diffraction patterns (intensity *vs* 2θ) were consistent with the respective structure simulations. The pressure dependences of the various transition temperatures determined by x-rays and Raman exhibit consistent behaviours. However, as shown in Fig.1, pressure discrepancies between the two determinations, may reach 1 GPa. These differences may arise from the difficulty to locate the transitions by x-rays (the various structures are similar). Also it is to be recalled here that Raman and x-ray probe the sample at different scales (the first is sensitive to short-range effects whereas the second to long-range effects, see also the note 2). This last remark is supported by the consistency between our x-ray and neutron diffraction results plotted also in Fig.1.[7]

ii) From the d-spacing data list the lattice parameters were computed by the refinement program U-FIT and their pressure dependences were obtained.

iii) The cell volume was then obtained (actually the pseudo-cubic cell volume) *vs* pressure along the various isotherms. These data were fitted to a Murnaghan equation of state. At room temperature the bulk modulus B_0 was found close to 150 GPa which is in relative good agreement to that deduced from Brillouin scattering experiment.[8] The fit of the whole volume data set lead to the temperature dependences of B_0 and of its pressure derivative B'. As expected B_0 decreases with temperature whereas B' increases. An analytical form for the complete EOS (v = v(p,T)) will be proposed. These data are of primary importance specifically for this important class of materials. They provide valuable information concerning solid-state theory and the behaviour of fundamental thermodynamics parameters such as expansivity under high pressure.



p-T phase diagram of $KNbO_3$.
Solid and dashed lines : from Raman scattering.
□ , △ , ◇ : x-rays, T-C, O-T, O-R.
■ , ▲ , ◆ : neutrons, T-C, O-T, O-R.

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8. From the elastic coefficients obtained from Brillouin scattering the computation yields B_0 = 172 GPa.