Polarized XAFS study of high-temperature phases of $NaNbO_3$

Victoria A.Shuvaeva,* Yusuke Azuma, Kenichiro Yagi, Kiyoshi Sakaue and Hikaru Terauchi

Advanced Research Center of Science, Kwansei-Gakuin University, Gakuen 2-1, Sanda, Hyogo, 669-1337, Japan. E-mail: vika@ip.rsu.ru

Temperature dependence of the Nb displacement relative to the center of oxygen octahedron in $NaNbO_3$ has been studied by polarized Nb K XAFS. Spectra were measured at two orientations of a single crystalline sample. Room temperature EXAFS data are in a good agreement with earlier X-ray diffraction data: Nb antiferroelectric displacements were found to be orthogonal to the b axis. Analysis of the temperature dependent EXAFS data didn't reveal any abrupt changes of Nb-O distances in the phase transition points. In all high-temperature paraelectric phases Nb appeared to be displaced to the off-center positions. Displacements, orthogonal to b axis, remained almost constant, while displacement along b axis gradually increased with temperature, so that in the cubic phase the displacements along all axes became equal. This shows, that disorder plays an important role in the high temperature phases. The above results are supported also by the analysis of the pre-edge structure, - the integral intensity of the pre-edge peak was temperature-independent when the polarization vector of the X-rays was orthogonal to b axis and gradually increased with temperature when the polarization was parallel to b.

Keywords: polarized XAFS; local structure; ferroelectrics; $NaNbO_3$; phase transitions.

1. Introduction

During last decades considerable attention has been paid to structural investigations of perovskite compounds (general formula ABO_3) since structural information is important for understanding mechanisms of phase transitions in these compounds. Considerable progress in these studies has been made recently by means of XAFS technique. It has been shown, that large local structural distortions are present in the cubic phases of many perovskite crystals undergoing ferroelectric, antiferroelectric and antiferrodistortive phase transitions, such as $PbTiO_3$, $BaTiO_3$, $KNbO_3$, $K_{(1-x)}Na_xTaO_3$ (Bell et al., 1991; Ravel et al., 1998, Yacoby et al., 1997). Unique opportunities for structural investigations of perovskite crystals are given by polarized XAFS. The method can provide structural details, which cannot be obtained by any other experimental technique, including XAFS obtained from powder samples. By coinciding the vector of X-ray polarization with each of the main perovskite directions in a single-crystal sample one can obtain from EXAFS spectra precise information on the direction and value of B atom displacement.

Additional possibilities are provided by analysis of the pre-edge structure of transition metal elements. The approach has been developed in detail for the analysis of Ti displacements in perovskite compounds (Vedrinskii et al., 1997; Skeath et al., 1987). The direct connection of the intensity of the pre-edge peak at the Nb K-XAFS spectra and the value of the Nb off-center displacement, determined by EXAFS analysis has been revealed in $KNbO_3$ (Shuvaeva et al., 1999). Application of polarized XAFS for the studying of the phase transitions in $KNbO_3$ made it possible to reveal quite complicated crossover of the displacive and order-disorder mechanisms of the phase transitions (Shuvaeva et al., 1997, Shuvaeva et al., 1998). It has been shown, that the direction of the Nb displacement from the center of oxygen octahedron at high temperatures deviates from the averaged macroscopic displacement. The value of this deviation is quite small at room temperature, but it increases abruptly in the phase transition points to the tetragonal and cubic phases.

Here we report results of temperature-dependent polarized XAFS study of Nb displacement in $NaNbO_3$, which is antiferroelectric at room temperature. Six phase transitions involving different types of tilts of the octahedra and displacements of the cations were reported to occur in this compound at 170, 620, 763, 790, 840, 906 K (Glazer et al., 1973). The room temperature structure is characterized by antiparallel off-center displacements of Na and Nb within (010) plane and oxygen octahedra tilting. At temperatures higher than 620 K the material is paraelectric. As it was believed previously, in paraelectric phases Nb atoms occupy positions at the centers of oxygen octahedra.

2. Experimental

Spectra from $NaNbO_3$ single crystals of about 1.5×1.5×0.04 mm in size were measured in a transmission mode at BL-10B Photon Factory of National Laboratory for High Energy Physics (Tsukuba), using a Si(311) crystal monochromator. Ring energy and current were 2.5 GeV and 300 mA, respectively. Spectra were obtained at about 35 temperature points in the range from 20 to 700 ^{o} C from the single crystal, oriented in two different ways, so that orientation of the vector of X-ray polarization was coincided with [101] and [010] directions of the orthorhombic cell. Data analysis has been performed using UWXAFS (Stern et al., 1995), and FEFF7 software (Zabinskii et al., 1995). EXAFS signal has been extracted via standard procedures. Fourier transform of the k^3-weighted spectra has been performed over the range $2.7<k<13.3$ A^{-1}.

3. Results and discussion

EXAFS

Temperature evolution of Fourier Transforms (FT) XAFS of $NaNbO_3$ are shown at the Figure 1. The room temperature spectra, measured for the two different orientations of the single crystal show clear difference, however at higher temperatures they are quite similar.

Single Nb-O peak at FT XAFS for e||[010] indicates, that the Nb displacement from the center of the oxygen octahedron in this direction is rather small. This is in agreement with the X-ray diffraction data (Sakowski-Cowley, 1969). As temperature grows, the peak becomes broader, more asymmetric and finally at T of about 370 it splits into two separate peaks. These two peaks persist in all high-temperature paraelectric phases including the cubic phase. Below T= fitting of the spectra can be successfully performed assuming single shell Nb-O distribution, however at higher temperatures a good agreement can be achieved only by involving two Nb-O shells.

* Present address:Institute of Physics, Rostov State University, Stachki 194, Rostov-on-Don, 344090, Russia

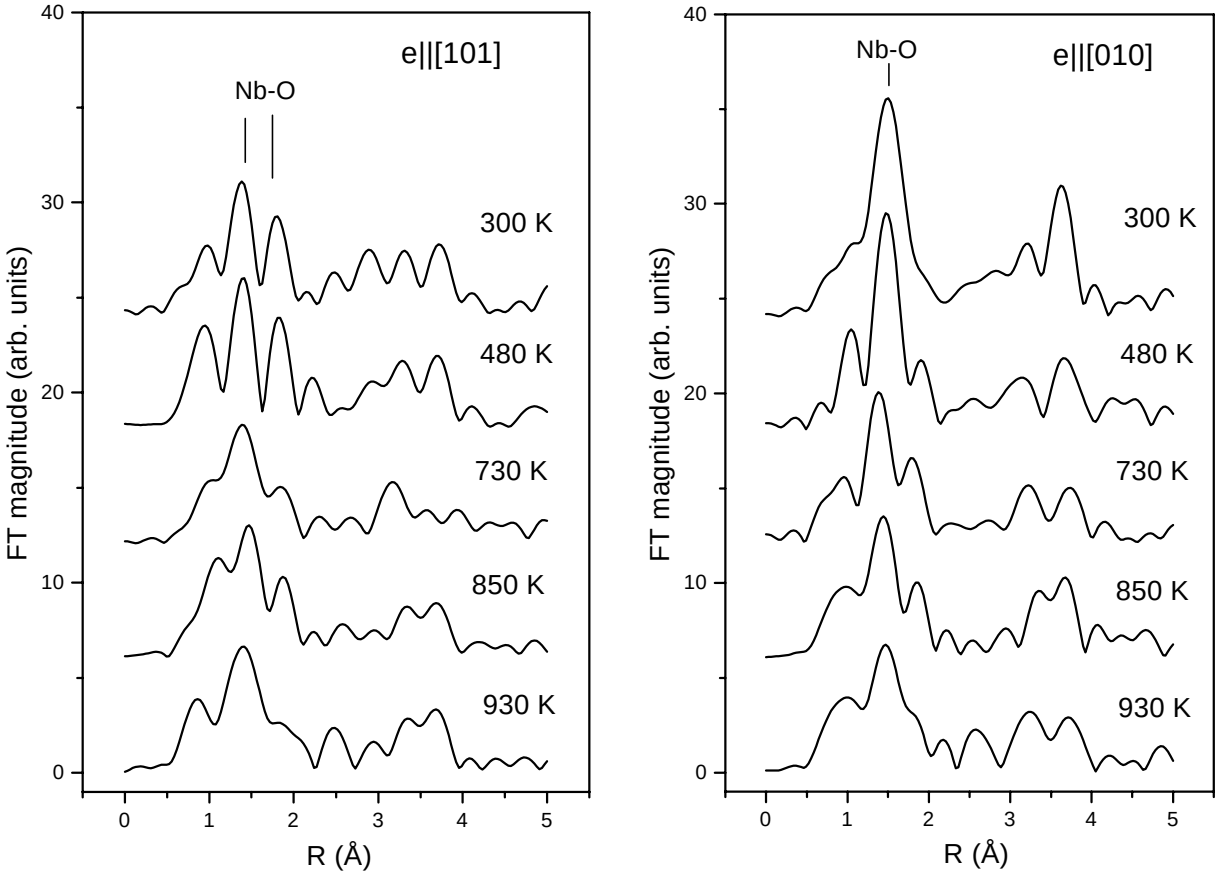

Figure 1
Absolute values of k^3-weighted Fourier transforms of the Nb K XAFS of $NaNbO_3$

At room temperature FT EXAFS for e||[101] two small separate peaks corresponding to two different Nb-O distances can be seen.

The best fit is obtained for two Nb-O distances which differ by 0.25 Å. Spectra for this orientation of the crystal display some subtle temperature changes. However two different Nb-O distances can be distinguished over the whole temperature range. Results of fitting show, that Nb off-center displacement decreases slightly with temperature, but they preserve in all high temperature phases.

According to the X-ray diffraction data (Darlington and Knight, 1999) structural distortions in $NaNbO_3$ at temperatures higher than 760 K are associated mainly with octahedra tilting whereas Nb are located at the centers of oxygen octahedra. However our EXAFS data show that this is not the case and changes of the value of Nb displacement in the phase transition points is not essential. Although the direction of the displacement changes with temperature, these changes are rather gradual. We didn't observe any dramatic changes in the phase transition points like those in $KNbO_3$ (Shuvaeva et al., 1998, Shuvaeva et al., 1999). In all paraelectric phases at temperatures higher than 760 K Nb displacements along two perovskite axes become equal. It should be noted, that due to the low symmetry of the three paraelectric phases the Nb displacement isn't really forbidden. So further investigations are needed to clarify the role of disorder in these phases. However the displacement in high-temperature cubic phase can be explained only by disorder of Nb atoms among equivalent positions.

XANES

The Nb K-XAFS near-edge region, measured at room temperature at two orientations of $NaNbO_3$ single crystal are shown at the Fig.2. Difference of the spectra in the energy range from 18980 eV to 18990 eV is seen clearly. As the peak is not clearly resolved we extracted it at all our spectra by taking the difference between them and the specter measured at room temperature for e||[010]. The temperature dependence of the integral intensity of this peak for two orientation of the crystal is shown at the Fig.3. It can be seen that it is rather temperature-independent at e||[101] and grow gradually with temperature at e||[010]. At temperature of about 750 K, at which the phase transition into paraelectric state occurs, the integral intensities of the pre-edge peak at two orientations of the crystal become equal.

So, the pre-edge structure analysis provides additional support to the conclusions, made on the basis of EXAFS. Here we observe the same correlation of the amplitude of the pre-edge peak at the Nb K XAFS to the Nb off-center displacement, which has been noticed at the Nb K XAFS of $KNbO_3$.

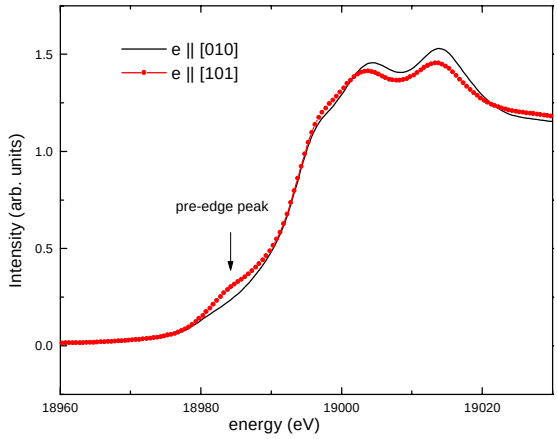

Figure 2
Polarized Nb K XAFS spectra of $NaNbO_3$ at the room temperature

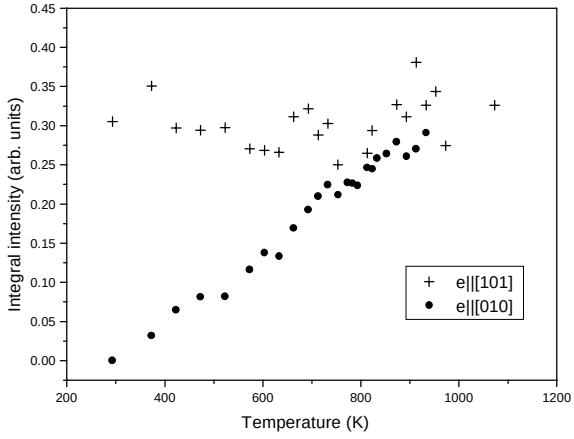

Figure 3
Temperature dependence of the integral intensity of the pre-edge peak

Conclusions

In summary, the analysis of EXAFS and near edge structure has allowed to make the following conclusions on the structure of $NaNbO_3$:

1. at room temperature the Nb displacement relative to the center of oxygen octahedron is orthogonal to [010] axis. This is in agreement with X-ray diffraction data.
2. as temperature increases, direction of the Nb displacement changes gradually. However its value remain almost constant. No any substantial changes of Nb-O distances at the phase transition points were revealed
3. in all paraelectric phases including cubic phase Nb is displaced to off-center positions. This shows, that the cubic phase is essentially disordered

References

Bell, M.I., Kim, K.H. & Elam, W.T. (1991). *Ferroelectrics* **120**, 103.
Darlington C.N.W. & Knight K.S. (1999). *Acta Cryst*., **B55**, 24.
Dougherty, P.T., Wiederrecht, G.P.& Nelson, K.A. (1995). *Ferroelectrics*, **64**, 253.
Glazer, A.M.& Megaw, H.D. (1973). *Acta Ctyst.* **A29**, 489.
Ravel, B., Stern, E.A., Vedrinskii, R.V.& Kraizman, V.L. (1998). *Ferroelectrics* **206**, 407.
Sakowski-Cowley, A.C., Lukaszewicz, K. & Megaw, H.D. (1969). *Acta Cryst*., **B25**, 851.
Shuvaeva, V.A., Yanagi, K., Sakaue, K.& Terauchi, H. (1997). *J. Phys. Soc. Japan*, **66**, 1351.
Shuvaeva, V.A., Yanagi, K., Yagi, K., Sakaue, K. & Terauchi, H. (1998). *Solid State Communications*, **106**, 335.
Shuvaeva, V.A., Yanagi, K., Yagi, K., Sakaue, K. & Terauchi, H. (1999). *J. Synchrotron radiation*, **66**, 1351.
Skeath, P., Elam, W.T., Burns, W.K., Stevie, F.A. & Briggs, T.H. (1987). *Phys. Rev. Lett.* **59**, 1950.
Stern, E. A., Newville, M., Ravel, B., Yacoby, Y. & Haskel, D. (1995). *Physica B* **208 & 209,** 117.
Vedrinskii, R.V., Kraizman, V.L., Novakovich, A.A., Demekhin, Ph.V., Urazhdin, S.V., Ravel, B. & Stern, E.A. (1997). *J. Phys. (Paris)*, IV, **7**, C2-107
Zabinskii, S. I., Rehr, J. J., Ankudinov, A., Albers, R. C. & Eller, M.J. (1995). *Phys. Rev. B* **52,** 2995
Yacoby, Y., Girshberg, Y., & Stern, E. A. (1997). Z. *Phys. B* **204,** 725.

Received 31 July 2000 • Accepted 20 November 2000