ESRF	**Experiment title:** Study of local atomic structure and phase transitions for lead-free piezoelectric solid solutions K(1-x)Na(x)NbO3 by XAFS	**Experiment number:** **HE-2192**
Beamline: BM29	**Date of experiment:** from: 12 April 2006 to: 18 April 2006	**Date of report:** 19 August, 2006
Shifts: 18	**Local contact(s):** Dr Olivier MATHON (e-mail: mathon@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Elena NAZARENKO Laboratoire de Cristallographie, CNRS, Grenoble, France. Institute of Physics, Rostov State University, Rostov-on-Don, Russia

Mikhail LEMESHKO Institute of Physics, Rostov State University, Rostov-on-Don, Russia

Dr. Yves JOLY Laboratoire de Cristallographie, CNRS, Grenoble, France

Prof. Rostislav VEDRINSKII Institute of Physics, Rostov State University, Rostov-on-Don, Russia

Report:

The most successful piezoelectric ceramics, which is widely used in sensors, actuators and other electronic devices, is based on $PbZr_{1-x}Ti_xO_3$ (PZT). Environmental concerns over PZT lead content could disappear with the advent of new lead-free ceramics. Recently Saito and colleagues [1] have found such compounds based on $K_{1-x}Na_xNbO_3$ (PSN) ceramics, whose piezoelectric properties are comparable to PZT. However, the mechanisms underlying the ultrahigh performance of these materials, and consequently the possibilities for further improvements, are not clear at present. The challenge of relating the PSNs piezoelectric properties to their microscopic structure is still open.

The main goal of this work is refinement of the local atomic structure parameters and its change near phase transition points for PSN solid solution using the extended x-ray absorption fine structure (EXAFS) spectroscopy. The Nb K-spectra obtained for powder samples are analyzed using the combination of two techniques: i) fitting of the EXAFS signal in the *R* space, and ii) the "differential EXAFS" method, i.e. the analysis of Fourier transform of the difference between $\chi(k)$ functions obtained for various temperatures or concentrations *x*. The last one allows finding out even the weak differences between local atomic structures, taking place with changes of temperatures or concentrations.

Experimental: Powder samples of $K_{1-x}Na_xNbO_3$ (PSN) solid solution were prepared for six different concentrations x=0.35, 0.50, 0.60, 0.70, 0.95 and 1.00 at the Institute of Physics at Rostov State University by standard solid-state reactions of Na_2CO_3, K_2CO_3 and Nb_2O_5. Several grindings and firings in air at temperatures up to 1150 ^oC were performed. X-ray powder diffraction measurements confirmed that the solid solutions were single phase ones. The samples were prepared from grinded PSN ceramic diluted with carbon and pressed into tablets. XAFS Nb K-edge spectra were collected for all the samples. The temperature dependence of the spectra in the range from 10 K to 1023 K was studied also.

The storage ring was run at energy 6.0 GeV with the electron current about 200 mA. Spectra were recorded in the transmission mode using a double-crystal Si(111) monochromator. Harmonic rejection is achieved with two Rh-coated mirrors, before and after the monochromator. The spectra were scanned in the range of 18.61-20.22 keV, with an energy depending step.

Results:

To study the local atomic structure of the NbO_6 octahedrons in PSN solid solution we performed the fitting of EXAFS signal using the iFEFFIT package. Scattering paths were determined by the FEFF7 code. The k-range for the Fourier transformation was 3.5-15.0 $Å^{-1}$, the R-range was 1.1-2.0 Å. Fitting of the EXAFS data was performed within different assumptions about the distribution of the Nb atom on the small sphere surface: eight-site model, six-site and 12-site ones. All these models are used to describe local atomic structure of perovskite-type crystals (see ref. [2] and refs. therein). The radius of the small sphere r_0 and the average distance from the center of this sphere to oxygen atoms R_0 were determined from the results of EXAFS fitting.

The results of the EXAFS analysis for the temperature far from the phase transitions are shown at **Fig. 1.** As an example, the fitting results are presented for x = 0.5 (see also **Table**). The results obtained for other x values are quite similar to these ones.

Table. Best-fit parameters of the 1st coordination shell of Nb atom for $K_{0.50}Na_{0.50}NbO_3$. R is Nb-O distance, r_0 is radius of the small sphere around immediate center of a NbO_6 octahedron and R_0 is average Nb-O distance determined from the full 1st shell pair radial distribution function. R-factor – statistical factor of fit quality.

T	R (Å)	r_0 (Å)	R_0 (Å)	R-factor (%)
10 K	1.89 2.12	0.193	2.00	0.9
50 K	1.90 2.12	0.194	2.00	1.5
300 K	1.88 2.02 2.16	0.195	2.02	0.5
423 K	1.88 2.02 2.16	0.195	2.02	1.8
553 K	1.91 2.13	0.195	2.02	1.5
623 K	1.91 2.14	0.195	2.02	1.8
773 K	1.93 2.16	0.196	2.04	1.4
953 K	1.93 2.15	0.195	2.04	1.9
1023 K	1.93 2.15	0.195	2.04	1.8

Fig. 1 The results of fitting performed for $K_{0.50}Na_{0.50}NbO_3$: Left panels - the absolutes values of the Fourier transforms of the k^3 weighted $\chi(k)$ (solid lines – experiment, dashed lines – fitting results), right panels - the pair radial distribution functions (PRDF). Fitting range is shown by the dashed line.

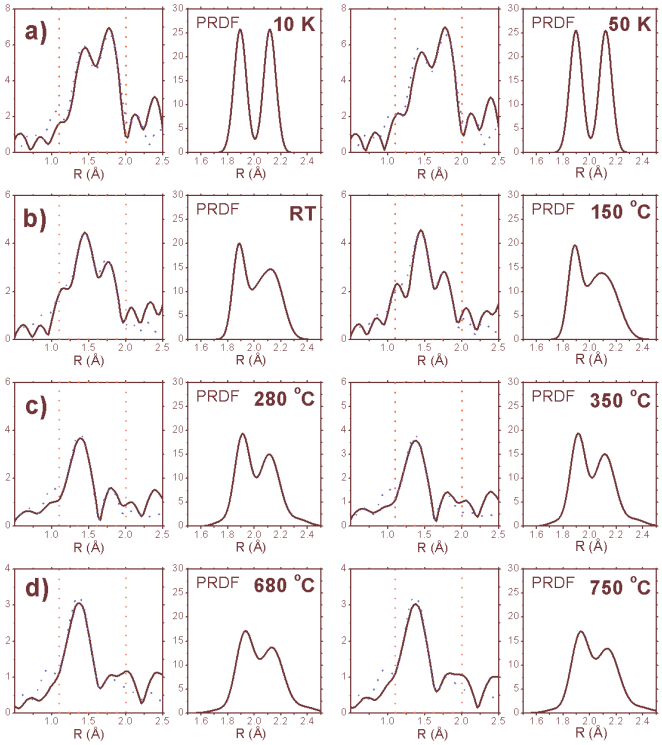
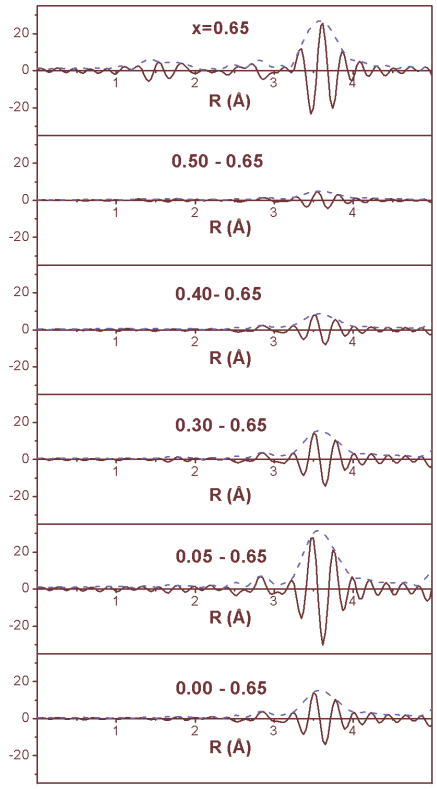


Fig. 2 Absolute values (dashed blue lines) and imaginary parts (solid black lines) of the k^3 weighted FT of the Nb K-edge EXAFS function measured for $K_{0.65}Na_{0.35}NbO_3$ at 10 K (on the top) and the differential FT at the same temperature. Concentrations are indicated in the figure.



We following results were obtained:
- in low temperature phase (10 K and 50 K) the eight-site model is the most suitable to describe the local structure of the NbO_6 octahedron, whereas fitting within six-site and 12-site models does not provide a reasonable *R*-factor. We also found out that in the orthorhombic phase (room temperature and 150 ^oC) the 12-site model is the only one providing a reasonable fitting. To describe the local structure of tetragonal (280 ˚C, 350 ˚C) and cubic (500 ˚C, 680 ˚C, 750 ˚C) phases we employed the anharmonic eight-site model.
- the value of Nb displacement r_0 is weakly depends on temperature and concentration *x*. This result is in good agreement with the spherical model of phase transitions in perovskite-like crystals proposed in previous work [2]. Within this model the Nb atoms are located on the surfaces of small spheres of constant radii r_0 surrounding the centers of NbO_6 octahedrons in all phases. The distribution of the Nb atom on this surface changes during phase transitions.
-the EXAFS data reveal that the R_0 values are almost independent on x at each temperature. These results enable to conclude that at constant temperature the NbO_6 octahedrons in PSN are rigid.
The last assumption is supported by the results of differential EXAFS analysis. For this purpose we performed Fourier transformation of the difference between normalized EXAFS functions $\chi_x(k) - \chi_{0.65}(k)$, where $\chi_{0.65}(k)$ is the function obtained for reference concentration x=0.65 at given temperature and $\chi_x(k)$ is that obtained for the concentration x at the same temperature. As an example, the absolute values and imaginary parts of the differential Fourier transforms obtained at 10 K for different x values are shown in **Fig. 2.** The differential EXAFS data obtained at other temperatures are close to these ones. It is clear that the differential signal in the 1st shell range is very weak, thus providing an unambiguous proof for rigidity of the NbO_6 octahedrons in PSN. On the other hand the differential signal in the 3^d shell range is strong. The most probable reason for the latter result is strong relative rotation of neighboring NbO_6 octahedrons taking place when sodium concentration increases. Such effect changes the geometry of Nb-O-Nb atomic chains and, as a result, influences on focusing processes and the 3^d coordination shell signal.

Summary: The local atomic structure of the lead free solid solution $K_{1-x}Na_xNbO_3$ (*x*=0.35, 0.50, 0.60, 0.70, 0.95 and 1.00) is studied in the temperature range 10 K – 1023 K using the Nb K-edge extended x-ray absorption fine structure (EXAFS) spectroscopy. To perform a precise investigation of small changes of local atomic structure during phase transitions we employed the combination of the fitting of all EXAFS spectra in the R-space, and the differential EXAFS method. It was shown that the: the Nb-O-Nb angles strongly depend on potassium concentration *x* at each temperature, but the NbO_6 octahedra keep rigid geometry. Furthermore, we have demonstrated the validity of new spherical model for phase transitions in piezoelectric ceramics $K_xNa_{1-x}NbO_3$. According to our previous investigation [2] one can conclude that this model may be common for all perovskite-like crystals.

Publication: A short communication (Letter) has been submitted on August 2006 to *Europhysics Letters.* A full paper reporting the EXAFS analysis is under preparation. The work on XANES calculations is in progress.

Abstract for *Europhysics Letters***:**

Phase transitions in lead-free piezoelectric ceramics: study of local atomic structure

M. P. Lemeshko, E. S. Nazarenko, A. A. Gonchar, L.A. Reznichenko, O. Mathon, Y. Joly, R. V. Vedrinskii

Local atomic structure of the piezoelectric ceramics $K_xNa_{1-x}NbO_6$ (*x*=0.35, 0.50, 0.60, 0.70, 0.95 and 1.00) is studied in all phase regions (10 K – 1023 K) using Nb K-edge extended x-ray absorption fine structure (EXAFS) spectroscopy. We have shown validity of new spherical model for phase transitions on the basis of both fitting of EXAFS signal in the *R*-space and differential EXAFS analysis. Within this model the Nb atoms are located on the surfaces of small spheres of constant radii surrounding centers of NbO_6 octahedrons in all phases. The distribution of the Nb atom on this surface changes during phase transitions. Besides the analysis of local structure revealed that the geometry of NbO_6 octahedra does not depend on *x* value at each temperature, but the octahedra rotation angles do.

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References

[1] Y. Saito et al. *Nature,* 432, p. 84 (2004).
[2] R. V. Vedrinskii et al. *Phys Rev B*, 73 p.134109 (2006).