EXAFS studies of isotopic effect in quantum paraelectric SrTiO$_3$

J. Purans, A. Anspoks, F. Rocca, D. Bocharov, V. Trepakov

Institute of Solid State Physics, University of Latvia, Kengaraga street 8, LV-1063 Riga, Latvia

SrTiO$_3$ (STO) is one of the most thoroughly studied materials in solid state physics [1, 2] with well pronounced anti-ferrodistortive cubic-to-tetragonal phase transition at 105 K caused by small rotation of the oxygen octahedra. In the low temperature region STO is a well known quantum paraelectric material, where ferroelectric ordering is suppressed by ion zero-point vibrations [3]. By controlling the balance between the dipole-dipole interaction and the quantum fluctuation through isotope exchange ($^{16}$O with $^{18}$O) [4], this material shows the so-called quantum ferroelectricity. Aim of our work was to study the STO16 and STO18 with X-ray absorption spectroscopy, giving insight into local structure of Ti atom.

In our study we used two samples: standard SrTi$^{16}$O$_3$ (powder and monocrystal) with $^{16}$O (STO16) and SrTi$^{18}$O$_3$ where 96 % of oxygen were substituted by $^{18}$O isotope (STO18) with preparation procedure described in [5]. The Ti K-edge x-ray absorption spectra were measured in transmission mode at the HASYLAB/DESY A1 bending-magnet beamline in the temperature range from 10 K to 300 K. The x-ray radiation was monochromatized by a 40 % detuned Si(111) double-crystal monochromator, and the beam intensity was measured using two ionization chambers filled with argon and krypton gases. The Oxford Instruments liquid helium flow cryostat was used to maintain the required sample temperature. To achieve the absorption Ti K-edge jump value $\mu \approx 1$ for transmission mode experiments, the proper amount of the STO powder was deposited on Millipore nitrocellulose membrane filter.

The Extended X-ray absorption fine structure (EXAFS) oscillations $\chi(k)$ and X-ray absorption near edge structure (XANES) data were extracted and analyzed following the conventional procedure [6, 7] using the EDA software package [8]. Theoretical EXAFS signal, backscattering amplitude and phase are calculated with FEFF8 [9].

Extracted EXAFS spectra and corresponding Fourier transforms are shown in Fig. 1 and 2. The peak corresponding to the first coordination shell (Ti–O$_1$) is less dependent from the temperature than the peaks corresponding to the second shell (Ti–Sr$_2$) and third shell (Ti–Ti$_3$). This is indication that the TiO$_6$ octahedra is relatively rigid compared, for example, with Sr sublattice.

Conventional analysis [7] of the first coordination sphere of STO16 gives us values of the mean square relative displacement of the first coordination shell of Ti (MSRD(Ti–O$_1$)) and corresponding bond distance $R_{Ti–O_1}$. Amplitude factor was kept constant (equal to the low temperature value), because the coordination number of Ti is assumed to be fixed. This allowed us to avoid well known correlation between MSRD and amplitude factor. Resolution of our spectra did not allowed us to resolve two different distances in the TiO$_6$ octahedra, so we have to concentrate on the behavior of the MSRD values seen in the Fig. 3, which contain dynamic part (thermal oscillations) and static part originating from the differences in average Ti–O$_1$ distance (static disorder).

Ti K-edge XANES spectra in perovskites contains characteristic pre-peaks [10] in the pre-edge region shown in Fig. 4 noted as “A”, “B”, and “C”. Only pre-peak “B” has some significant temperature behavior, because it originates from transitions of Ti 1s electron to the p-d hybrid orbitals originating from the titanium 3d orbital mixing with the oxygen 2p orbitals due to the Ti displacement from the center of the octahedra. The intensity of pre-peak “B” is proportional to the squared displacement of the Ti atom from the center of the oxygen octahedra [10]. Data shown in Fig. 5 confirm this suggestion and give us confidence about our data and methodology.

In contradiction to STO16, STO18 has noticeable deviations from the Debye model in the low temperature region, where STO18 has higher pre-peak “B” and corresponding MSRD of Ti-O$_1$...
This correlates also with the optical second harmonic signal which also drops sharply at $T_v$. With the increase of the oxygen mass the oscillation amplitudes phase. At the same time in the low temperature region we do not expect increase in the Ti–O bond with optical second harmonic signal, that is an indicator of the non-centrosymmetric ferroelectric static off-center shift compared with STO16. One can see that these deviations strongly correlate bond then STO16, which can be caused by larger Ti atom vibration amplitude or/and additional static off-center shift compared with STO16. One can see that these deviations strongly correlate with optical second harmonic signal, that is an indicator of the non-centrosymmetric ferroelectric phase. At the same time in the low temperature region we do not expect increase in the Ti–O bond vibration amplitude, even more, with the increase of the oxygen mass the oscillation amplitudes should decrease. This leads us to the conclusion that there is off-center position of the Ti atom in the TiO$_6$ octahedra which is increasing when temperature is decreasing. This phenomena starts at least at 100 K, which is far above suggested ferroelectric phase transition temperature $T_c = 25$ K. This correlates also with the optical second harmonic signal which also drops sharply at $T_c$ to the non-zero value which slowly decreases until vanishes at about 100 K. This is clear indication that the ferroelectric phase transition in the STO18 is not pure order-disorder type, because in this case the local off-center displacement of Ti atom does not change, and MSRD should follow Debye model and be flat in the low temperature region.

References