X-ray Single Crystal Study of $Na_{0.5}Bi_{0.5}TiO_3$

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Introduction:

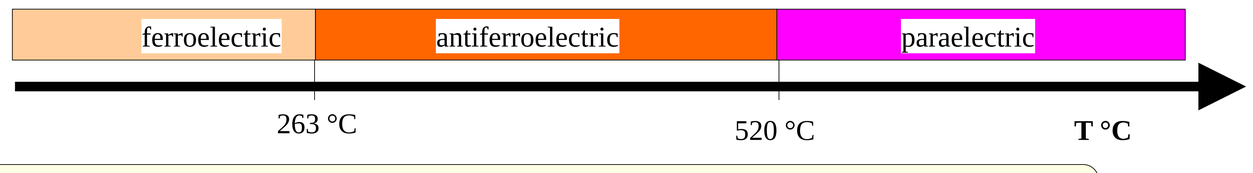
The perowskite structure ABO_3 became of great interest for compounds with two different cations on A- or B-positions, because of the formation of different ordering schemes. $Na_{0.5}Bi_{0.5}TiO_3$ belongs to the case where the A-positions are occupied by two inequevalent cations Na^{1+} and Bi^{3+}.

The compound exhibits two structural phase transitions according to the adjacent schematic.

Problems:

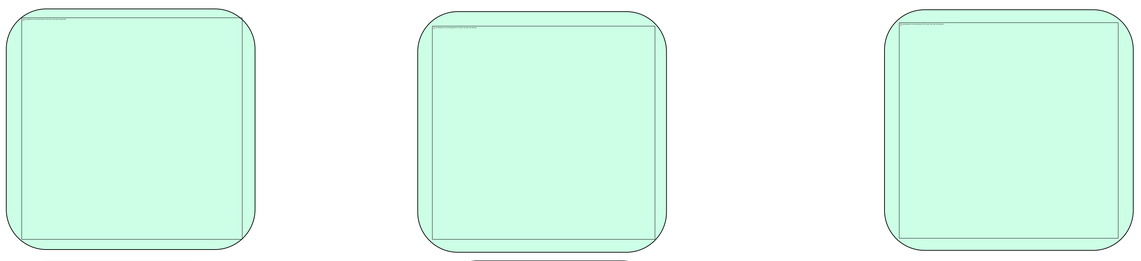
1. The weak superstructure reflections which have been observed by neutron diffraction experiments [1] have not been found yet by X-ray experiments.
2. In the literature the range of co-existing phases at the transition ferroelectric-antiferro-electric is beeing discussed controversaly.
3. The space group Fm3m as postulated from Raman scattering experiments for the cubic phase has not been verified yet by diffraction experiments [4]. Here the space group Pm3m must be assumed.

Phase transitions for perowskite $Na_{0.5}Bi_{0.5}TiO_3$

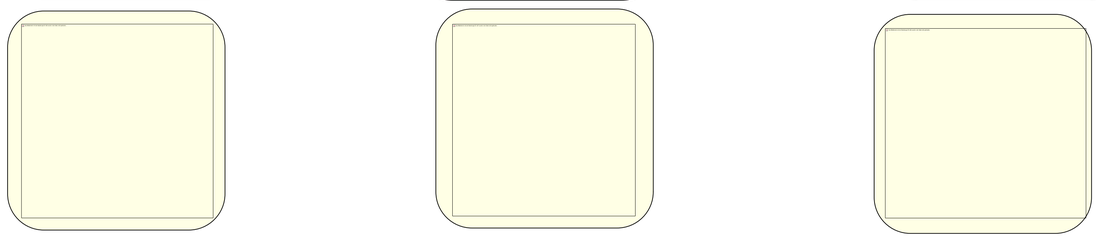


Lattice parameters:	rhombohedral [2]	tetragonal [2]	cubic [2]
Space groups:	R3m [2] , R3c [3]	P4mm [2]	Pm3m [2]

Schematic picture of the diffraction pattern with superstructure reflections:



Schematic picture of the structure:

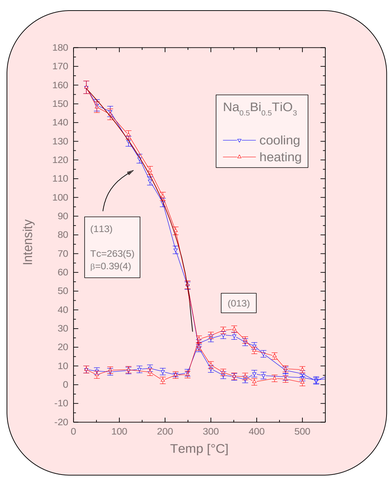


Experiments and Results:

Experiments :

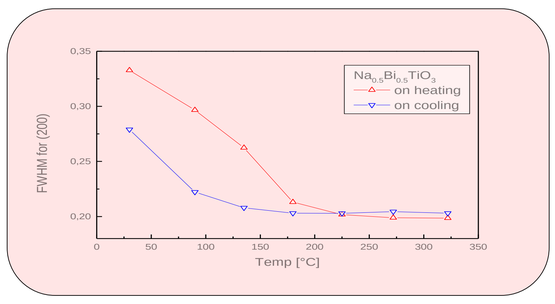
The $Na_{0.5}Bi_{0.5}TiO_3$ single crystals were grown by flux and Czochralski methods. The diffraction experiments were carried out on the 4-circle diffractometers KM-4 and CAD-4 using graphite monochromators and MoKα. A heating device was used for the high temperature experiments (up to 750 °C). The temperature stability was ±1°.

Phase Transitions :

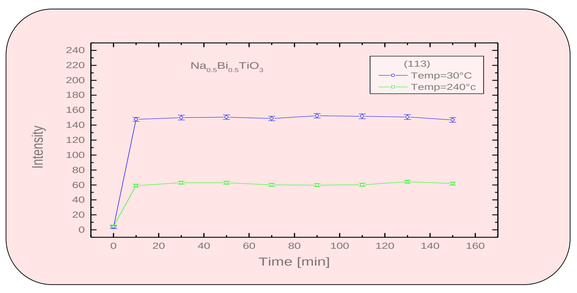


Variation of satellite intensities with temperature upon cooling and heating

Ferroelectric Phase :

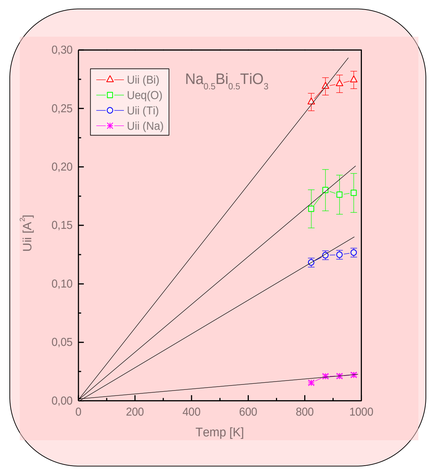


Variation of the FWHM with temperature



Intensity evolution of the satellite (1 1 3) with time of the rhombohedral phase after quenching from 600 °C.

Paraelectric Phase :



Temperature dependence of the mean square displacements of the thermal probability tensor (in Pm3m)

Referernces :

[1] S. B. Vakhrushev et al. ZhETF, **35** (1982) 111

[2] J. A. Zvirgzds et al., Ferroelectrics, **40** (1982) 75

[3] S. B. Vakhrushev et al., **FTT**, 25 (1983) 2613

[4] I. G. Siny et al., Ferroelectrics, **124** (1991) 207

Coclusion:

1. The ferroelectric-antiferroelectric phase transition does not exhibit any hysteresis in the satellite intensities with temperature. This is different from neutron experiments reported in the litterature [1]. There is obviously a co-existence of the two phases in the range between 250 °C and 300 °C.
2. The transition temperature as derived from the fit of the experimental data with the function $I(T)=A\,(Tc-T)^{ß}$ is found: Tc = 263(5) °C; ß = 0.39(4) .
3. There is a broadening of the reflections below 180 °C; the FWHM decreases with increasing temperature but it increases again upon cooling. This is very likely to be due to the formation of micro-domains.
4. The intensity evolution of a satellite reflection with time indicates that the kinetics for the formation of the rhombohedral phase is not sluggish.
5. The mean square displacements of the thermal probability tensor indicate that their variation is not proportional with temperature. This means that the large values are not due to harmonic motion but rather due to disorder. This is consistent with the results of Raman spectroscopy [4].