



	Experiment title: Coupling of spin, charge and structure in the multiferroic bismuth ferrite	Experiment number: HE-1950
Beamline: ID31	Date of experiment: from: 29 June 2005 to: 02 July 2005	Date of report: 4 September 2007
Shifts: 9	Local contact(s): Dr. Irene MARGIOLAKI	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Radosław PRZENIOSŁO* M.Sc. Andzej PALEVIC* Prof. dr. Izabela SOSNOWSKA Institute of Experimental Physics, Warsaw University, Hoża 69, PL 00-681 Warsaw, Poland		

Report:

The crystal structure of BiFeO_3 was studied by using the beamline ID-31 operating at wavelength 0.40006 \AA . The BiFeO_3 powder sample was sealed in a 0.3 mm diameter quartz capillary mounted inside a helium flow cryostat (low temperatures) or above a hot air blower (high temperatures). The measurements were performed at temperatures from 5 K up to 1073 K.

Complementary measurements with the same polycrystalline BiFeO_3 have been performed at RT by using the microdiffraction beamline ID-11 (ESRF Grenoble) operating at 0.15368 \AA wavelength. The SR microbeam of $20 \mu\text{m} \times 20 \mu\text{m}$ dimensions passed perpendicularly through the centre of a 1 mm diameter glass capillary filled with polycrystalline BiFeO_3 . The diffracted X-rays were recorded on a position sensitive image plate while the capillary was rotated around its axis (perpendicular to the beam).

Measurements gave narrow Bragg peak widths with $\Delta d/d \approx 6 \times 10^{-4}$ in whole temperature range, close to the instrumental resolution limit of the beamline ID-31. The presence of numerous weak Bragg peaks due to the distortion of the FeO_6 octahedra [1] confirmed the description of BiFeO_3 within the space group R3c. The R3m space group used in earlier BiFeO_3 structural studies [2] assumed regular FeO_6 octahedra.

A powder diffraction pattern measured at 5 K did not show any additional maxima as compared with the room temperature pattern (nor the pattern measured at 700 K, i.e. above T_N). From background point

fluctuations, it was estimated that there were no additional peaks with an intensity larger than 1/1500 of the strongest (110) Bragg peak. Therefore, we conclude that there is no crystal symmetry breaking due to, e.g., charge modulation or strain modulation in BiFeO₃.

Thermal evolution of the BiFeO₃ lattice constants has been obtained by Rietveld refinements involving the programme FullProf [3]. The refined values of the lattice parameters are shown in Fig. 1. The points denote the experimental data while the lines show fitted third order polynomials. The values of a_{hex} and c_{hex} agree well with the earlier data of Bucci et al. [4]. We did not study the temperature range near $T_N = 640$ K at a sufficient number of temperatures, so we were unable to reproduce the small discontinuity of the lattice constants observed by Bucci at T_N . The maximum of the thermal expansion coefficient [5] and the minimum of α_{th} occur at the same temperature as the strong anomalies of the phonon frequencies in BiFeO₃ Raman studies [6], indicating strong spin–lattice coupling in this compound.

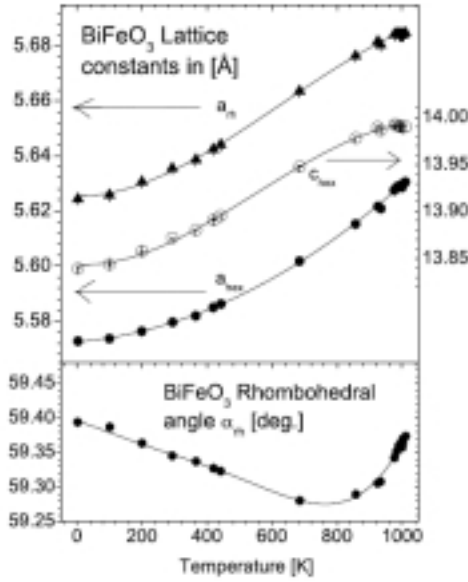


Fig. 1 Temperature dependence of the BiFeO₃ lattice parameters given both hexagonal and rhombohedral settings.

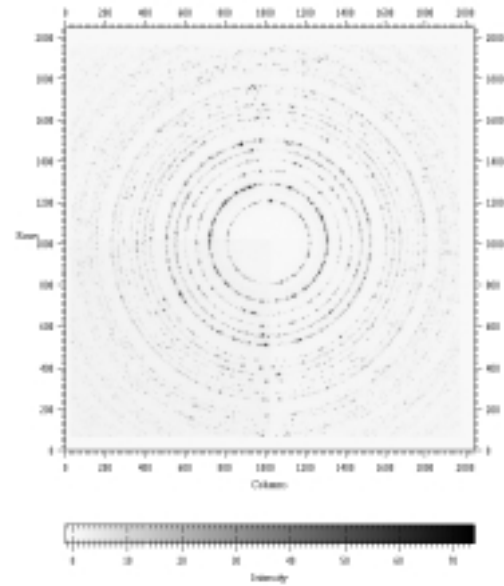


Fig. 2 SR microbeam diffraction pattern obtained for a polycrystalline BiFeO₃ sample.

The Bragg peak intensities observed in different measurements showed, in all cases, large discrepancies. Repeated SR diffraction measurements could not provide reliable values of the Bragg peak intensities. In order to look into the crystallite morphology of BiFeO₃ we conducted complementary SR microbeam diffraction studies. The SR microbeam diffraction (beamline ID-11) involving the sum of all the 160 scans obtained in the rotation of the sample capillary by the angle φ from 0° up to 40° , in $\Delta\varphi=0.25^\circ$ steps, is shown in Fig. 2. Instead of continuous Debye-Scherrer rings we have clearly separated spots. It can be concluded that BiFeO₃ polycrystalline powder has large aggregates and that there is no proper averaging over grain

orientations, similarly as in the case of a strong texture. This result (Fig. 2) explains why it is complicated to interpret the high resolution SR diffraction results, in particular atomic positional parameters.

Acknowledgments

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