A.12: $BiFeO_3$ prepared by rapid liquid-phase sintering method and its properties

$BiFeO_3$ (BFO) is a model multiferroic which shows ferroelectric and antiferromagnetic ordering well above room temperature (RT) and thus have the possibility to show magneto-electric coupling at RT. Hence, is expected to be a useful material for developing potential devices based on magneto-electric coupling at RT. However, high leakage current which lowers the resistivity of these samples hampers the observation of useful ferroelectric loop in this material. Therefore, precise control on stoichiometry is very important during sample preparation. Keeping this in mind; Material Research Lab (MRL) of Indus Synchrotrons Utilization Division (ISUD) RRCAT, has undertaken the present study with an intention of preparing high quality BFO sample and to study the effect of heat treatment on its properties. Further, synchrotron x-ray diffraction (XRD) data on an image plate has been used to detect the impurity contents which otherwise go un-noticed using conventional lab sources.

Sample preparation was carried out by modified rapid liquid-phase sintering technique (MRLPS). In this method a pellet of homogenously mixed raw materials (Bi_2O_3 and Fe_2O_3), is inserted in a preheated furnace. Temperature and duration, for which the materials were kept in the furnace, were optimized for minimum impurity levels. Based on these optimizations, the pellet was kept at 910°C in the furnace for 300 secs after which it is quenched. A part of this prepared sample was kept as it is (BFOQ) and other part of the sample was sintered at 860°C for 1hr (BFOS). Fig. A. 12.1 shows the refined lab source XRD pattern of the samples. XRD pattern shows that using this method, BFO samples with ~1% of impurity (*) were successful prepared.

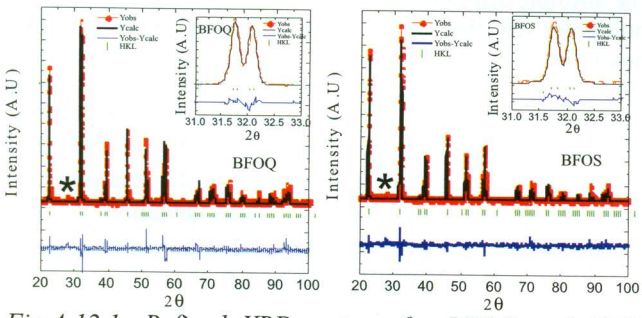

Fig.A.12.1: Refined XRD pattern for BFOQ and BFOS samples.

Polarization measurements (P-E) at room temperature show a well-defined P-E loop with very low dielectric losses for BFOQ sample. However, for BFOS sample, P-E loop is of unwanted balloon shape with dielectric losses two orders of magnitude higher than that of BFOQ sample. Detailed analysis of XRD data obtained at room temperature and the parameters obtained using Rietveld refinement shows no appreciable difference between the two samples, to give such a large difference in the dielectric properties. Hence, to check the quality of sample beyond the detection limit of the lab x-ray source, XRD measurements were performed at BL-12, Indus-2 synchrotron source. The measurements were performed at the photon energy of 11 keV. Fig. A. 12.2 shows the XRD patterns of both the samples obtained using synchrotron x-ray source.

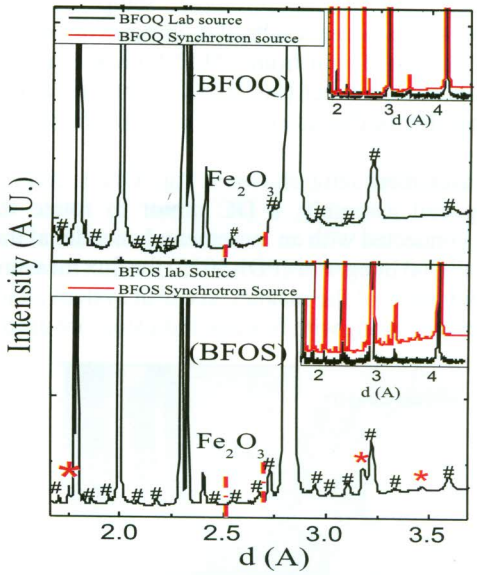

Fig.A.12.2 XRD pattern of BFOQ and BFOS samples obtained using synchrotron x-ray source. Inset shows XRD data obtained using lab and synchrotron x-ray source for both the samples.

Respective insets show a comparison of XRD data obtained using lab and synchrotron source. Presence of large number of peaks from secondary phases can be seen (#), which were not clearly visible in lab source XRD data. The number/intensity of these impurity peaks is higher in BFOS sample. Peaks from Bi_2O_3 phase are also present in BFOS sample (*), which are not visible in BFOQ sample. Bi_2O_3 creates low resistance percolating paths, leading to an increase in conductivity, which hampers the observation of well defined P-E loop in the system. It should be noted that the peaks from the secondary phases are ~1%, goes unnoticed when seen using lab source. The presence of these phases may be the reason for the observance of different P-E properties in both the samples. Thus, XRD results obtained using synchrotron source explain the polarization results obtained in BFOQ and BFOS samples very well. Further XRD data obtained using synchrotron source leads us to conclude that samples prepared by MRLPS method are not in the chemical equilibrium state. This is conclusively shown from the fact that on heat treatment, a number of secondary phases appear.

Reported by:
Archna Sagdeo (archnaj@rrcat.gov.in)
and A.K. Sinha