Opportunities of research in multiferroic materials using Angle Dispersive X-ray Diffraction (ADXRD) beamline on Indus-2 synchrotron source

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Abstract. Synchrotron beamlines have advantages of higher flux and wide tunability of photon beam compared to laboratory based equipment for performing x-ray diffraction and x-ray absorption spectroscopy (XAS). In this paper we report capabilities of angle dispersive x-ray diffraction beamline (BL-12) on Indus-2 synchrotron source for structural and spectroscopic characterisation of multiferroic materials. Brief description of the beamline along with the photon beam specifications at the experimental station is given. Results on low temperature XRD measurements on mixed spinel system (\(\text{Fe}_{1.5}\text{Co}_{1.5}\text{O}_4\)) between 30K and 300K and subsequent Reitveld refinement reveal that there are no phase changes but the lattice parameter show anomalous changes between 100 and 150K. It has been explained how XANES spectra on a type II multiferroic, \(\text{Co}_3\text{TeO}_6\), and \(\text{Fe}_{1.5}\text{Co}_{1.5}\text{O}_4\) can be used for the determination of charge and spin states of transition metal ions.

1. Introduction

Single phase compounds and multiphase composites, which posses simultaneously, two or more ferroic orders among ferroelectric, ferromagnetic (FM), ferroelasticity or ferrotoroidicity are called multiferroic (MF) materials. An important class of MF materials are magnetoelectric (ME) MF materials, which consists of ferromagnetic and ferroelectric orders. In modern day definition of ME MF materials, other magnetic orders like antiferromagnetic (AFM) and ferromagnetic are also included, in addition to FM order. From application point of view of ME MF materials, the coupling between the magnetic and the ferroelectric orders (the ability to control the ferroelectricity using the magnetic field and vice versa) is important. ME MF having coupling between FE and FM orders are called type II or proper MF materials. More often than not, type II MF materials have weaker magnitude of individual orders and also the MF properties are observed at very low temperatures. Current research efforts in MF research are directed towards enhancing the magnitudes of magnetic and ferroelectric orders, increasing the onset temperature of coexistence of the two ferroic orders and physics understanding of the magnetic transition as well as appearance of the two orders simultaneously in these materials. Bulk (both single crystals and powder) as well as thin film multilayers are being explored by various groups worldwide to achieve the above mentioned goals [1-5].

In order to understand the ME properties and magnetic transitions at low temperatures, the structural as well as the spectroscopic properties are important inputs. Structural techniques like low and high temperature x-ray diffraction (XRD), anomalous XRD and extended x-ray absorption fine structure (EXAFS) give changes in lattice parameters as a function of temperature, exact positions of the atoms in unit cell [6], distortion in lattice and neighborhood of a chosen atom [7]. These techniques along with neutron diffraction, magnetic and ferroelectric measurements have been used to
solve a number of very interesting phenomena like charge ordering [8], Verway transition [9] and Jahn- Teller transition [10], in different systems. The behavior of lattice parameters as a function of temperature reveals the origin of magnetic transition. The refinement of large Q (momentum transfer vector) XRD data using Reitveld refinement technique is useful in revealing small distortions in the unit cell [11]. In addition, the low temperature lattice parameters have been used for first principle theoretical calculations for density of states [12]. Spectroscopic techniques like x-ray absorption near edge spectroscopy (XANES), soft x-ray absorption spectroscopy (Soft-XAS) and x-ray photoemission spectroscopy (XPS) are used to study the charge/spin states of transition metal ions [13], electronic structure, hybridization of various levels etc. XANES, in particular, has been applied to estimate average charge state of Co ions in Co$_3$TeO$_6$ [13]. It has been reported that Co is in mixed oxidation state (both Co$^{2+}$ and Co$^{3+}$) in Co$_3$TeO$_6$. This explains the possibility of small ferromagnetic nano regions in Co$_3$TeO$_6$ in majority AFM matrix, giving rise to the so called Griffiths phase [14]. Also the pre-edge of the XANES spectra have been used to comment on the spin states of Co ions [13]. Therefore, it is important to perform temperature dependent high Q XRD, anomalous XRD and XANES measurements on MF materials. These measurements in wide temperature range (3 - 450K) can be performed in ADXRD beamline, in order to correlate the structural and spectroscopic properties with magnetoelectric properties.

In this paper, we present brief description of ADXRD beamline on Indus-2 synchrotron source [15]. Its capabilities for performing high resolution XRD measurements both at low and high temperatures will be discussed with the help of some examples. The measurements can be done for polycrystalline and single crystal samples in the form of powder, bulk as well as thin films. High resolution XANES as a function of temperature can also be performed in the same beamline. The capability of XANES measurements to estimate charge and spin states of transition metal ions in MF and magnetic systems will also be discussed with the help of some examples.

2. Description of ADXRD beamline

The beamline is the instrumentation which processes the photon beam emitted by synchrotron source according to the requirement of the experiment. ADXRD experiments require monochromatic beam with high energy resolution ($E/\Delta E = 10^4$), wide tunability ($5 - 25$ keV), high collimation and high photon flux. Ideally the polycrystalline bulk/single crystal and powder samples need different experimental stations. We have designed the beamline in such a way to accommodate two experimental stations, for the two different experiments. ADXRD beamline (BL-12) consists of Si (111) crystal pair based double crystal monochromator (DCM). A pair of plane Pt coated Si mirrors, bendable in the form of cylinders and coated with 400 – 500 Å of Pt are used as collimating/focusing elements. These mirrors have dimension of 1200mm (L) x 60mm (W) x 40mm (H) and are used for collimating/focusing the photon beam in the meridional direction. The bender placed with the second crystal of the DCM is used for focusing the photon beam in the sagittal direction. DCM, thus, is used for the dual purpose of monochromatisation as well as for focusing in sagittal direction. Decoupled meridional and sagittal focusing reduces optical aberration and therefore improves both focusing and energy resolution. In figures 1, we show the optical layout of the beamline. Important parts of the beamline are marked in the figures. In table I, we summarize important photon beam parameters delivered at the experimental station of the beamline.

The experimental hutch of the beamline consists of two experimental stations in tandem. First, a six circle diffractometer (Huber 5020) along with a scintillation point detector is a high angular
resolution set up and is used mostly for single crystal diffraction. The diffractometer is equipped with Eulerian cradle ($\chi$-axis) and also $\phi$ axis, to orient the single crystal samples or the epitaxial films. The diffractometer is also equipped with Mythen strip detector for fast and high resolution measurements. Another experimental station in tandem with the diffractometer is the Image plate area detector (MAR 345 dtb). The setup is quick but has moderate angular resolution and is used for powder diffraction. For low temperature XRD (LTXRD), we have liquid He based cryostat which operate between 3K and 450K. The set up contains beryllium (Be) heat shield and Be vacuum enclosure. Innovative arrangements have been made to stop Be diffraction peaks in the set up. The beamline is also equipped with a Cry free closed cycle He refrigerator (CCR) with Kapton window. The CCR works between 30K and 450K. The photographs of two LTXRD set ups are shown in figures 2 and 3. The software for interfacing the DCM for energy scan and data acquisition has been developed in-house. More details of the beamline can be found in our earlier publication [16].

![Fig. 1: Schematic representation of the optical lay-out of ADXRD beamline on Indus-2](image)

Table 1: Photon beam parameters at the experimental station

| Parameter              | Value             |
|------------------------|-------------------|
| Spectral Range         | 5-25 keV          |
| Energy Resolution      | $10^{-4}$         |
| Beam Size              | 0.5 x 0.5 mm$^2$  |
| Flux                   | $10^9$ to $10^{10}$/sec |
| Angular Resolution     | 15° (single crystal) |

1. Be Window
2. Slit
3. Wire Monitor
4. Pre-mirror
5. Double Crystal Monochromator
6. Post-mirror
7. ionisation Chamber
8. Six Circle Diffractometer
9. Scintillation Detector
10. Image Plate area Detector

### 3. Typical Results

3.1. Low temperature XRD studies in Cobalt Ferrite $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$

$\text{Co}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ are direct and inverse spinels, respectively. The formula unit for the two may be written as $(\text{Co}^{2+})[\text{Co}^{3+}]_2\text{O}_4$ and $(\text{Fe}^{3+})[\text{Fe}^{3+}\text{Fe}^{2+}]\text{O}_4$, where ( ) and [ ] represent the tetrahedral and octahedral sites, respectively. Magnetic properties of the two spinel structures are also quite different. $\text{Co}_2\text{O}_3$ shows antiferromagnetic behavior, whereas, $\text{Fe}_2\text{O}_3$ shows ferrimagnetic interaction. $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ is partially inverted spinel and in a recent publication [6], based on anomalous x-ray diffraction technique we propose its formula unit to be $(\text{Co}^{2+}_{0.45}\text{Fe}^{2+}_{0.15}\text{Fe}^{3+}_{0.40})[\text{Co}^{2+}_{0.30}\text{Co}^{3+}_{0.75}\text{Fe}^{3+}_{0.95}]\text{O}_4$. These compounds show very interesting properties like charge ordering [8], Verway transition etc. [9] at low temperatures. Here we present the low temperature XRD measurements and subsequent Reitveld analysis of LTXRD data on $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$. Figure 4 shows the measured and calculated XRD...
profiles at various temperatures between 30 K and 300 K. Also shown in the figure is the difference (between the measured and the calculated) curves. The theoretical XRD pattern was generated using Reiveld analysis software FulProf [17]. For calculation, Pseudo-Voit (P-V) profile shape was assumed and the lattice parameter, occupancy and position of the atoms, P-V profile parameters were refined. The background was manually picked and the background between the manually chosen points is extrapolated using a high order polynomial. We find that all the XRD patterns can be fitted with Fd3m space group with no extra peaks. Therefore, there are no phase changes in the sample in the measured temperature range. However, the values of lattice parameters plotted as a function of temperature (shown in figure 5), show anomalous behavior between 100K and 150K. Actually the sample shows negative thermal expansion in this temperature range. This clearly shows that the lattice is undergoing some rearrangement like charge ordering, J-T distortion or some transition. More experiments are required to be done to ascertain the exact reason for negative thermal expansion.

3.2 X-ray absorption near edge spectroscopy (XANES)

Figure 6 shows Co K-edge normalized XANES spectra for $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ along with the spectra of two standards, CoO (oxidation state +2) and $\text{Co}_3\text{O}_4$ (oxidation state +8/3). The spectra consists of four features marked “A”, “B”, “C” and “D” in the figure. The feature “A” represents Co 1s-3d quadrupole allowed transitions. Since this is a dipole forbidden transition, these are normally weak but they get enhanced because of hybridization between TM 3d and Oxygen s and p states and also because of the distortion in oxygen polyhedra. The feature marked “B” is monopole transitions (1s-4s) and are used to estimate average charge state of the absorbing atom. Although we attribute these transitions to 1s-4s, there is some controversy regarding the assignment of these transitions. Some authors attribute this feature to 1s-4p transitions [18]. The edge shifts towards higher energies with the increase in the oxidation states. The feature “C” is called the white line and has important information on the disorder present in the system. The feature marked “D” in the figure represents the absorption at unoccupied density of states beyond 4s and is modified by the multiple scattering. We have used the main edge part of the spectra (feature “B”) to estimate average oxidation state of Co and also Fe using Fe K-edge XANES spectra. It is found that in sample $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ the average Co and Fe oxidation states are 2.5 and 2.9, respectively.

In our earlier publication [19], we use the pre-edge part (feature “A”) of Co K-edge XANES spectra of type II multiferroic system $\text{Co}_3\text{TeO}_6$ to obtain information on the spin states of Co ions. We observe from the analysis of main edge (feature “B” in figure 6) that Co is in mixed oxidation state of +2 and +3. The pre edge shows two absorption bands attributed to splitting of 3d band of Co into t2g...
and eg bands due to crystal field splitting. The observed splitting is 1.26 eV between these two bands (see Fig. 4 of Ref 19) prefers high spin state of Co$^{2+}$ as well as Co$^{3+}$. It is known from literature that the splitting in the case of Low spin Co$^{3+}$ is 2.2 eV, much larger than 1.23 eV observed by us. Also the value of crystal field splitting in the case of high spin Co$^{2+}$ in tetrahedral site is 1.14 eV.

Finally the white line intensity has been used by us to to study Pt incorporation in LaMn$_{0.96}$Pt$_{0.04}$O$_3$ and LaFe$_{0.94}$Pt$_{0.06}$O$_3$ perovskite [20]. Synchrotron XRD data pattern for the system LaMn$_{0.96}$Pt$_{0.04}$O$_3$ showed that Pt does get incorporated in the matrix but remains in the metallic form, as the XRD peaks corresponding to metallic Pt is observed in the XRD pattern. No Pt peaks are observed in LaFe$_{0.94}$Pt$_{0.06}$O$_3$. This gives indication that Pt is incorporated in the matrix. However, to confirm this we have performed Pt L–edge XANES measurements (shown in Fig. 2 of Ref 20). The white line of LaMn$_{0.96}$Pt$_{0.04}$O$_3$ sample is very small indicating metallic form of Pt, in agreement with XRD data. On the other hand the white line for the sample LaFe$_{0.94}$Pt$_{0.06}$O$_3$ is very prominent suggesting the fact that Pt has been incorporated in the matrix and therefore, we don’t observe XRD peaks of Pt metal. White line intensity also increases when defects are induced by some perturbation like Ar implantation or γ ray irradiation, which results in donor density of states.

4. Conclusions
Structural and spectroscopic characterization like Low and high temperature XRD, XANES are extremely useful in the field of research in multiferroic materials. ADXRD beamline on Indus-2 synchrotron source is well equipped with these measurements. In this paper, we provide a brief description of the beamline and experimental station. The photon beam specifications at the

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Fig. 4: Calculated, measured and difference XRD pattern at 30K for Fe$_{1.5}$Co$_{1.5}$O$_4$

Fig. 5: Lattice parameter as a function of temperature

Fig. 6: XANES spectra at Co K-edge for Co$_{1.4}$Fe$_{1.5}$O$_4$ (CFO) along with those of standards Co$_3$O$_4$, CoO and Co metal foil. The metal foil XANES is used for photon energy calibration
experimental station are given for the benefit of potential users. Anomalous changes in mixed spinel cobalt ferrite with composition Fe1.5Co1.5O4 between temperatures 100 K and 150 K have been discussed. The pre-edge and main edge features of XANES spectra have been used to estimate the average charge state and spin state of transition metal ions. The white line has been used to comment of the incorporation of Pt in $\text{LaMn}_{0.96}\text{Pt}_{0.04}\text{O}_{3-\delta}$ and $\text{LaFe}_{0.94}\text{Pt}_{0.06}\text{O}_{3-\delta}$ perovskite systems.

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