

X-ray Absorption Spectroscopy of magneto-electric $\text{PbTi}_{1-x}\text{Fe}_x\text{O}_3$

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The phase $\text{PbTi}_{0.5}\text{Fe}_{0.5}\text{O}_3$ was first identified by Palkar et al [1], and shown to have ferromagnetic properties, together with ferroelectricity similar to PbTiO_3 . It was also shown that the room temperature magnetic moment of the $x = 0.5$ phase responded directly to the applied poling electric field, indicating a strong coupling between magnetism and ferroelectricity. To better understand the nature of magnetism and cationic oxidation states in this system, we have synthesized and studied the entire series $\text{PbTi}_{1-x}\text{Fe}_x\text{O}_3$ [2]. Here, we report our results from x-ray absorption spectroscopy down to 15K.

We performed XANES and EXAFS measurements at the Fe K -edge (13035eV) and the Pb L_3 -edge (7112eV) in transmission mode at the MR-CAT beamline 10-ID [5], at the Advanced Photon Source, Argonne National Laboratory. The samples were spread on tape. Several layers were stacked so that the thickness t of the samples was corresponding to $\Delta\mu t = 0.5$, where $\Delta\mu$ is the jump of the absorption coefficient at the Fe K -edge, or the Pb L_3 -edge energy, as applicable. The samples were then loaded in a closed cycle cryostat, and cooled to 10 K. Monochromator energy was calibrated by simultaneously collecting XAFS spectra from an iron foil and lead foil respectively. The Si(111) double crystal monochromator was scanned continuously, so that the data was collected in quick EXAFS mode. The incident and transmission photon intensity were measured by using ion chambers filled with appropriate mixtures of He:N₂, and N₂, respectively. The size of the incident x-ray beam on the sample was 500 μm^2 . The transmission measurements for the Fe K -edge were collected over the scanned energy range of 6900 to 8400 eV with a step size of 0.4 eV and a dwell time of 0.5 second. Scanning range for the Pb L_3 -edge was from 12900 eV to 14100 eV with a step size of 0.4 eV and a dwell time of 0.5 second.

We used XANES to determine the valence state of Fe ions and Pb ions by comparison with published data for FeO (Fe^{2+}), Fe_2O_3 (Fe^{3+}), PbO (Pb^{2+}) and PbO_2 (Pb^{4+}) [3,4]. We found that the relative ratio of near-edge features at the Fe- and Pb- edge varies significantly with varying Fe-content ($0.2 < x < 1$). The EXAFS data were analyzed through structural model fitting to obtain coordination numbers and nearest-neighbor distances. Possible structural changes in dependence of temperature were investigated in a range of 10K~300K.

1. V.R. Palkar et al, *Solid State Comm.* 134, 783 (2005); *Appl. Phys. Lett.* **90**, 172901 (2007).
2. S. Sen et al, *Synchrotron Radiation Center Users' Meeting Abstracts* (2007)
3. S. Sasaki, *Rev. Sci. Instrum.* 66, 1573(1995)
4. Z.N. Akhtar et al, *J. Phys.: Condensed. Matter* 5, 2643(1993)
5. C.U. Segre, et al. *Synchrotron Radiation Instrumentation: Eleventh U.S. Conference CP521*, 419-422 (2000).