

Electronic and Magnetic Properties of $\text{Fe}_{1.3}\text{Mn}_{0.7}\text{O}_3$ Nanoparticles using Soft X-Ray Magnetic Circular Dichroism

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1. **INTRODUCTION:** The nanocrystalline perovskite ferrites have attracted interest among due to its adverse range in the technological field of sensors, catalysts, pigments, magnetic storage, spintronic devices, magnetic resonance imaging, and so on [1, 2]. The perovskite structures are found to be more flexible for their structural phase transition properties particularly at lower temperature. Nanostructured manganese ferrite materials among those perovskites are acknowledgeable for their remarkable electrical and magnetic properties. Iron-Manganese oxide or commercially known Bixbyite (FeMnO_3) based mixed systems have an essential application as superparamagnetic materials, oxidation catalysis and thermistors [1-3]. The Fe-Mn-O nanocrystalline systems are also interesting due to the fact that Mn is an element generally found in iron ore. The incorporation of Mn in steel greatly influences its metallurgical properties [3]. Fe-Mn based oxide systems are also well in demand for their catalytic properties [3]. The electronic as well as the magnetic properties of the cubic FeMnO_3 are related to the distribution of cations from one lattice site to the other influencing the hopping of electrons which nurtures the conductivity of the material. Therefore, multivalence state becomes possible that plays a major role in varying the magnetic and electronic properties. In FeMnO_3 , hopping is between $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ and $\text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+}$ results in the occurrences of oxygen vacancy and creation of defects. In the present case, we have prepared Fe-Mn-O system in complex cationic configuration of $\text{Fe}_{1.3}\text{Mn}_{0.7}\text{O}_3$ through sol-gel combustion process to study its cationic distribution that enhances its magnetic and electronic variations. In FeMnO_3 , Fe and Mn have distinct crystallographic sites, and at each site, 50% of the occupant is either Fe or Mn. In

this very study, sample combination is resulting in a ratio of 65:35 for Fe to Mn. Such a strong anti-site disorder for both sites in FeMnO_3 is expected to come out with some interesting physical properties which can also be further modified for technological importance. According to previous temperature-dependent magnetism studies of FeMnO_3 is found to be antiferromagnetic at low temperature $\sim 36\text{K}$, in room temperature it shows ferrimagnetism. Thus, it motivated us to study the magnetic properties of $\text{Fe}_{1.3}\text{Mn}_{0.7}\text{O}_3$ nanoparticles by means of synchrotron-based X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD). It is well known that XAS and XMCD are one of the most sensitive techniques for detecting the influence of local structure on magnetic ions, and temperature dependent magnetic phase transitions.

2. **EXPERIMENT:** Polycrystalline $\text{Fe}_{1.3}\text{Mn}_{0.7}\text{O}_3$ powder was synthesized by a facile sol-gel combustion method. The precursor solution was prepared by taking stoichiometric quantities of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and manganese acetate tetrahydrate ($(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$). These ingredients were dissolved thoroughly in the deionized water, and succinic acid was added dropwise to the solution as a chelating agent. The solution was stirred continuously to ensure homogeneity at 70°C heating until the gel formation. The obtained gel was dried at 120°C for 12 hours. It was then calcined at 300°C in the air for 4 hours to vapour-out the organic constituents and finally the powder was sintered at 900°C for 4 hours. The crystallinity and phase formation of the sample is verified by X-ray Powder Diffraction.

To study further the element specific electronic and magnetic properties, X-ray spectroscopy, scattering,

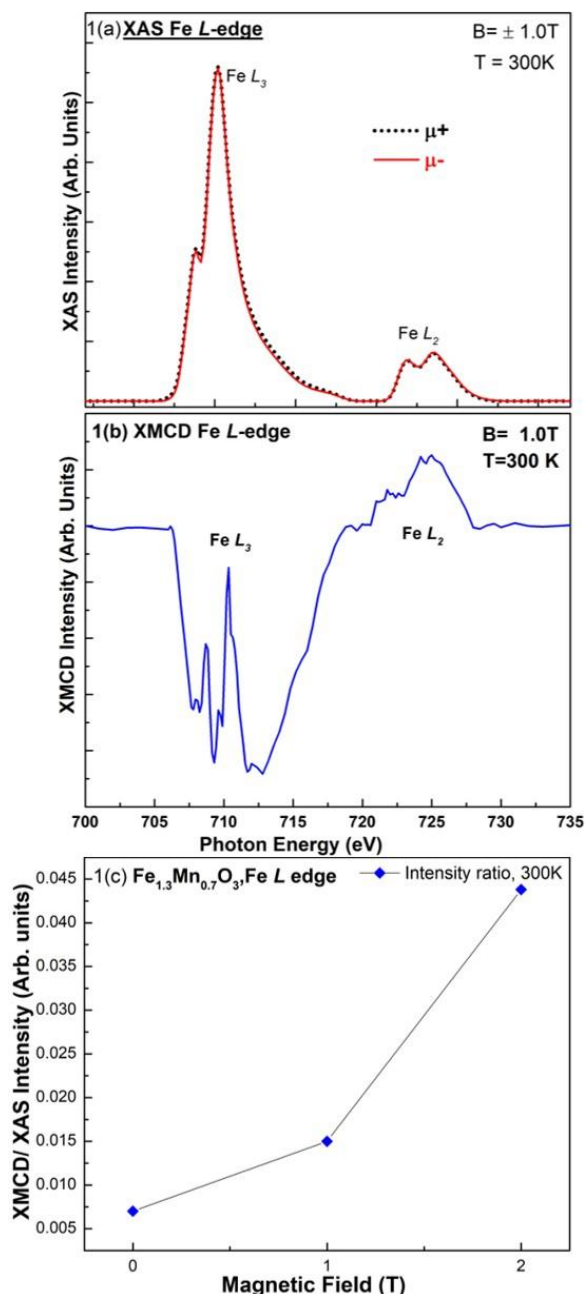


Fig 1(a) Normalised XAS spectra and 1(b) Normalised XMCD spectra of Fe L-edge w.r.t. applied magnetic-field $\pm 1.0T$. 1(c) XMCD/XAS Intensity ratio w.r.t. applied magnetic-field $0T$, $\pm 1.0T$ and $\pm 2.0T$ @ Fe L-edge.

and imaging experiments were performed at the variable-polarization soft x-ray beam-line BL-16A of the Photon Factory (KEK, Japan). Experimental geometry of soft x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) experiments are shown in Fig. 1 and 2. The sample was placed in the vacuum chamber with a pressure of 10^{-9} Torr equipped with a 5 T superconducting magnet. XAS and XMCD signals were measured at $0T$, $\pm 1T$ and $\pm 2T$ with varying magnetic-fields (only the data of

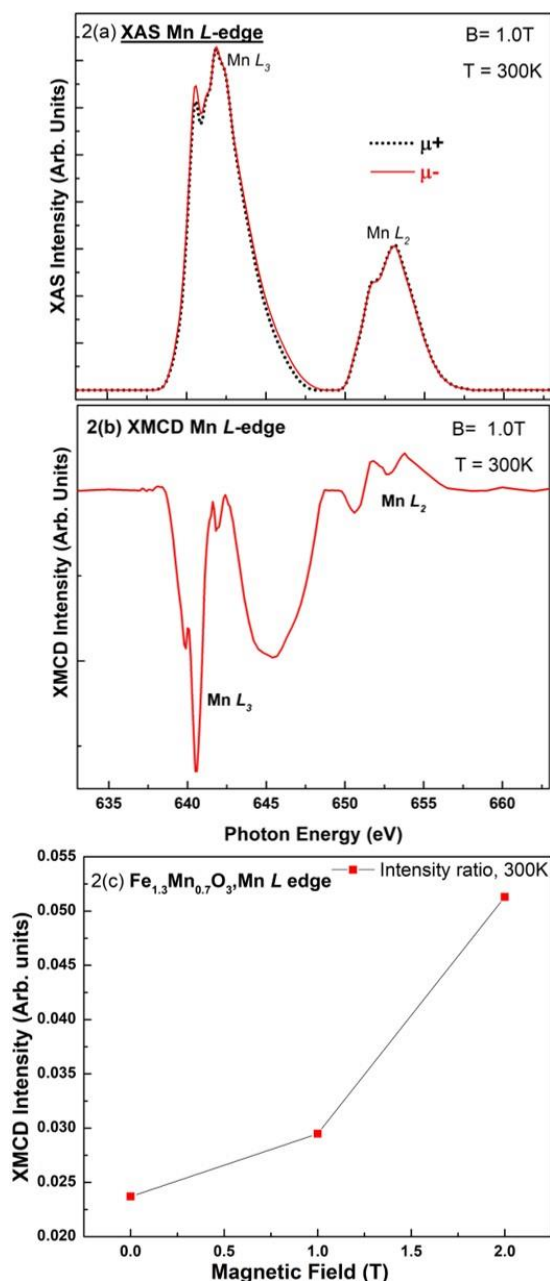


Fig 2(a) Normalised XAS spectra and 2(b) Normalised XMCD spectra of Mn L-edge w.r.t. applied magnetic-field $\pm 1.0T$. 2(c) XMCD/XAS Intensity ratio w.r.t. applied magnetic-field $0T$, $\pm 1.0T$ and $\pm 2.0T$ @ Mn L-edge.

$\pm 1T$ has been produced here) with right and left circularly polarized (RCP and LCP) x-rays having an energy resolution of 0.1 eV using the surface-sensitive total electron yield (TEY) method near Fe and Mn $L_{2,3}$ absorption edges with right and left circularly polarized (RCP & LCP) x-rays.

RESULTS AND DISCUSSIONS: The XAS spectra obtained with applied magnetic fields of +1.0 and -1.0 T are denoted by μ^+ and μ^- which represent left and right circularly polarized light, respectively as

shown in Fig 1. The XMCD spectrum was recorded by taking a difference between the XAS spectra with negative and positive helicity of the circular polarized light. In the $\text{Fe}_{1.3}\text{Mn}_{0.7}\text{O}_3$ polycrystalline sample, the Fe absorption spectra shows a multiplet structure at the L_3 and L_2 edges. Well-resolved peaks at the absorption maxima at $E = 710.22$ eV and 708.85 eV exhibits a doublet structure at the L_3 edge, whereas, maxima at $E = 722.83$ eV at L_2 edge is clearly observable. This verifies that the fine structures of Fe $2p \rightarrow 3d$ transition should result from the localization of Fe $3d$ electrons with $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ oxide formation. Since Fe $3p$ can be further oxidized to higher valence states, oxygen-rich secondary phases can emerge. Fe $3d^6$ was assumed as an initial state and Fe $3d^3$ was the final configuration. The observed fine structure of the XAS spectrum of Fe also corresponds to the one calculated from the multiplet effects [Fig. 1(a)]. XMCD signal measured in a magnetic field of $B = 1.0$ T as shown in Fig.1(b) for Fe-edges. Despite that the magnitude of the XMCD measured at the $L_{2,3}$ edges of Fe is clear that the signs of the dichroic signals are the same. The XMCD signal at the Fe L_2 edge is notably suppressed, indicating magnetic ordering due to fully occupied t_{2g} level. The XMCD/XAS intensity ratio w.r.t. the variable magnetic field with $\pm 0\text{T}$, $\pm 1.0\text{T}$ and $\pm 2.0\text{T}$ are shown in Fig 1(c) for Fe-edges. This result is quite relatable with the XMCD graphs. Fig 1(c) exhibits that the intensity ratio of XMCD/XAS is decreasing with increasing magnetic-field. In a same manner, Mn $L_{2,3}$ edge shown in Fig 2(a). Mn absorption shows a multiplet structure at the L_3 and L_2 edges at $E = 641.81$ eV and 653.17 eV doublet splitting is clearly observable. This verifies that the fine structures of Mn $2p \rightarrow 3d$ transition should result from the localization of Mn $3d$ electrons with oxide formation of Mn^{3+} . Mn $3d^5$ was assumed presence of Oxygen K-edge is shown in Fig 2(a). XMCD measured at the $L_{2,3}$ edges of Mn show dichroic signals at the same. If anyone wants to calculate quantitative spin and orbital magnetic moment then using sum-rule [4-8] it can be derived.

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References:

- [1] S. D. Kaushik, P. D. Babu, and V. Siruguri, Structure and magnetism of FeMnO_3 , S. Rayaprol, AIP Conf. Proc. **1512**, 1132 (2013).
- [2] S. Rayaprol, S.D. Kaushik, Magnetic and magnetocaloric properties of FeMnO_3 , Ceramics International 0272-8842 (2015).
- [3] T. Herranz, S. Rojas, M. Ojeda, F.J. Pérez-Alonso, P. Terreros, K. Pirota, J.L.G. Fierro, Synthesis, structural features, and reactivity of Fe–Mn mixed oxides prepared by micro-emulsion, Chem. Mater. **18** (2006) 2364.
- [4] V. R. Singh, V. K. Verma, K. Ishigami, G. Shibata, A. Fujimori, T. Koide, Y. Miura, M. Shirai, T. Ishikawa, G. f. Li and M. Yamamoto, “Electronic and magnetic properties of off-stoichiometric $\text{Co}_2\text{Mn}_\beta\text{Si/MgO}$ interfaces studied by x-ray magnetic circular dichroism” J. Appl. Phys. **117**, 203901 (2015).
- [5] M. Kumar, V. K. Verma, and V. R. Singh, “Magnetic Anisotropic of Thermally Evaporated FeNi Thin Film: A Soft X-Ray Magnetic Circular Dichroism study”, Surf. Interfac. Ana. **53**, 808-813 (2021).
- [6] R. Dawn, M. Zzaman, R. R. Bharadwaj, C. Kiran, R. Shahid, V. K. Verma, S. K. Sahoo, K. Amemiya and V. R. Singh, “Direct Evidence to Control the Magnetization in Fe_3O_4 thin films by N_2 Ion Implantation: A Soft X-Ray Magnetic Circular Dichroism Study”, J. Sol-gel Sci. and Tech. **99**, 461 (2021).
- [7] R. Dawn, M. Zzaman, F. Faizal, C. Kiran, A. Kumari, R. Shahid, C. Panatarani, I. M. Joni, V. K. Verma, S. K. Sahoo, K. Amemiya, V. R. Singh, “Origin of Magnetization in Silica-coated Fe_3O_4 Nanoparticles Revealed by Soft X-ray Magnetic Circular Dichroism” Brazilian Journal of Physics **52** (99), 1-12 (2022).
- [8] A. Kumari, A. Kumar, R. Dawn, J. Roy, S. Jena, R. Vinjamuri, D. Panda, S. K. Sahoo, V. K. Verma, S. Mahapatra, A. Rahaman, A. Ahlawat, M. Gupta, K. Kumar, A. Kandasami and V. R. Singh, “Effect of Annealing Temperature on the Structural, Electronic and Magnetic Properties of Co doped TiO_2 Nanoparticles: An Investigation by Synchrotron-Based Experimental Techniques” J. of All. and Comp. **933**, 167739 (2023).

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