

# Comparative Studies of X-Ray Absorption Studies of Ni Doped $\text{GdFe}_{1-x}\text{Ni}_x\text{O}_3$ ( $x \leq 0.5$ ) and $\text{SmFe}_{1-x}\text{Ni}_x\text{O}_3$ ( $x \leq 0.5$ )

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## Abstract

We present the comparative study of X-ray absorption spectroscopy (XAS) studies on O K edges of  $\text{GdFe}_{1-x}\text{Ni}_x\text{O}_3$  ( $0 \leq x \leq 0.5$ ) and  $\text{SmFe}_{1-x}\text{Ni}_x\text{O}_3$  ( $0 \leq x \leq 0.5$ ) samples along with the reference compounds to bestow the exact chemical states of functioning ions. The pre-peaks show the mixing of d states between different atoms, through hybridization with the oxygen p-band. The peaks present the  $t_{2g}$  and  $e_g$  symmetry bands denoting the bare (ionic) crystal field splitting plus hybridization. The XAS studies confirm the complete imbibing of the Ni in the Fe matrix.

**Keywords: X-Ray Absorption, O K-edge NEXAFS**

## I. INTRODUCTION

The transition-metal oxides are inviting an enormous attention from the material science community due to their diverse structural, magnetic, transport, and optical properties [1]. These oxides have well defined crystallographic and magnetic sublattices within the same compound that usually leads to very interesting phenomena. The strong interplay between localized moments, itinerant electrons, magnetic ordering and other important features characterize each one of the competing phases existing within the system. In particular, the rare earth transition metal oxides from the perovskite family are well known due to their striking properties, which are related to exchange mechanisms and the competition between different phases.  $\text{GdFeO}_3$  is an important transition metal oxide belonging to perovskite family exhibiting the prototype material for  $\text{GdFeO}_3$  (Pbnm space group) family structures.  $\text{GdFeO}_3$  crystallizes in an orthorhombic lattice which contains pseudo cubic sub-cells where  $\text{Gd}^{3+}$  and  $\text{Fe}^{3+}$  ions occupy sites at pseudocube corners and body centres in a perovskite structure [2-5]. The nickelates and orthoferrites are very interesting system to study the relation between structural, electronic and magnetic degrees of freedom, which are strongly depending upon the rare-earth element [6-8]. Among these,  $\text{SmFeO}_3$  can be used as a novel sensing material for detecting ethanol vapour.  $\text{SmFeO}_3$  sensor has good selectivity, stability and response recovery characteristics, but its optimal operating temperature is still unsatisfactory (around 370 °C) [9- 11]. In this paper, a comparative analysis of the O K edge of the Ni doped  $\text{SmFeO}_3$  and  $\text{SmFeO}_3$  has been made to discover the electronic states of the two systems.

## II. EXPERIMENTAL DETAILS

The polycrystalline bulk samples of chemical composition  $\text{GdFe}_{1-x}\text{Ni}_x\text{O}_3$  ( $0 \leq x \leq 0.5$ ) and  $\text{SmFe}_{1-x}\text{Ni}_x\text{O}_3$  ( $0 \leq x \leq 0.5$ ) were synthesized by solid-state reaction technique. The stoichiometric amounts of high purity (99.99%)  $\text{Sm}_2\text{O}_3$  or  $\text{Gd}_2\text{O}_3$ , FeO and NiO powders were ground into fine powder in an agate mortar. The mixtures were pressed into pellets and then calcinated in air at 1000°C for 12 h. Calcinated samples were sintered twice at subsequently higher temperatures followed by intermediate grinding and pelletizations, at 1250 °C and 1300 °C for 12 h and 24 hours, respectively. To understand the crystal structure, powder x-ray diffraction measurements were performed using Rigaku Rotaflex x-ray diffractometer with Cu K $\alpha$  radiation at room temperature (RT) in the  $2\theta$  range of 20° to 80°. The NEXAFS experiments at O K edge were performed at the soft X-ray beamline 7B1 XAS KIST of the Pohang Light Source (PLS), operating at 2.5 GeV with a maximum storage current of 200 mA. All the scans were collected simultaneously in both total electron yield (TEY) and total fluorescence yield (TFY) modes, ensuring both surface (TEY) and bulk (TFY) sensitivities. The close similarity of the spectra taken with these methods verifies that the TEY spectra are representative for the bulk material. The spectra were normalized to incident photon flux and the base pressure of the experimental chamber was better than  $1.2 \times 10^{-8}$  Torr.

### III. RESULTS AND DISCUSSIONS

O K-edge NEXAFS spectra, representing the orbital nature of the spectral features of the O 2p unoccupied states in the conduction bands and its hybridization with different Fe and Gd orbitals, can be efficiently used to explore all kinds of possible hybridizations with different cations normalized to incident photon flux. Figure 1 represents the normalized O K-edge NEXAFS spectra at different Ni concentration. The spectra can be studied at different energy values starting with the pre peak carrying a substantial information at 529 eV marked by an inverted arrow in the figure. The pre-peak structure is ascribed to  $1s \rightarrow 3d$  transitions either quadrupole-allowed or dipole-forbidden, where the latter becomes allowed due to a strong mixing of O 2p and Ni 3d states. The pre-peaks have their origin in the density of d-states of the neighbouring transition metal atoms, showing the mixing of d states between different atoms, through hybridization with the oxygen p-band [12, 13]. Similar pre-edge features have been reported in the oxides mainly in cuprates, manganites and Ni doped  $SmFeO_3$  and  $NdFeO_3$  [14, 15]. Since this feature originates with Ni doping, it is ascribed to dipole transitions from O 1s to O 2p states that are hybridized with the unoccupied states of Ni 3d. Thus, the intensity of this peak represents the Ni 3d density of states. A continuous increase of this peak with Ni doping indicates more unoccupied states at the Ni 3d levels and hence reflects the presence of more charge carriers, electrons or holes.

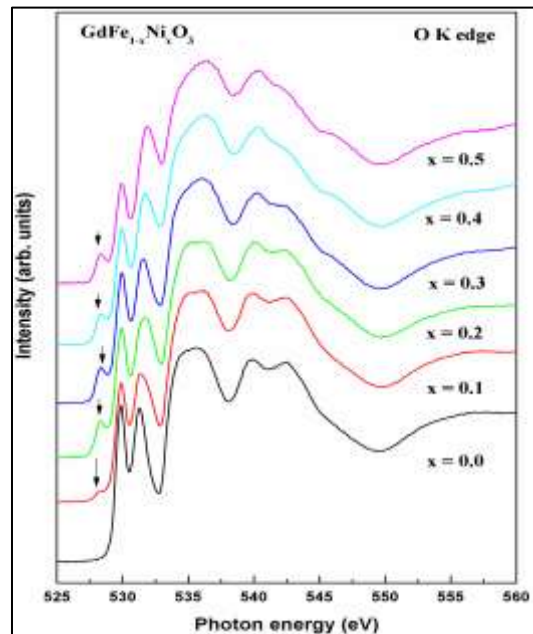


Fig. 1: Normalized O K edge NEXAFS spectra of  $GdFe_{1-x}Ni_xO_3$  ( $0 \leq x \leq 0.5$ ) samples.

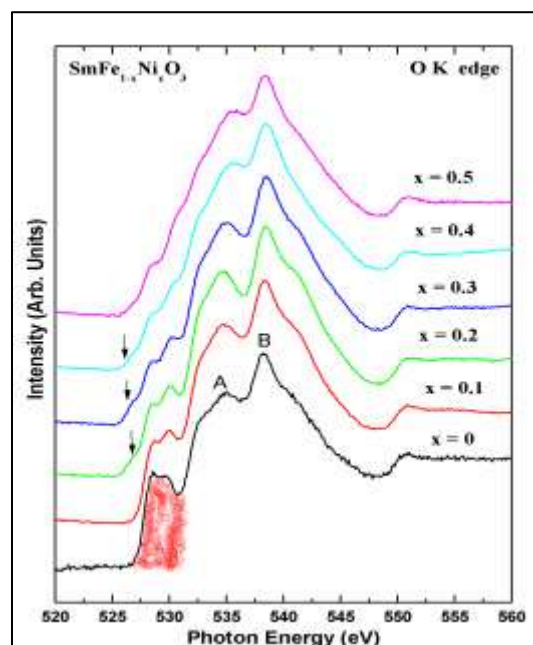


Fig. 2: Normalized O K edge NEXAFS spectra of  $SmFe_{1-x}Ni_xO_3$  ( $0 \leq x \leq 0.5$ ) samples.

The peaks marked (a) 529.92 eV and (b) 531.112 eV, where the peak separation mirrors the ligand field splitting, identified as the  $t_{2g}$  and  $e_g$  symmetry bands denote the bare (ionic) crystal field splitting plus hybridization [16]. The spectral intensity shown by (c) at 537 eV and the doublet shown by (d) in the range of 539-542 eV which gets merged into a single peak as the Ni concentration increases giving a clear evidence that the Ni ions are incorporated in the system and responsible for change in the electronic structure. The spectral features above 545 eV are quite similar and nearly independent of Ni concentrations, and dominated by the contribution from multiple scattering effects. This suggests that Ni ions are incorporated in the system.

Figure 2 shows the O K-edges of  $SmFe_{1-x}Ni_xO_3$  ( $0 \leq x \leq 0.5$ ). The spectra originate from the transition into unoccupied states with O-2p character hybridized with the metal states. While analyzing the spectra, the parent compound  $SmFeO_3$  in which the shaded doublet is shown. This shaded doublet (at  $\sim 528.56$  eV and  $529.57$  eV) above threshold is attributed to the bands of minority Fe 3d states split by octahedral crystal field into  $t_{2g}$  and  $e_g$  orbitals. This signature can be compared with the  $LaFeO_3$  energy level diagram where it clearly impresses on the fact that the peaks should directly represent the crystal field splitting parameter  $10 Dq$  [17]. In the present system, the observed crystal field splitting parameter is around 1.01 eV. The peaks marked A at 534.85 eV are attributed to the bands of primarily Sm 5d-character while the peak B at 538.45 eV is due to correlation effects associated with the hybridization of O 2p and Sm 5d effects. One more prominent feature of the spectra is the appearance of the clearly separated pre-peak in the low energy region, marked by vertical arrows, which becomes prominent as the Ni concentration is increased. The pre-peak can be attributed to new-states containing the O-2p character. This feature has also been found in transition metal mono oxides due to the O 2p weight in states of predominantly Fe 3d character [18].

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