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The Influence of Cerium Doping on the Crystal and Electronic Properties of FeBO₃ Oxides

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Abstract. Cerium substituted FeBO₃ samples were investigated according to their crystal and electronic properties via the general formula Ce_xCuFe_{1-x}BO₃. With the doping of the heavy fermion “Cerium”, samples were determined in polycrystalline structure. With the increasing Ce in the samples, disturbances on the Cu-Fe planes became more clear that supports the formation of geometrically different crystal structures. To obtain the electronic mechanisms in the crystals, X-ray Absorption Fine Structure Spectroscopy (XAFS) technique were used to study the electronic properties of the samples in coordination with the X-ray diffraction (XRD) patterns. As a result of the analysis, *f*-levels of the Cerium atoms were determined as the main playground of interplays and strongly correlated electrons of *4f-3d* levels were determined to emerge dominant interactions causing phase transitions.

INTRODUCTION

Recent technological applications show a high impact on the importance of studies on materials to improve their properties, such as electrical, optical, crystal, magnetic, electronic etc. [1-3]. Especially, interplay between the *3d* transition metals (TM) due to their partly filled *d* shell and *4f* levels of the rare earth (RE) lies in the center of the studies due to their many interesting physical phenomena. In this manner, transition metal oxides (TMO) have high demand in technological applications. The parent oxide of this study, Ferric Borate (FeBO₃), is a popular member of the TMO group. FeBO₃ was reported in some papers with a weak antiferromagnetic ordering above the room temperature ($T_N=350$ K) [3]. Recent studies on TM and RE containing materials were reported interesting interactions between the outer shell electrons of *3d-4f* system altering the electronic and magnetic properties of the materials [4,5]. So this study was aimed to probe the influence of Cerium substitution on the crystal and electronic behaviors in the FeBO₃ samples with the general formula of Ce_xFe_{1-x}BO₃ for $x=0.2$ and 0.8 .

Rare-Earth Oxiborate samples, in this study, with general Formula Ce_xFe_{1-x}BO₃, where x has value as 0 , 0.2 and 0.8 , were prepared in MEITAM laboratories of Mersin University (Mersin, Turkey). Samples were synthesized from the stoichiometric mixtures of CeO₂, Fe₂O₃ and B₂O₃ powder compounds with high purity (>99.99%). Powders were mixed and milled for 30 minutes and annealed in the furnace at 550 °C for 4 hours. In the second step, powders were milled again for 30 minutes and annealed in the furnace at 950 °C for 48 hours. To study the crystal properties of the samples, XRD patterns were taken at the MEITAM laboratories with Rigaku Smartlab and electrical resistivity of the samples were measured with the four probe technique at room temperatures (RT). Further analysis on the crystal structure were performed by the MAUD software [6]. Also, to support the vague details appeared during the crystal structure analysis, additional EXAFS (Extended X-ray Absorption Fine Structure) measurements were performed for Fe K-edge of the Ce_xFe_{1-x}BO₃ samples at Beamline-BL8:XAS of SIAM Photon facility (SLRI) (Nakhon Ratschaisima, Thailand) at room temperature in transmission mode [7, 8]. Additionally, electronic structure study of the Ce_xFe_{1-x}BO₃ compound were performed by the collected X-ray Absorption Near Edge Spectroscopy (XANES) measurements at MAX-Lab synchrotron radiation facility of Lund

University in Sweden. Fe $L_{3,2}$ -edge and O K-edge data were collected at Beamline I1011 on MAX-Lab in TEY (Total Electron Yield) mode [9]. XANES measurements were performed at room temperature and under ultra-high vacuum (UHV) ($\sim 10^{-10}$ Torr) conditions. XANES technique provides rich data collection for detailed electronic and crystal structure analysis of the interested materials [10].

RESULTS AND DISCUSSION

Electrical resistivity of the samples were estimated between $2.0\sim 14.0 \times 10^6 \text{ ohm.cm}$. which fall in the category of weak semiconductors. Electrical resistivity of the materials are highly related to the crystal morphology and structural properties of the samples. As it is known that porous materials provide more distances to electrons to hop and increase the conductivity of the material. To estimate the average crystallite sizes for the samples, Scherrers formula was used by using the data from the XRD patterns given in figure 1. The average crystallite sizes were determined as: 43.77 \AA and 58.17 \AA for the samples $x=0.2$ and $x=0.8$, respectively. In the figure, XRD patterns of the samples are given in comparison and the results of the XRD analysis by the MAUD software. According to the patterns, smooth character of the samples for $x=0.8$ (i.e. formula as $\text{Ce}_{0.8}\text{Fe}_{0.2}\text{BO}_3$) highlights a uniform crystal structure and addressing a single crystal structure in the entire bulk. According to the crystal structure analysis, the sample was determined to form CeBO_3 crystal in orthorhombic geometry with a space group of “ $Pnma$ ”. However, the sample for $x=0.2$ has noisy pattern and determined in polycrystalline structure with two structures: a) FeBO_3 (as the parent oxide) with trigonal geometry, “ $R-3c:H$ ” space group b) CeBO_3 with monoclinic geometry and “ $P21/m$ ” space group.

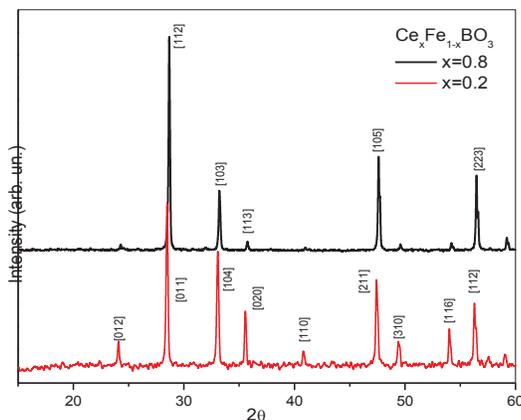


FIGURE 1. The compared XRD patterns of the samples.

To probe the background information of the crystal structure properties, electronic structure analysis were performed on the Fe $L_{3,2}$ -edge XANES spectra of FeBO_3 sample with the FeBO_3 structure containing sample ($x=0.2$) and given in figure 2. The L_3 -edge spectra is due to the $2p_{3/2}$ electrons' transitions to unoccupied $3d$ levels, while L_2 -edge spectra is due to transitions to unoccupied levels of $2p_{1/2}$ electrons'. The L_3 -edge spectra begin to rise at 705 eV and have maxima at 706.5 eV and 708 eV , respectively. However, the main absorption edge spectra for the sample $\text{Ce}_{0.2}\text{Fe}_{0.8}\text{BO}_3$ ($x=0.2$) has two peaks. While the main peak preserving its symmetry with its parent oxide FeBO_3 (confirming dominant FeBO_3 structures in the bulk), the weak edge has an energy shift to lower energy side. The shift and low intensity of the peak highlights different electronic behaviors of iron domains under the influence of neighboring Ce atoms in the bulk via $3d-4f$ hybridization. Fe L_2 -edge also has two peak feature, like the L_3 -edge and begin to rise at 718 eV and have maxima at 719.5 eV and 721 eV , respectively. To confirm the f -level contribution in the molecular bands, Ce $M_{5,4}$ level XANES spectra are given in figure 3. The two peak pre-edge picture reflects the existence of low (t_{2g}) and high energy (e_g) levels. Both of the Ce $M_{4,5}$ ($3d \rightarrow 6p$ or $4f$) edge XANES spectra of the $\text{Ce}_x\text{Fe}_{1-x}\text{BO}_3$ structure carries the tetravalent sign of a satellite located above the main edge where; $\text{Ce}^{4+} \sim 3d^0 \rightarrow 4f^1$ transition occurs [11].

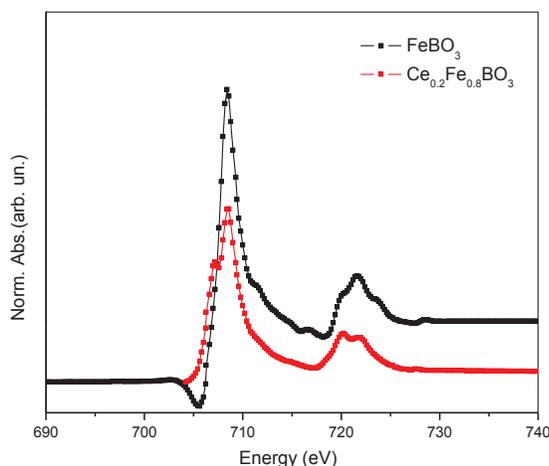


FIGURE 2. Fe L_{3,2}-edge XANES spectra of FeBO₃ and Ce_{0.2}Fe_{0.8}BO₃ samples

The sharpness of the M_{4,5} edge peaks reflects the abundance of the unoccupied states for a dipole allowed transitions from 3*d* levels. The weak slope below the main edge is also confirms the hybridization with 3*d* levels of iron because transition from *d* level to a *d*-level is also forbidden according to the quantum selection rules.

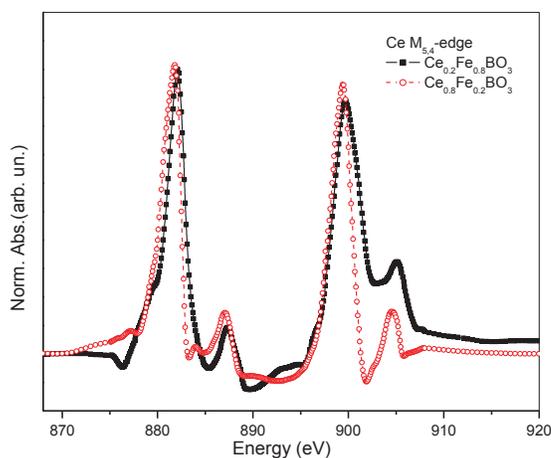


FIGURE 3. Ce M_{5,4}-edge XANES spectra of C_xFe_{1-x}BO₃ samples

Exact iron coordinations in the sample $x=0.8$ is still vague. So, a more elaborate study should be fulfilled with a powerful technique: EXAFS. the crystal structure study, the EXAFS (Extended-XAFS) study was performed for the sample $x=0.8$. The main goal of this part is to find a trace of Fe atoms in the bulk where only one type of crystal structure (orthorhombic CeBO₃) was determined. The EXAFS data can be extracted from the measured XAFS spectra and its fourier transform can be used to find the atomic distances, coordination in the sample (called as RDF (radial distribution function)). In the figure 4, the atomic coordination around a Fe atom in the sample is given on an 1D axis location. The peak intensities are related to the atomic weight and the number of the atoms at the locations. The nearest neighbors were estimated at 2.183 Å, 3.026 Å and 3.658 Å, as the closest Oxygen, Boron and Iron atoms, respectively. For the sample $x=0.2$ where the iron atoms could not determined in the XRD analysis. the atomic types are assigned on the figure. There should be no peak around 1 Å for the given Ce_{0.8}Fe_{0.2}BO₃ sample. The result is double checked from literature and crystallography databases for CeBO₃ structure. This figure does not match with the crystal structure of Orthorhombic CeBO₃, unless a substituted Fe sit in Ce coordination. So, the peak around 1 Å is a proof that indicates Fe atoms in the bulk sits in Ce coordination to preserve its structure.

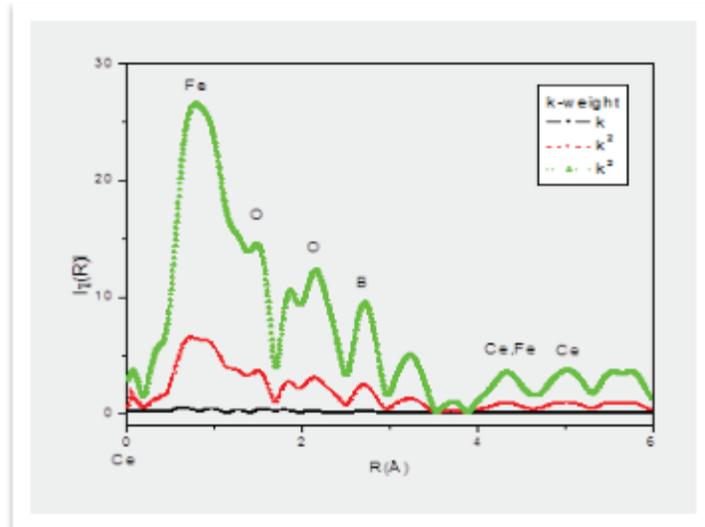


FIGURE 4. EXAFS spectra of $\text{Ce}_{0.8}\text{Fe}_{0.2}\text{BO}_3$ samples given in “ k ” powers.

CONCLUSIONS

In this study, Cerium substituted FeBO_3 samples were investigated according to their crystal and electronic properties for the general formula “ $\text{Ce}_x\text{CuFe}_{1-x}\text{BO}_3$ ”. With the Cerium substitution, disturbances on the Cu-Fe planes observed that supports the formation of geometrically different crystal structures. To obtain the electronic mechanisms in the crystals, X-ray Absorption Fine Structure Spectroscopy (XAFS) technique were used to study the electronic properties of the samples in coordination with the X-ray diffraction (XRD) patterns. For the analysis, f -levels of the Cerium atoms were selected as the main playground of interplays and strongly correlated electrons of $4f$ - $3d$ levels were determined to emerge dominant interactions causing phase transitions in crystal structures of the samples.

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