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Temperature Dependent XAFS Study of $CrFe_2O_4$

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ABSTRACT. $CrFe_2O_4$ (CFO) is a multifunctional magnetic, optoelectronic, and energy conversion material with research interest of current technology. The aim of the study was to test the CFO material against heat treatment and to analyze the electronic and crystal response when the material exposed to heat. To this aim, crystal and electronic properties of CFO material were investigated by x-ray absorption fine structure (XAFS) spectroscopy technique calculations for temperatures of 300, 373, 423, 473, 523, and 573 K. According to increasing the temperature, not so high reaction has been determined in Fe coordination. However, Cr atom has been affected by the temperature more than the Fe atoms. The obtained data at 523 K have been found the most fascinating for analysis.

KEYWORDS. Thermoelectric material; Metal oxide; Absorption spectroscopy; Transition metal.

INTRODUCTION. Being abundant in the earth crust and applicability in many technological applications due to the electronic properties, 3*d* transition metals attracted attention for many studies.[1] Unoccupied 3*d* levels of the transition metals could yield many interesting phenomena that inspires several desired electronic interactions that carries out the mechanisms of the physical phenomena such as; promising materials in optoelectronic technologies, semiconductor materials, vacuum technologies, thermoelectric devices, energy storage devices, etc.[2-5]

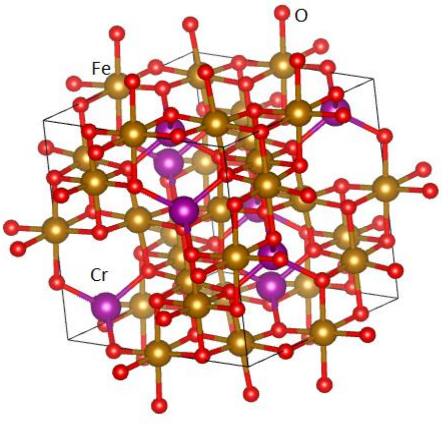

Fig. 1: The cubic CrFe2O4 in "*F d -3 m*" crystal structure.

$CrFe_2O_4$ (CFO) is a member of transition metals that exhibits multifunctional magnetic and optoelectronic, thermoelectric properties and especially interested in the applications for energy conversion and data storage technologies.[6] CFO is a transition metal oxide which is popular especially its semiconductor properties exhibiting photoconductivity under visible light. Besides, the thermoelectric properties of the CFO material was reported by Assadi et al.[7] with ambient seebeck coefficients at ~±700 μVK^{-1}. CFO material crystallizes in cubic geometry with "*F d -3 m*" space group and sketched in Fig. 1.[8]

This study was carried out to probe the temperature dependent change in the electronic and crystal structure properties of the CFO materials at a range of room temperature (300 K) to 573 K. For this aim, x-ray absorption fine structure (XAFS) calculations were performed by the commercial code FEFF 8.2 which is a real space multiple scattering approach.[9] XAFS technique is a richer version of the x-ray absorption spectroscopy and contain extra tail part in the spectra. Due to the extended (tail) part of the spectra, XAFS data can be analyzed in two parts, x-ray near edge

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spectroscopy (XANES) and the extended-XAFS (EXAFS). The XANES part yield data for the chemical bonding, local geometry, electronic structure properties, while EXAFS data yields information about the atomic coordination and bond distances between the atoms.[10]

METHODOLOGY. The calculations on the electronic structure properties of the $CrFe_2O_4$ (CFO) material were performed by the commercial XAFS code FEFF 8.2. The main aim of the calculations study are to probe the electronic properties of 3*d* metals against the increasing temperature conditions. Besides, XAFS calculations supported the crystal structure properties by defining the atomic environment and also the atomic coordinations of the calculated metals. The input file for the calculations were generated with the ATOMS program in the IFFEFIT package for CFO material where Cr and Fe atoms have been selected as the photon absorber and photoelectron emitter.[11] The lattice parameters of the studied CFO material were used as; $a=b=c=8.515$ Å and $\alpha=\beta=\gamma=90^{\circ}$. For the calculations, input files were generated for the cluster with the size of 13 Å containing 925 atoms (Cr, Fe and O) at the temperatures of 300, 373, 423, 473, 523, and 573 K where one Cr atom (sitting at the origin) was selected as a photon absorber and a photoelectron emitter. The Debye-Waller factors (σ^2) of Cr for the temperature were estimated as; 0.001214 Å^2 (300 K), 0.001470 Å^2 (373 K), 0.001649 Å^2 (423 K), 0.001829 Å^2 (473 K), 0.002011 Å^2 (523 K), and 0.002194 Å^2 (573 K). Same calculation procedures were also performed for the Fe atoms and an input data were generated for 908 atoms where one Fe atom was selected as a photon absorber and photoelectron emitter. The σ^2 factors of Fe for the temperature are calculated as; 0.001740 Å^2 (300 K), 0.002120 Å^2 (373 K), 0.002384 Å^2 (423 K), 0.002650 Å^2 (473 K), 0.002917 Å^2 (523 K), and 0.003185 Å^2 (573 K). According to the σ^2 factors, both Cr and Fe atoms have increase parallel to the temperatures. During the calculations, backscattering and phase shifts with single and multiple scattering paths have been calculated to obtain the EXAFS spectra for different temperature condition. Indeed, this work was done based on advantage of computer-based works to investigate the electronic and structural properties of matters at the lowest atomic scale to provide insightful information in complementary to experiments.[12-21]

RESULTS & DISCUSSION. The calculated XAFS spectra analysis were carried by the ATHENA and the ARTEMIS programs.[11] The XANES data of the XAFS method provides the most valuable data for research on the electronic structure of materials. In Fig. 2, Cr K-edge of the CFO absorption spectra is given in comparison with the spectra calculated at temperatures of 300, 373, 423, 473, 523, and 573 K. Cr K-edge absorption spectra is a result of the 1*s* electron's transition to unoccupied levels above the Fermi level. The ground state electronic configuration of the chromium atom is $[Ar]3d^5 4s^1$. In CFO material the Cr atom has Cr^{2+} ionic state and the electronic state became $[Ar]3d^4 4s^0 4p^0$. When one *s* electron is excited from the core state, an unoccupied state can provide convenient states as a final state, but the transition should obey the quantum selection rules, i.e., $\Delta l=\pm 1$.

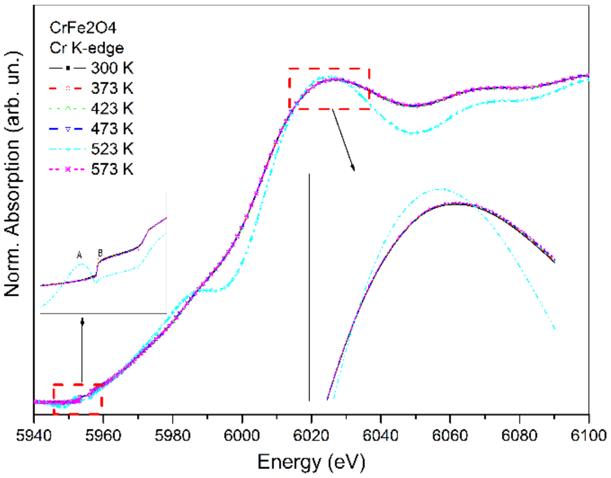

Fig. 2: Cr K-edge XANES spectra comparison of $CrFe_2O_4$ for different temperatures.

According to Fig. 2, the Cr K-edge has high agreement on the peak features. Cr K-edge XAS spectra begin to rise at 5944.3 eV and gave weak step-like pre-edge structure at 5953.4 eV which is assigned as "B" in the inset. The pre-edge is a result of low amount of transition probabilities to the unoccupied levels above the Fermi level which do not obey the quantum selection rules. The pre-edge feature is a result of a quadrupole transition of the 1*s* electrons to the hybridized 3*d*-2*p* levels as a result of the molecular bonding between Cr and O atoms. Apart from other spectra, the spectra calculated for 523 K has an extra and stronger pre-edge structure, assigned as "A" at 5952 eV. Among the temperature dependent spectra, spectra calculated at 523 K has totally different spectral feature where peak points have stronger structures. This peak points out richer molecular bonding with oxygen and possibly due to 4*s*-3*p* hybridized band. The main absorption peak of the Cr K-edge spectra have a maximum at 6024 eV. The K-edge of Cr atoms is a result of 1*s* electrons' transition to unoccupied levels of 3*d* or 4*s* or 4*p*. 3*d* and 4*s* levels do not obey the quantum selection rules and the only route for the s electrons seem to be the 4*p* levels. Just below the main absorption edge emphasizes different site symmetries presence in the crystal structure. As given in Fig. 3, Cr sites mainly have tetrahedral site symmetries, while Fe atoms have octahedral site symmetries. The low energy peak feature of the CFO material at 5986.3 eV emphasize the presence of the partly octahedral site symmetry formation on Cr atoms in the sample. Calculation at 523 K seem to triggers structural change in the molecular bonding via the atomic vibrations. To probe the influence of the increasing temperature on Fe atoms, FEFF 8.2 calculations were also performed for Fe atoms in the CFO materials.

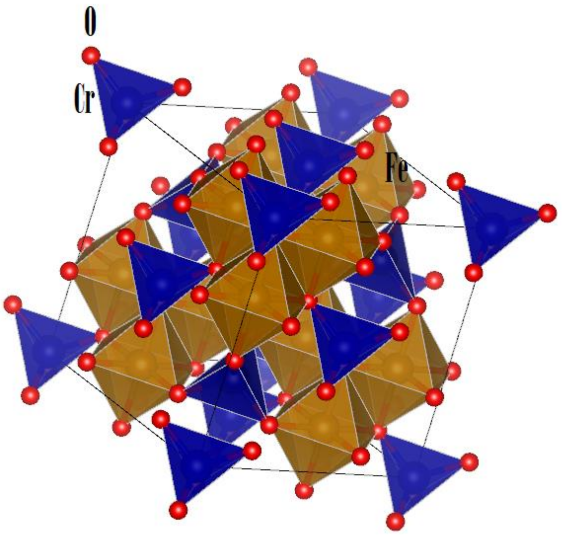

Fig. 3: Polyhedral structure of the $CrFe_2O_4$ material.

In Fig. 4, Fe K-edge XANES spectra of the CFO material is given in comparison with the data calculated for increasing temperature degrees. Fe K-edge absorption spectra has risen at 7071 eV and gave a satellite at 7075 eV, like Cr atoms. However, in Fe K-edge absorption spectra no disturbance were observed during increasing temperature which points out the stable position of Fe atoms in the cluster with a high resistivity against annealing. The main absorption edge, which is shown with a dashed line as a guide, has given a peak at 7136.3 eV. The binding energy of the Fe 1*s* electrons are 7112 eV and the peak energy beyond the energy reported in the literature addresses the excited 1*s* electrons transition to higher energy levels, i.e. 1*s*-->4*p* (like in Cr atoms). It is clear that, Cr atoms in the CFO materials are the main act players in the bulk against heat treatment.

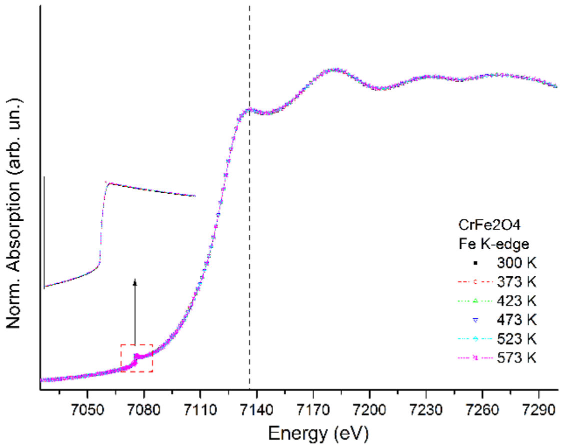

Fig. 4: Fe K-edge XANES spectra comparison of $CrFe_2O_4$ for different temperatures.

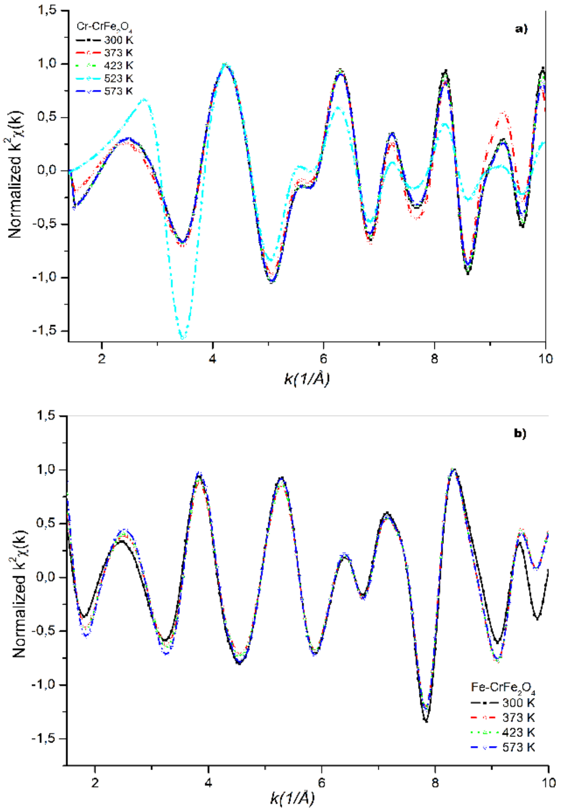

Fig. 5: EXAFS scattering data comparison of CFO sample against temperature; a) From Cr K-edge, b) From Fe K-edge.

The response of the atoms in the CFO material and their environment can be best probed by the EXAFS technique, in which the data are extracted from the tail part beyond the XANES region. The tail part spectra of the XAFS data has fluctuations as a result of the interactions with the incoming photoelectrons' wave functions at the scattering mechanism and the outgoing x-rays. When the interactions are "in phase" positive peaks (constructive) are created, while they are "out of phase" negative peaks (destructive) are created. The source of the photoelectrons' travel are; when a photon with an energy more than the binding energy of the excited core electrons, the excess energy is used as the kinetic energy of the photoelectron to travel among its neighboring atoms.

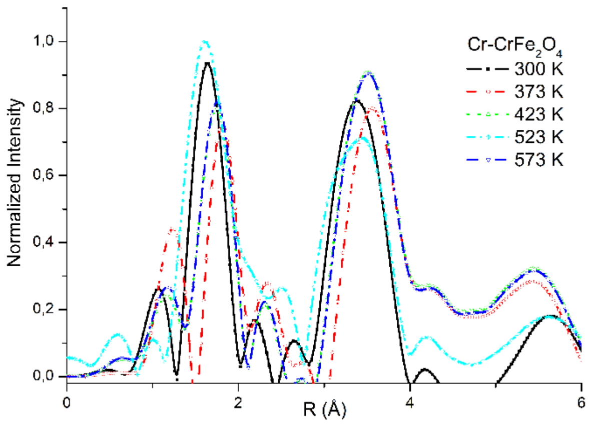

Fig. 6: Compared RDF data of CFO sample against temperature from Cr K-edge.

The data of the scattering mechanism is called the EXAFS "χ" scattering intensity. In Fig. 5, χ data is given for the CFO material at different temperatures. According to the data given in Fig. 5a, photoelectron emitted from the Cr atom has agreement on peak positions. However, a small peak intensity reduction over 300 K was observed at high K values beyond K= 7 (1/Å) and more reduction observed at 523 K confirming the disturbance given in Fig. 2. In Fig. 5b, EXAFS scattering data of the Fe K-edge is given. The scattering peak features confirms the XANES data (given in Fig. 4) and emphasizes the high stability of the iron atoms in the CFO material. The atomic interactions with the increasing temperature can be probed by the Fourier transform of the scattering data. By using the Fourier Transform for the scattering data, is also called as the radial distribution function (RDF), the atomic locations on a one dimensional axis can be determined. At the origin of the axis, the source atom sits and so the atomic locations give us the atomic distances with each other. RDF data from the Cr K-edge is given in Fig. 6.

Shifts at the peak positions according to the data for different temperatures are clearly seen in Fig. 6. The shifts have pointed out the atomic instabilities during temperature change and with the influence of the annealing, atoms have changed their locations to more distant position with the increasing temperatures. However, at 523 K, the RDF peak of the data seems to have a high agreement with the data at 300 K. According to the analysis results, the first peak with the peaks around 1.80 Å, are belonging to oxygen atoms (degeneracy 4) which are located between the source Cr atom and the Fe atoms that are located at a distance of 3.45 Å (degeneracy 12). The reason of the broader peak feature of that peak is its being an overlapped peak of Fe and Cr atoms. The peak also contains signals from the Cr atoms (degeneracy 4) located at a distance of 3.64 Å from the source Cr atom.

CONCLUSION. In this study, crystal and electronic properties of CrFe$_2$O$_4$ (CFO) material were investigated by calculated XAFS analysis. The input file for the calculations were generated for the CFO material in cubic geometry with "*F d -3 m*" space group. Calculations performed for temperatures of 300, 373, 423, 473, 523, and 573 K compared in each sections for electronic structure and crystal structure properties. According to the increasing temperature conditions, Cr atoms were determined as the most reactive metal in the CFO material, especially at 523 K. Stability in absorption data of Fe atoms pointed out the high resistance of Fe atoms against annealing procedure. However, at 523 K, the electronic response of Cr atom was found as the most valuable data for the analysis.

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