



Electronic Structure Study of Fe Substituted RuO₂ Semiconductor

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ABSTRACT. RuO₂ (ruthenium oxide) material is a popular semiconductor used for a wide technological interest. The influence of Fe substitution on the Ru coordination in the RuO₂ material has probed by the x-ray absorption (XAFS) calculations. Calculations were performed for Ru K-edge absorption spectroscopy in the RuO₂ material. To study the influence of Fe atoms on the electronic structure of the Ru atoms, parent RuO₂ material calculation has been used as reference material during the analysis. In the RuO₂ material, the analyses have shown that unoccupied 5s levels of the Ru atoms were hybridized with 2p levels of the oxygen and 3d levels of the iron atoms to build up molecular bands. The electronic bandgap of the RuO₂ semiconductor was determined as 0.32 eV.

KEYWORDS. Electrode; Oxides; Semiconductors; Absorption spectroscopy.

INTRODUCTION. Materials from RuO₂ are included in many applications; such as super capacitors, hybrid capacitors, solid state sensors, dynamic memory capacitors.¹ Rutile Ruthenium(IV) oxide is mostly used as an electrocatalyst for producing chlorine, chlorine oxides, and O₂ catalyst is ruthenium (IV) oxide in chemical reactions.^{2, 3} Ruthenium is a member of the transition metal column of the periodic table. Due to the active presence of transition metals in technological applications, they have become prominent in the study of all fields of science. RuO₂ oxide electrode has attracted attention as an electrode with its ferroelectric properties.^{4, 5} RuO₂ crystallizes in

tetragonal geometry with “*p 42/m n m*” space group and possesses properties such as; high thermal stability, diffusion barrier capability, and low bulk resistivity.⁵

The electronic structure properties of RuO₂ and Fe substituted RuO₂ materials were studied by the x-ray absorption fine structure (XAFS) spectroscopy technique calculations. XAFS is a superior technique with rich data content such as; crystal geometry, atomic types, and atomic bond lengths in a single data as well as providing electronic, chemical bonding and molecular interaction information. Apart from the fundamental absorption spectroscopy, the XAFS data

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has a long energy spectrum range and the extended part gives its name to the technique EXAFS. The XAFS spectra can be studied in two parts: XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended-XAFS). XANES part of the spectra is related to the electronic structure and bond properties of the material and lays between 20 eV below and 50~70 eV above the absorption process. However, the EXAFS part is the tail part of the XAS spectra with an energy range of 400~800 eV.

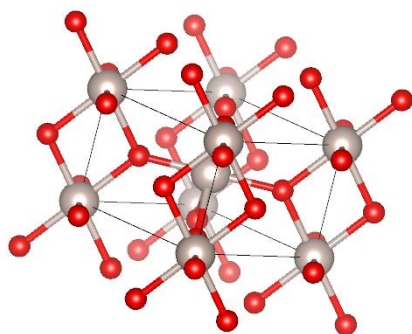


Fig. 1: Tetragonal (*p 42/m n m*) RuO₂ crystal.

METHODOLOGY. The electronic properties of RuO₂ and Fe substituted RuO₂ materials have been studied with the performed XAFS calculations. In the calculations, a ruthenium atom was chosen as the source atom in the calculated materials and parent RuO₂ was used as the reference material. Calculations were performed by using the real-space multiple scattering approach FEFF8.20 code.⁶ For the calculations, input files were generated which provides the calculation steps, calculation cards, crystal data, and electronic energy details adapted for the ambient conditions. The crystal structures in the input files for use in the calculations were created using the TkATOMS package, which is part of the IFEFFIT Shell interface.⁷ For the calculations, an input files has been created for the RuO₂ material in tetragonal geometry with “*p 42/m n m*” space group for 10 Å thick cluster, containing 385 atoms (Ru (Fe) and O) with the lattice parameters; *a*: 4.51 Å, *c*: 3.11 Å and Ru (*x, y, z*): (0.0, 0.0, 0.0), Fe (0.0, 0.0, 0.0), and O (0.30, 0.30, 0.0).³ The crystal structure of the studied RuO₂ material is given in Fig. 1.⁸ All calculations were performed at the room temperature. It is important to comment here that computer-based works could interpret achievements in addition to experiments, which both could evaluate insightful information to find a better solution for the

investigated problems.⁹⁻¹⁶ Moreover, details of such electronic structure systems could be obtained very well by performing computer-based calculation and simulation works.¹⁷⁻²¹

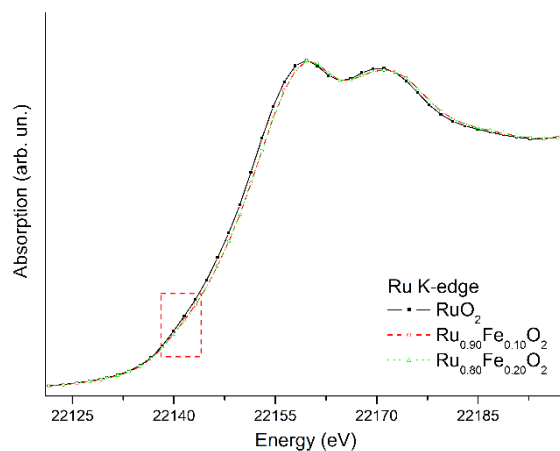


Fig. 2: Ru K-edge XANES spectra comparison of RuO₂ and Fe substituted RuO₂ materials.

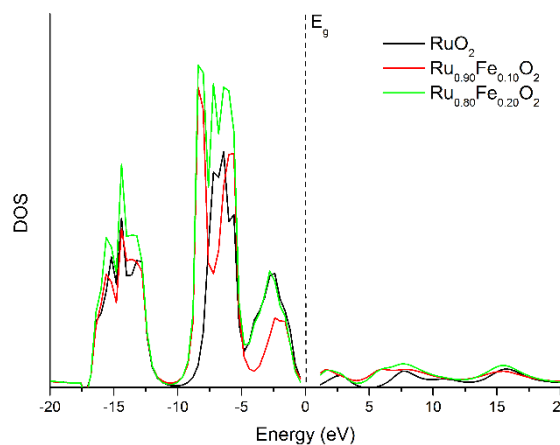


Fig. 3: Comparison of the density of states (DOS) of the RuO₂ and Fe substituted RuO₂ materials.

RESULTS & DISCUSSION. The XAFS technique is the best tool among techniques on the electronic structure probe method due to its capability to provide rich and valuable data for research on the electronic structure of materials. For the electronic structure study of the materials, Ru K-edge absorption data were produced with the code FEFF 8.2. In Fig. 2, the XANES absorption spectra of Ru K-edge in RuO₂ and Fe substituted RuO₂ materials are given in comparison. High agreement between the absorption spectra of the Ru K-edges of the materials indicates similar oxidation states of Ru atoms in each material. The ground state electronic configuration of the ruthenium atom is [Kr] 4d⁷ 5s¹, so electronic configuration for Ru⁴⁺ become [Kr] 4d⁴ 5s⁰ 5p⁰. Ru K-edge absorption spectra is a result of the excited 1s electrons' transitions to unoccupied

levels as a final state. The transition of the s electrons should be the d - or s - level according to the given electronic configurations. However, the route for the excited s electrons to unoccupied s or d levels are forbidden due to the quantum selection rules, i.e., $\Delta l = \pm 1$. The smooth rise (from 22122 eV) in the spectra points out the transition occurs as; $1s \rightarrow 5p$ obeying the quantum selection rules. However, a very weak pre-edge feature was observed on the Fe substituted samples at 22140.6 eV and this pre-edge gives the traces of the Ru $5s$ - Fe $3d$ - O $2p$ hybridization (spd) and the lower contribution comes from the ruthenium atoms. The main absorption edge peak of the Ru K-edge has a maximum at 22160 eV. However, the obtained Ru K-edge spectra have a broader spectra than the Fe substituted RuO_2 material. This is an indication of the iron atoms' presence reduced the influence of ruthenium atoms.

The density of states (DOS) is the best way to probe the electronic localizations in a molecular interplay. In Fig. 3, DOS data of the RuO_2 material is given. As a guide for eyes, a line showing the Fermi level (EF) is given in the figure. The DOS figure confirms the d -level contribution to ruthenium atoms by iron atoms which pushed the d -levels back. Besides, the semiconductor properties of the Fe-substituted RuO_2 materials become better than the parent RuO_2 material. The energy bandgap of the RuO_2 material was determined as 0.32 eV and the bandgap for the 20% Fe-substituted material is 0.27 eV.

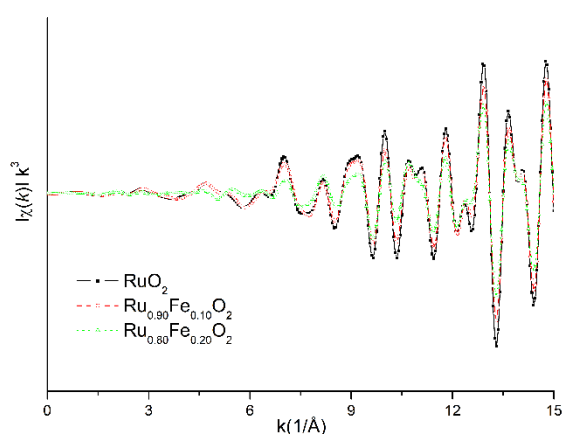
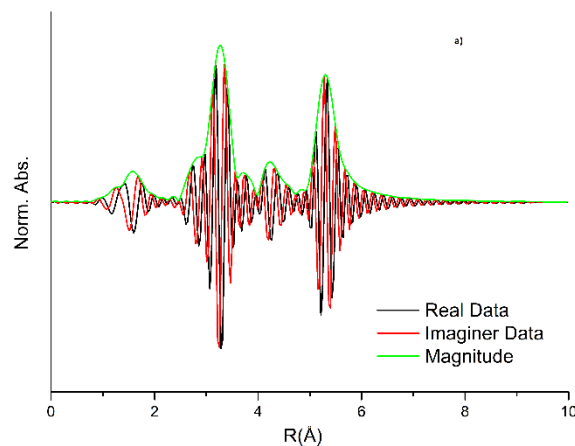


Fig. 4: EXAFS scattering data comparison of in RuO_2 , $\text{Ru}_{0.90}\text{Fe}_{0.10}\text{O}_2$, and $\text{Ru}_{0.80}\text{Fe}_{0.20}\text{O}_2$.

The best way to analyze the effects of the electronic interplays on the atomic environment and the crystal order is the EXAFS study. In Fig. 4, the χ scattering intensities of the photoelectrons emitted from the Ru

atoms are given in comparison. Scattering intensities of the studied materials have high agreement pointing out the stable crystal environment of the Ru atoms. The decrease in the scattering intensities is related to the decreasing amount of ruthenium atoms in the materials.

a)



b)

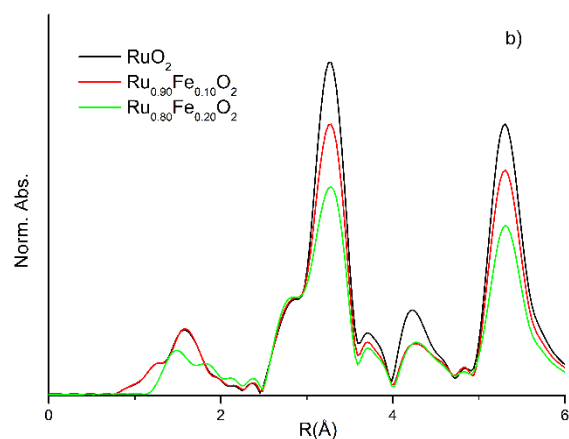


Fig. 5: Radial Distribution Function (RDF) results of a) RuO_2 , b) Comparison of the RuO_2 and Fe substituted RuO_2 materials.

The reason for the decay in the intensities are due to the interstitial potentials provide by the atoms on the way of the traveling photoelectrons. This phenomenon can be explained by the iron substitution process which is lighter than the ruthenium atoms and contribution of the iron atoms lower the interstitial potential that supports the photoelectrons mean free path with longer range. By analyzing the data in real space, the Fourier Transform should be performed on the scattering data which yields the Radial Distribution Function (RDF). RDF data gives atomic distances that mean the bond lengths from the source atom (Ru) on a one-dimensional axis. In Fig. 5, the radial distribution function of the RuO_2 atom with its real and imaginary parts. To determine atomic types and the coordination

numbers, fitting of the scattering paths were performed which was produced during the EXAFS calculations. Weak multiplet peak features are results of the overlapped signals of the multiple scattering mechanisms.

In the RuO₂ material, oxygen atoms were determined as the closest atom group as that are located at a distance (bond length) of 1.92 Å (Ru-O). Nearest Ru atoms coordination were located at a distance of 3.11 Å (Ru-Ru). The decay in the peak intensities of the Ru atoms is due to the iron atoms that were sitting in the Ru atoms coordination. Therefore, the importance of atoms substitution was shown by this work.

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