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Heat Treatment Calculations of $CaTiO_3$ Material to Probe the Oxygen Non-Stoichiometry

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ABSTRACT. $CaTiO_3$ (CTO) is a popular material that has a wide application in electronics and its thermoelectric potential has led to its application in related fields. In this study, the electronic structure response of atoms in the CTO material to the temperature increase was probed by means of the x-ray absorption fine structure spectroscopy (XAFS) calculations. Very high stability was determined in the material against the temperature increase. However, decay at both calcium and oxygen atom data were determined as a response to the temperature increase which can give us clues about the oxygen non-stoichiometry in $CaTiO_3$ materials reported in the literature. Besides, with increasing temperature, a very slight increase at pre-edge features was observed. In this work, systematic calculations of XAFS features were performed to achieve the purpose of such CTO material characterization.

KEYWORDS. $CaTiO_3$; Thermoelectric potential; XAFS; X-ray; Computational.

INTRODUCTION. Using the waste heat, which is produced during mechanical or chemical reactions, has become one of the most important study topics nowadays. Especially for the automotive industry, it is intended to use the waste heat generated by active engines to compensate the energy used in automobiles or to recharge the batteries of electric vehicles, and such studies are collected under the title of thermoelectric. Calcium titanate with the formula of $CaTiO_3$ (CTO) is a well-known semiconductor material besides its thermoelectric properties. CTO is an amphoteric semiconductor showing both *p*-type and *n*-type conductivity; here, non-oxygen stoichiometry has the main role in revealing such properties.[1] Imperfections in semiconductor materials have an important role to be considered a gift rather than a defect.[1-4] Similarly, in some reports, defects in the CTO material due to loss of oxygen have been viewed as a gift because of the electrical properties defects revealed.[1] In several nano-based materials, existence of defects or impurities is almost an advantage for producing novel electronic properties for specified purposes, in which several works reported such case at the molecular scale computations.[5-10]

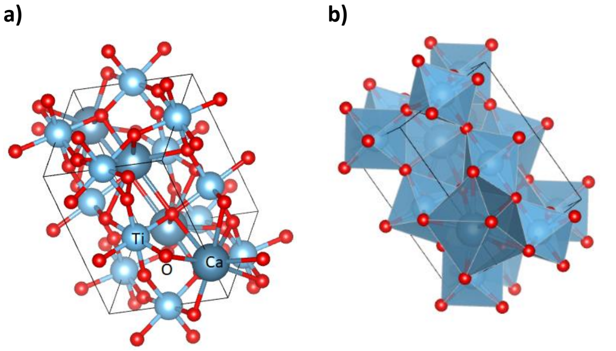

Fig. 1: Qualitative a) Crystal structure CTO and b) Octahedral site symmetry of Ti atoms.

CTO itself crystallizes in orthorhombic perovskite geometry with the space group of "*P b n m*" as sketched in Fig. 1.[11] The crystal lattice parameters are; *a*: 5.4043 Å, *b*: 5.4224 Å, *c*: 7.6510 Å, and $\alpha=\beta=\gamma=90^o$. The atomic positioning in the crystal is: Ca (x: 0.99160,

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y: 0.01230, z: 0.25000), Ti (x: 0.50000, y: 0.00000, z: 0.00000), O1 (x: 0.05860, y: 0.46870, z: 0.25000), and O2 (x: 0.71300, y: 0.28800, z: 0.03710).[12]

In the study, electronic responses of CTO to increasing temperature were investigated by x-ray absorption fine structure (XAFS) spectroscopy calculations performed at different temperatures (300, 400, and 500 K). Studies were conducted with the commercial code FEFF 8.2, which is one of the most reliable codes for the XAFS technique.[13-19] The XAFS data of 3*d* transition metals could provide detailed information about electronic reactions to conditions applied on the atom and its environment. The first part of the XAFS spectrum, so called x-ray near edge absorption spectroscopy (XANES), is one of the best techniques for studying the electronic structure of materials. The tail part of the XAFS spectra, which lays at the high energy part of the spectrum, is called the expanded XAFS (EXAFS) region consisting of the tail part where spectral fluctuations take place as an indication of the interruption of the travel between high kinetic energies. As a consequence, advantages of such technique were used to achieve the purpose of this work based on computer-based approaches.[20-25]

METHODOLOGY. The electronic structure properties of CTO material were examined using the FEFF8.20 code.[26] The XAFS calculations were performed with real space multiple scattering approach. The "feff.inp" file is the input file read by the FEFF code containing initial values of electronic energy details, crystal data and ambient conditions. The input files of calculations for this work were created using the TkAtoms package.[27-30] For studying the CTO material, calculations were performed on two atoms as the source located at the origin in real space. For the calculations, the input files were generated for 10 Å thick cluster containing 393 atoms (Ca, Ti, and O) for a calcium atom first part and a titanium atom for the second part. Calculations were made for 300, 400, and 500 K temperatures.

RESULTS & DISCUSSION. The XAFS technique could provide very efficient data for investigating the properties of atoms in detail. The calculated data was processed in two parts: electronic analysis-XANES study and atomic coordination and distance analysis-EXAFS study. XANES spectra relate to traces of electronic (bond) interactions of the source atom with its neighbors; where the EXAFS section (about 40 ~ 80 eV beyond the main absorption edge) yields atomic arrangements around the source atom by way of ripple spectra. Fluctuations in spectra are the result of scattering interactions of photoelectrons.

In the CTO material, Ca atoms have the ionic state of Ca^{2+}, while Ti atoms have the ionic state of Ti^{4+}. The ground state electronic configuration of calcium is [Ar] $4s^2\ 3d^0\ 4p^0$ and the Ca^{2+} ion has [Ar] $4s^0\ 3d^0$, i.e., the electronic configuration of the noble gas Argon. So, it is difficult to ionize them further. This information is useful for providing better information during non-stoichiometric analyzes of oxygen atoms. In order to see the electronic structure of the calcium atoms in the CTO material, the Ca K-edge XANES spectra were given in Fig. 2 by comparing 300, 400, and 500 K calculations.

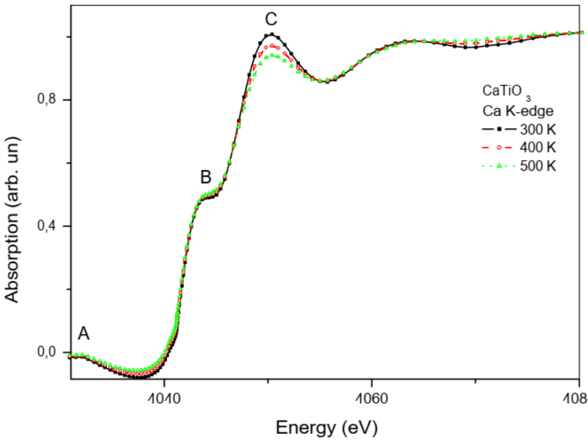

Fig. 2: Comparison of the Ca K-edge XANES spectra of CTO material at 300, 400, and 500 K.

The Ca K-edge absorption spectra of CTO material showed a strong pre-edge at 4031.5 eV, a forbidden transition to Ca 3*d* / O 2*p* hybridized molecular state. K-edge absorption spectra are a result of core 1*s* electrons transition to unoccupied levels as a final state over the Fermi level. However, unoccupied *d* and *s* levels are forbidden due to the quantum selection rules. Therefore, the main pathway for the excited s electrons is the unoccupied 4*p* levels above the unoccupied 3*d* and 4*s* levels, giving the main absorption spectra assigned as “C”. The peak just below the main edge “C” is due to the transition of the *s* level electrons’ to the low energy levels of the Ca-O molecular bands above the *dp* hybridized level, and this level is the Ca 4*s* and O 2*p* hybridized level (4043.64

eV). Spectra for different temperatures have high symmetry in peak properties, but poor distortion at peak intensities. Similar peak properties with decreasing peak intensities accentuate electron release with increasing temperature. Therefore, it can be said that with increasing temperature, Ca atoms tend to separate electrons from the crystal, that is, from thermoelectricity. Because the XANES spectra of materials that do not show thermoelectric properties may increase in peak density with increasing temperature.[27] In addition, the thermal increase seems to give a slight boost to the forbidden transitions on the leading edges designated "A" and "B". For more detailed analysis, the Ti K-edge XAFS spectra were calculated under the same conditions (Fig. 3).

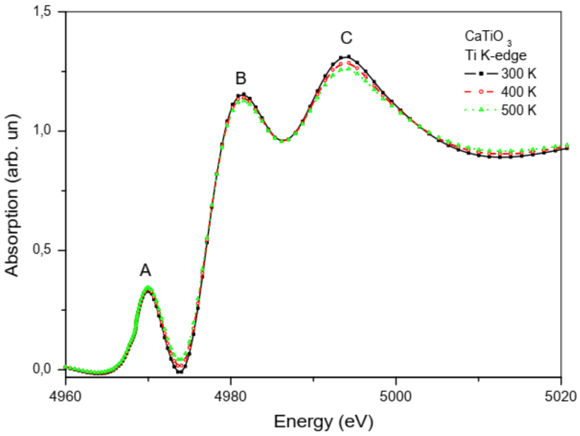

Fig. 3: Comparison of XANES spectra with Ti K-edges of CTO material at 300, 400, and 500 K.

Ti K-edge XANES spectrum was calculated for the CTO material showing edge properties similar to Ca atoms. The ground state electronic configuration of Ti is [Ar] $4s^2$ $3d^2$ $4p^2$ and Ti^{4+} ion has [Ar] $4s^0$ $3d^0$, which is the same for Ca^{2+} ions in the CTO material similar to the electronic configuration of the noble gas Argon. Ti K-edge XANES spectra were given in comparison with calculations at 300, 400, and 500 K. The low level pre-edge peaks of the forbidden transitions Ti 3*d* - O 2*p* (assigned as "A") and Ti 4*s* - O 2*p* (assigned as "B") were also appeared like on the Ca K-edge XANES spectra. The peak positions of the pre-edge peaks were 4969.8 eV (peak A) and 4981.2 eV (peak B), respectively. The main absorption edge energy was determined as 4993.7 eV. The symmetry on peak positions and the similarity on peak structure confirm the high stability of the crystal structure against temperature changes. Also, a decrease in the peak intensities with the increasing temperature confirms the electron release with the increasing temperature, as in the Ca K-edge spectra. The spectral decrease in Ti atoms data was weaker than Ca atoms (Fig. 4).

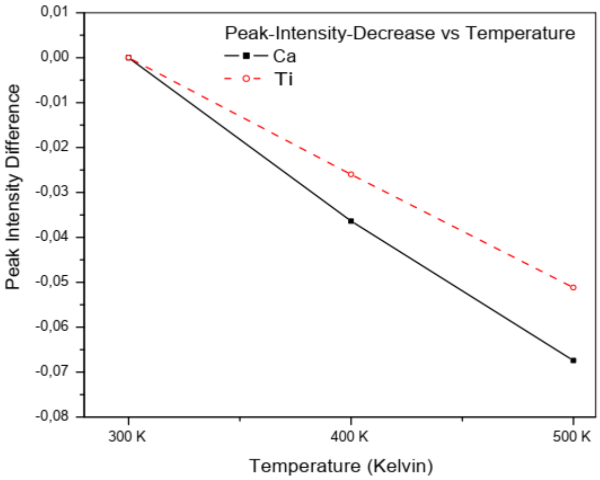

Fig. 4: Comparison of the peak density difference of the Ca and Ti K-edges of CTO material at 300, 400, and 500 K.

According to Fig. 4, the electronic activity of Ti atoms showed a monotaneous decrease with increasing temperature, while Ca atoms had stronger decay in curved electronic activity. To investigate the effect of increasing temperature on the crystal structure of CTO material, EXAFS data yielded from the emitted photoelectrons that travel between the atoms that are neighbors of the source atom, give us the best tool for analysis. EXAFS data could be extracted from the XAFS spectra using the ATHENA program. The data could be processed by the ATHENA program for electronic structure and for the determination of the atomic coordinations with the help of the ARTEMIS program for fitting, which are parts of the Demeter shell.[26] The EXAFS scattering data of CTO extracted from the Ti K-edge XAFS data are given in Fig. 5 for comparison. In this figure, the high symmetry in the scattering peak properties emphasized the stability to heat in the crystalline structure. Also, a decrease in peak density confirms absorption spectra, where Ca atoms and O atoms are the atoms most affected in the material by increasing temperature, but not at all peak properties. The best view of the atomic response to temperature increase can be provided by the Fourier Transform (FT) of scattering data, also called the radial dispersion function (RDF).

In Fig. 6, the FT of the scattering intensity taken from the Ca K-edge XAFS spectra was given in comparison with the data calculated for 300, 400, and 500 K. No shift or noise was observed which can be the trace of any distortion in the crystal structure for the RDF of the Ca K-edge. According to the analysis results, each peak is named with the atoms from which the signal came from. In Fig. 6, a calcium atom is sitting at the origin and the nearest neighbors were determined as the oxygen atoms that are sitting at various distances. The inhomogeneous distribution of the oxygen around the calcium may be the key to understanding the oxygen loss during the heat treatment that were reported in the literature.[1] While a decay observed at Ca and O atoms, Ti atoms seem to have less influenced by the heat treatment.

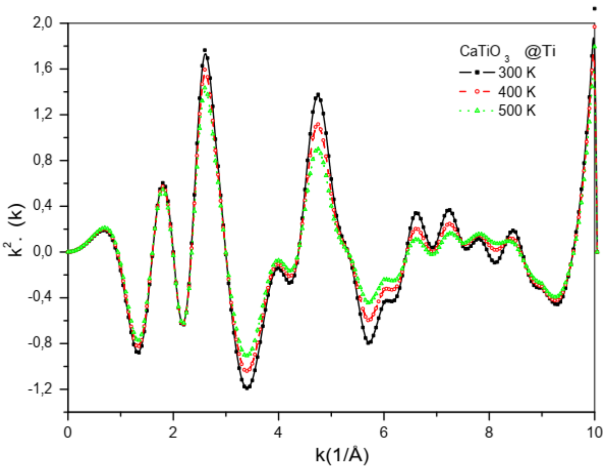

Fig. 5: Comparison EXAFS spectra of CTO material at 300, 400, and 500 K.

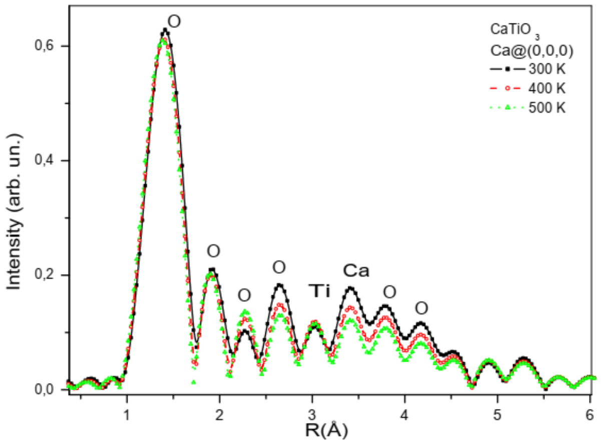

Fig. 6: Comparison of RDF data of CTO at 300, 400, and 500 K.

Decay at the O and Ca sites but low decay at Ti sites highlights increasing O stoichiometry due to electron loss that ruins the bonds between Ca-O and let O atoms leave the crystal with the increasing temperature. The loss of the O sites shows itself with decay at peak intensities. According to carefully analyzing the obtained results, O atoms were sitting at different distances (Ca-O) as described here; 2.32 Å (2 O atoms), 2.44 Å (1 O atom), 2.50 Å (1 O atom), 2.68 Å (2 O atoms), 2.73 Å (2 O atoms), 2.97 Å (1 O atom), 2.98 Å (1 O atom), and 3.16 Å (2 O atoms) were determined around the source Ca atoms.

CONCLUSION. In this study, electronic and crystal structure response of CaTiO3 (CTO) material to the increasing temperature conditions was investigated by XAFS technique. The study was performed on both Ca K-edge and Ti K-edge spectra of the CTO material. High stability against thermal treatment was determined in the material. However, from the spectral data, a decay at the absorption intensities on Ca, Ti and O atom coordinations parallel with the increasing temperature was observed. However, Ti atoms have less decay than both Ca and O atoms. Metals become the electron donor during the bonding in oxides due to the higher electronegativity of oxygen, and oxygen becomes the acceptor. In means of the electronegativity values, Ca atoms have the lowest electronegativity among the atoms that are the members of CTO, so Ca atoms lose their electrons more easily that make them the one more affected from the heat application. The electronic degree of the heat treatment confirmed by the absorption spectra of the Ca K-edge and Ti K-edge, where the pre-edges on both have a slight increase in intensity the main peak intensities have decay. The picture on the electronic structure is confirmed with the decay on both Ca and O sites by the RDF data.

DISCLOSURE STATEMENT. The author(s) did not report any potential conflict of interest.

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