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Electronic and structural properties of SnO and SnO_2 thin films studied by X-ray-absorption spectroscopy

O. M. ÖZKENDİR, Y. UFUKTEPE*
Physics Department, University of Cukurova, 01330 Adana-Turkey

Tin oxide thin films have been investigated by X-ray Absorption Fine Structure spectroscopy (XAFS). XAFS provides a description of the structure of the films. The paper also presents a structural characterisation of the SnO_2 thin films and their crystallisation behaviour by annealing at increasing temperatures. The x-ray absorption fine structure (XAFS) of Sn L_{III} -edge in SnO and SnO_2 have been investigated. The full multiple scattering approach has been applied to the calculation of Sn L_{III} edge XANES spectra of SnO. The calculations are based on different choices of one electron potentials according to Tin coordinations by using the real space multiple scattering method FEFF 8.2 code. The crystallographic and electronic structure of the SnO and SnO_2 are tested at various temperature ranges from 300 to 873 K. We have found prominent changes in the XANES spectra of Tin oxide thin films by the change of the temperature. Such observed changes are explained by considering the structural, electronic and spectroscopic properties. The results are consistent with experimental spectra.

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1. Introduction

The electronic structure of Tin and its oxides SnO and SnO_2 has been a subject of enduring interest due to the potential use of such materials as transparent electrical conductors, heterogeneous catalysis, gas sensing devices, solar energy cells, and lithium ion batteries [1-4]. These materials are increasingly studied in nanostuctured forms or thin films [5,6]. For these applications the films have to be stoichiometric and especially for optical/conductivity applications, they must have a high density. Doping with different elements is also necessary, if a conducting/transparent coating is required [3]. SnO and SnO2 are two stable oxides and exist in tetragonal crystalographic form, SnO2 is a n-type semiconductor with a band gap of ~ 3.6 eV [4]. SnO is a metastable materaial at ambient condition when heated up at certain temperature it changes to more stable SnO2 structure. In order to understand the origin of various features by the change of temperature it is necessary to calculate the observed fine structures from a suitable theoretical model. The aim of this study is to investigate the electronic and crystal structure response of Tin oxides to a annealing process.

One of the most useful methods serving the electronic structure of materials is the X-ray absorption fine structure (XAFS) spectroscopy. The method XAFS, especially over the last two decades, became an important way for electronic structure calculations, bondings, valency properties, catalytic properties, orbital and atomic configurations [7]. Near-edge structure, observed in x-ray absorption of inner-shell ionization process, can be sensitive to interatomic distances, local coordination and local electronic structure. The shape of absorption spectrum in this region is related to the electronic structure of the material, while the oscillation observed in the high energy part of the spectrum, called as the extended X-ray absorption fine structure (EXAFS) region, is associated with the arrangement of the atoms. It contains signals of interference of outgoing electron wave functions and scattered electron wave functions, gives information about the neighboring atoms, their regional configurations, atomic distances, coordination numbers etc. The amplitudes of the fine structure is related to the number of atoms that surround the absorbing atom. It is known that these amplitudes exhibit a dependence on temperature which is caused by thermal vibrations of absorbing and scattering atoms. To understand the origins of various features it is necessary to calculate the observed fine structures from a suitable theoretical model.

In this paper, oxide metallic compounds and more precisely SnO, SnO_2 are investigated using X-ray Absorption Fine structure spectroscopy with a particular emphasis on the numerical simulations of the L-edge in the absorption spectra of Sn. With this purpose we have performed full multiple scattering calculations.

2. Material and method

Sn L_{III}-edge x-ray absorption fine structure calculations of tetragonal cassiterite SnO_2 and tetragonal SnO were performed using FEFF 8.2 code, which is based on real space multiple scattering approach [8]. In the calculations, the FEFF input file was generated by the ATOMS package. The full multiple scattering calculation for 10 angstroms thick SnO_2 thin film, containing 349 atoms cluster (Sn, O) and SnO thin film, containing 725 atoms cluster (Sn, O) were performed with self-consistent potential. We have calculated backscattering and phase shift with single and multiple scattering paths to obtain X-ray absorption spectrum. Calculations performed as one Sn atom selected as an x-ray absorber is also a photoelectron emitter at 300, 673, 873 K temperatures. Mainly, bonding effects while obtaining a Tin oxide and thermal effects on SnO_2 and SnO are investigated. In ordet to show the effects of annealing at various temperatures are investigated by XAFS and Debye Waller factors calculated for related temperatures.

3. Results and discussion

SnO can be obtained at the initial state of metal tin oxidation as intermediate phase. Oxygen forms a very thin layer at the surface while obtaining SnO_2 [9]. Charactheristics of SnO are not yet well investigated. Semiconductors, like SnO_2, have wide band gap that make them a major material for optoelectronic devices [11-12].

Metallic Sn atom has electronic configuration of $[Kr]4d^{10}5s^{2}5p^{2}$ with completely filled 4d level. Empty 5d levels are located well above the Fermi level. Thus, for metallic Sn, transition from 2p level to empty d level (5d) can not be seen but transitions to unoccupied 5p level are possible. On the other hand, electronic configurations of SnO and SnO_2 are $[Kr]4d^{10}5s^{2}5p^{0}$ and $[Kr]4d^{10}5s^{0}5p^{0}$, respectively. Because of O bonding with Sn 5p level is empty in SnO and additionaly double O bonding in SnO_2 also 5s level is empty. Empty 5p levels of Sn atom in SnO and SnO_2 cause whitelines in the spectra. Whitelines in metals are results of the transition of the electrons from the core level to the unoccupied final states above the Fermi level. Whitelines in L_{III}-edge indicate the unoccupied d-symmetry orbitals (5d) and reflects the charge transfer [13].

5d levels of oxides have 5 degrees of degeneracy and bonding with neighboring O atoms cause splittings in bands with new levels. When small atoms (O) locate closer distances to heavy atoms (Sn), wave functions of outer shell electrons of the neighboring atoms overlap. In case of resonance and if the overlapping levels (i.e. Sn 5d-2p O) have close energies, the interaction and the following overlap would be more strong and establish a large hybrid molecular band with new high and low energy levels [14]. Peaks beyond the main absorption edge of oxides are corresponding to transitions to higher energy levels in the new energy levels in the band as told above. These levels are called as e_g and t_{2g} . t_{2g} levels are the low energy levels, e_g are the higher energy levels. Energies of the levels of bonds established between Oxygen and tin atoms are generally low. Also in 5d bands above the Fermi level, there are low energy levels which can be the final state for an excited electron. 5d levels have more convenient transition symmetries than empty s-level [13]. Thus, the properties of 5d levels support transitions to these levels.

In Fig. 1, energy calibration was performed using XANES calculation of Sn L_{III} edge absorption spectra in Sn, SnO and SnO_2. On the pre-edge region of the first absorption maximum at metallic Sn and also the whiteline of SnO at 3944 eV which correspond to the excitation of electrons 2p level to empty 5p levels above the Fermi level. However, Sn L_{III} edge of SnO_2, has two white lines at 3926 eV and 3958 eV energies. The first one is the result of 2p-5s and the second is due to 2p-5p transitions. Pre-edge structure of XANES region has an important role to investigate the electronic and bonding properties of the interested material. Previous studies have showed that structural properties of materials influence the pre edge region [18].

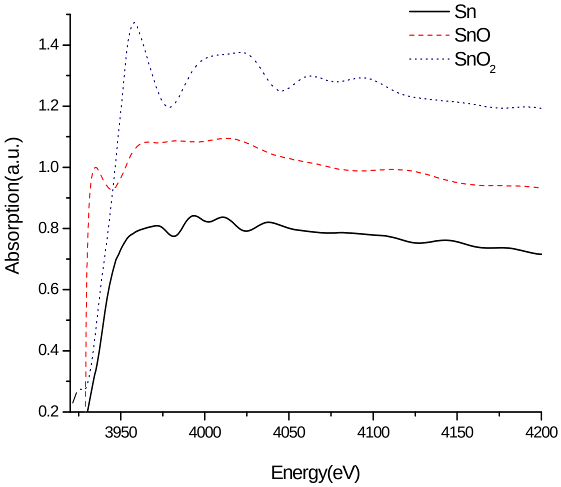

Fig. 1 . XANES spectra of Sn L_{III} –edge.

The pre-edge structure in SnO is a result of asymmetry and weakly overlapped O 2p outer shell electrons and Sn 5p level which have close energies. The main absorption peak beyond the pre-edge peak begin to rise at 3929 eV. This peak corresponds to the absorbed energy while transition from $2p_{3/2}$ level to empty 5d levels according to selection rules. High symmetry properties support Sn L_{III}-edge electron transition to 5d levels as a final state.

In Fig. 2, calculated Sn L_{II} -edge absorption peaks of SnO and SnO_2 are given. The same results of the process as explained above are shown. The wide absorption peaks of SnO_2 are the evidences of strong overlap and wider bands than in SnO. In the inset of the figure, oxygen K-edge absorption spectra in SnO and SnO_2 are shown. The features of the absorption peaks support the process in Sn L_{III} -edge and Sn L_{II} –edge spectra as a picture taken from the side across.

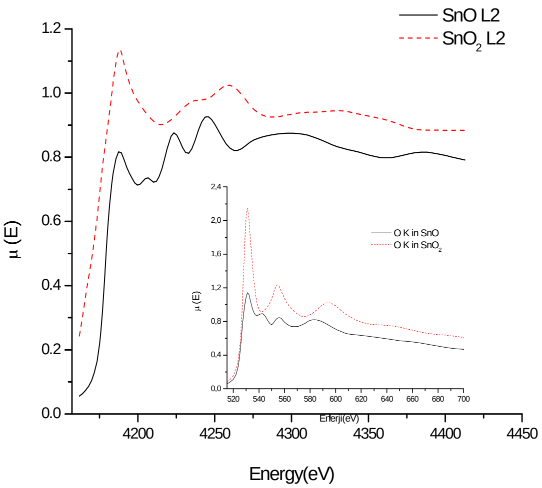

Fig. 2. Sn L_{II}–edge absorption spectra of SnO_2 and SnO. Inset, Oxygen K–edge absorption of SnO_2 and SnO.

Energy fluctuations beyond the main absorption edge is subject to EXAFS. Interference of incoming and outgoing waves of scattered photoelectrons cause fluctuations in absorption spectra beyond 30-40 eV of the main edge absorption edges. These fluctuations are also traces of atomic locations in crystals.

In Fig. 3, results of bonding process between tin (Sn) and Oxygen (O) in the trace of photoelectrons while its travelling out from the source (Sn) atom and back is given. We compared the scattering intensities (χ) of metallic Sn with SnO_2 structure as a function of wave number, *k*.

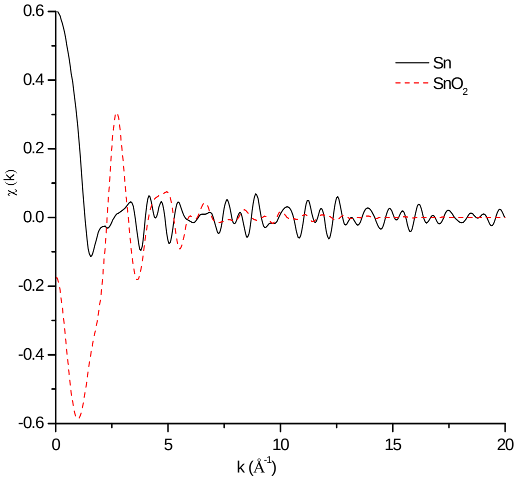

Fig. 3. EXAFS Scattering intensity function (χ) of Sn and SnO_2.

In Fig. 3, the emitted photoelectron from the source Sn atom in metallic Sn travels with its high kinetic energy because heavy Sn atoms are located in far distances from the others and Coulombic forces acting on each other. Large distances and weak intermedia potentials provide a long free path to the photoelectron emitted from a Sn atom with high kinetic energy. However, in SnO_2 structure, the photoelectrons lost its energy in short limit because of the O potentials which occupies the interatomic field and provides a continuous potential. When light O atoms located in the empty spaces between heavy Sn atoms, they fill the space with their weaker potentials. Thus, emitted photoelectrons suffer extra scatterings from weak O potentials which cause extra decrease in its kinetic energy. Scattering from varying but continuous potentials decrease the kinetic energy and cause decay in a short distance.

The fourier transform of EXAFS scattering intensity calculations give the atomic locations in real space and known as Radial Distribution Function (RDF). In figure 4, RDF of SnO_2 is given. The peaks are attributed to the nearest neighboring shells which surrounds the absorbing Sn Atom in 6 Angstroms distance. The peak distances are related with the atomic distances between the source Sn atom and the neighboring Sn or O atoms. Each peak contains information about the spherical localization of atoms in the crystal. However, informations at close distances to the source atom may superpose! In order to differentiate the information of in superposed peaks, one has to make fits! Table 1 shows various fitted atomic locations in SnO2 which are deduced from the result of Fig. 4.

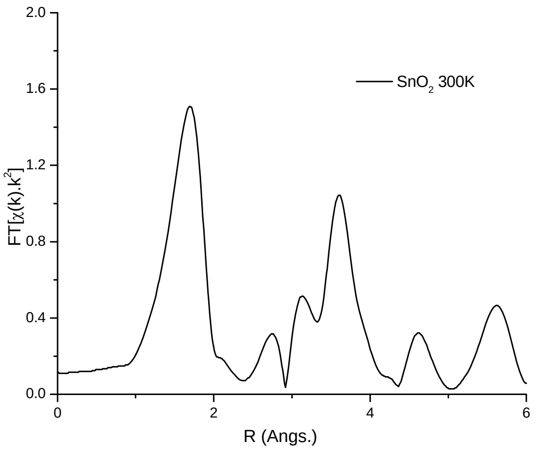

Fig. 4. RDF calculation of SnO_2.

In order to specify certain atomic locations and types of atom, fits with the scattering paths should be made. We need fits because signals from different atomic shells which are located closely may superposed. In table 1, fitted atomic locations up to 5 angstroms distance are given for SnO_2.

Table 1. Atomic locations in SnO_2.

Compound	Coordination Sphere**	Number of atoms	Type of atom	R (Å)*
SnO_2	Sn-O	6	O	2.07
	Sn-Sn	2	Sn	3.22
	Sn-O	4	O	3.62
	Sn-Sn	8	Sn	3.74
	Sn-O	4	O	3.83
	Sn-O	8	O	4.28
	Sn-Sn	4	Sn	4.78
	Sn-O	8	O	4.84
	Sn-O	4	O	5.0

**Inter-atomic distances (±0,02 Å) ; **Sn is the source atom*

4. Temperature dependence

Heating a crystal may cause changes in its crsytal geometry and electronic structure of atoms [15, 16]. In finite temperatures, atoms oscillates around their point of equilibrium. Raising temperature increase the oscillation frequency and force the atoms to vary their displacements. This process may cause distortions in their crystal structure. Distortions as a result of increasing temperature weaken the bonds and make changes both in electronic properties and geometry of the crystal. In SnO_2 structure, short and strong bonds which are established by occupation of light O atoms in the interatomic distances of heavy Sn atoms would prevent the structure to external effects. So the response to the increasing temperature would be weak and slow [17]. In figure 5, Sn L_{III}-edge XANES calculation of SnO_2 at 300 K, 673 K and 873 K temperatures are given.

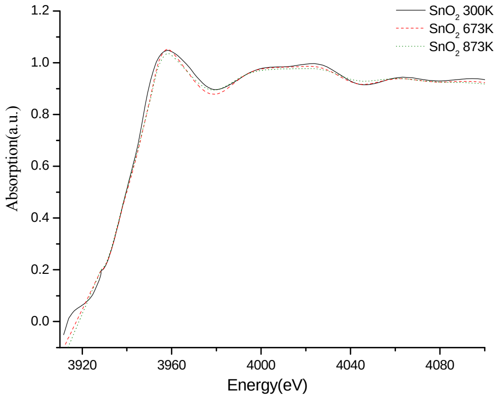

Fig. 5. Sn L_{III}-edge XANES calculation of SnO_2 at 300 K, 673 K and 873 K.

In figure 5, the pre-edge structure which is a result of 2p-5s transition at 300 K decay with the increasing temperature. When temperature increase, the atoms begin to vibrate strongly around their equilibrium lattice sites. They slightly alter the interference pattern between Sn and O [19]. This process leads a strong overlapping between p-like 5d level of Sn with its 5p level. Thus, supported wide bands increase transitions from 2p level to p-like 5d levels of Sn-O bonds which cause decay in pre-edge structure at high temperatures. However beyond pre-edge region, we could not observe any shift to asymmetry or high damping in their absorption intensity which is a sign of stable and strong SnO_2 crystal structure.

Also, in order to demonstrate the effect of high temperature on SnO_2 structure, EXAFS calculations of scattering intensities at 300, 673 and 873 K temperatures are given in Fig. 6.

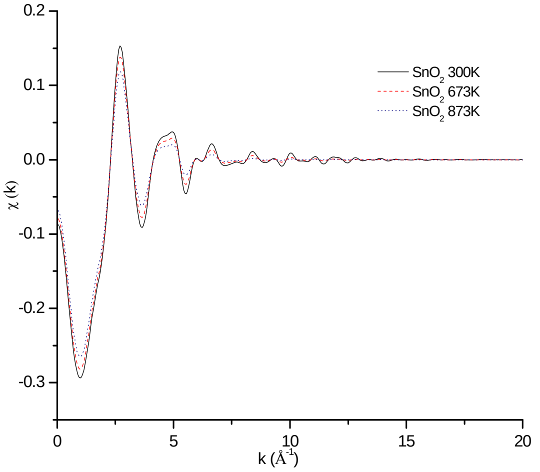

Fig. 6. Scaterring intensities of SnO_2 at various temperatures

The tiny damping of scattering intensity χ(k) is apparent in the spectrum. As a characteristic of thermal effects, intensity peaks become weaker and gaussian shaped. Anyway, symmetry in the damping of intensity, reflects the structural strength of SnO_2 against thermal effects.

5. Defects

Regional imperfections in a crystal is called “defect”. Most of the crystalline materials have some defects which may be a problem or sometimes a gift. In order to investigate the defects on a sample, we performed XANES calculation using FEFF 8.2 code. To obtain a defected sample we have rondamly taken out several O atoms in the list of tetragonal SnO_2 structure. Then we performed the XANES calculations for the Sn L_{III}-edge at various temperatures and the result of calculations are given in Fig. 7.

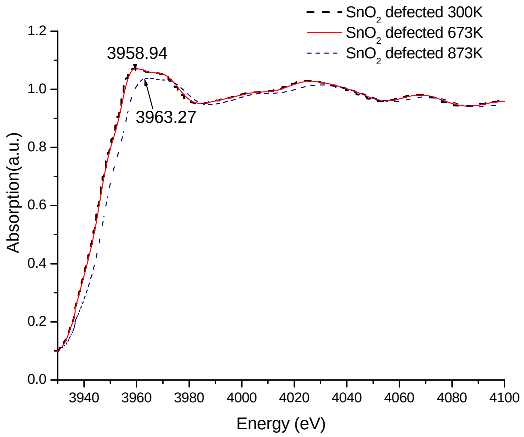

Figure 7. XANES calculations for Sn L_{III}-edge of defected SnO_2 at various temperatures

In figure 7, defected SnO$_2$ at 300 K and 673 K have similar absorption spectra which points out the SnO structure as measured by Z. Liu et al. [13]. These spectra is evident that in case of defects, the first step in obtaining a crystalline structure of Sn and O is SnO. SnO can be obtained at the initial state of metal tin oxidation as intermediate phase.

Above 673 K, thermal vibrations cause atomic displacement and forcing the structure to establish a more stable geometry. As shown in figure 7, also above 673 K increasing temperature give rise to phase transition of SnO to SnO$_2$.

6. Conclusions

We have investigated the electronic and crystal structure of SnO and SnO$_2$ by the spectral change of thin films with change of temperature ranges from 300 to 873 K. Because of phase transition from SnO to SnO$_2$ above 673 K temperature, thermal distortions and damping of EXAFS oscillations observed due to atomic vibrations. Our calculations showed strong structural geometry of Sn L_{III} edge against annealing. To observe the phase transitions, a defected SnO$_2$ sample obtained and calculations performed for various temperatures. By this calculation at above 673 K, it is observed that thermal vibrations cause atomic displacement and forcing the structure of SnO to establish a more stable SnO$_2$ geometry. Metastable SnO decomposes to SnO$_2$ structure by the increase of temperature. Oxygen bonding with Sn causes strong Coulombic foce and weak bond gives weak response to elevated temperature. Calculations are consistent with the previous experimental results.

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*Correponding author: ufuk@cu.edu.tr