Influence of Sn substitution on the electronic structure of ThGeO$_4$ semiconductors

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ThGeO$_4$ (TGO) material is an actinide semiconductor with a wide bandgap. The influence of Sn substitution in the Ge coordinations has probed by the x-ray absorption fine structure (XAFS) spectroscopy calculations. Calculations were performed for Th L$_3$-edge and O K-edge to study the influence of both Ge and the substituted Sn atoms on the electronic structure of the thorium atoms. ThO$_2$ material's calculation has been used as reference material during the analysis and the analysis have shown that unoccupied *6d* levels of the Th atoms' were hybridized with *2p* levels of the oxygen to build up molecular bands.

1. Introduction

Thorium is a metallic element that is in the first place of the Actinides group and is known for its radioactive properties [1-3]. Due to the active presence of actinide materials in the field of nuclear energy and radioactive materials, have become prominent in the study of energy materials. While it is generally taken into consideration in nuclear studies such as Uranium, it is considered that these materials cannot be used only on the basis of energy and that their technology use is possible due to the features required by the latest technology [2]. In this sense, the investigation of the electronic properties of actinide structures has become a priority in actinide research [4]. Apart from nuclear studies, thorium is included in various technological material research due to its electronic and crystal structure features. Among the thorium oxide materials, thorium germanate ThGeO$_4$ (TGO) is a well known wide bandgap semiconductor and a member of the family with the general formula ABO$_4$ and crystallizes in tetragonal structure. It creates compounds that display different properties with two types of space symmetry in tetragonal structure. The first and most notable of these is the structure with the space symmetry "*I41 / amd*", which is defined as the type of "zircon", and the second form with the space group of "*I41 / a*", called the "skheelite" type [4].

TGO material is a combination of ThO$_2$ and GeO$_2$ materials. Initially, the effects of germanium on the electronic and crystal structure of thorium atoms in TGO structure were studied by the x-ray absorption fine structure (XAFS) spectroscopy technique. And, as the second step, Sn substitution in Ge atoms to probe the electronic response of the TGO materials to a substitution process was studied. Moreover, the ThO$_2$ base material has been used as a reference to monitor the change of the electronic properties of thorium atoms in the Thorium Germanate material.

Mainly, the known properties of the materials are the result of the electronic interactions of the neighboring atoms during building a molecular band. Technological improvements lie in the detailed analysis of the electronic, magnetic, optical, and similar properties of atoms or molecules during the scientific studies on learning what interaction mechanisms lie in the background of their properties. Among the properties of the materials, the electronic structure has major importance to understand the background mechanisms. The XAFS technique has an important place among other techniques for electronic structure analysis [5-8]. In this study, XAFS calculations were performed to analyze the electronic structure of TGO (ThGeO$_4$) material. XAFS data has rich content than most of the other techniques and can yield informations 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. The XAFS data has a long energy spectrum range and it can be divided into two parts: XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended-XAFS). The XANES data provides information for the analysis of the electronic structure and bond properties of the material. The spectra lays between 20 eV below and 50~70 eV above the main absorption edge. However, the data range of the EXAFS part arises beyond the XANES spectra. It is sometimes called as the tail spectra of the XAS (x-rays absorption spectroscopy) data and the range can be elongated to an energy range of 400~800 eV. This part has spectral fluctuations which are a result of the photoelectrons' travel that are emitted from the source atom (an excited atom with photons).

2. Materials and methods

The electronic properties of the TGO and ThO$_2$ materials have been studied with the performed XAFS calculations. In the calculations, a thorium atom was chosen as the source atom in the TGO (ThGeO$_4$) and ThO$_2$ materials. ThO$_2$ material was used as the reference material for a better understanding of the interactions in the electronic structure of thorium atoms. Calculations were performed by using the FEFF8.20 code, which is based on real-space multiple scattering approach [5]. In order to perform the calculations, the code needs an input file providing the calculation steps, electronic energy details, crystal data, and calculation cards 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 [8]. For the calculations, two input files have been created for i) ThGeO$_4$ ii) ThO$_2$ materials. The first input file was prepared for the ThGeO$_4$ (TGO) material in tetragonal (I41 / amd) geometry for 10 Å thick cluster, containing 411 atoms (Th, Ge, and O) with the lattice parameters; a:7.230 Å, c: 6.539 Å and Th (x, y, z): (0.0, 0.0, 0.0), Ge (0.0, 0.0, 0.5), and O (0.0, 0.1803, 0.3214) [9]. The second input file was prepared for the 10 Å thick reference ThO$_2$ material with a cubic "F m -3 m" crystal geometry, containing a set of 295 atoms (Th and O). Crystal parameters of ThO$_2$ material; a: 5.5997 Å; Th (x, y, z): (0.0, 0.0, 0.0), and O (0.25, 0.25, 0.25) [10]. The crystal structure of the studied crystals a re given in Fig. 1. a. and b. for ThGeO$_4$ and Figure 2.a. and b. for ThO$_2$ materials [11]. Calculations were performed for room temperatures.
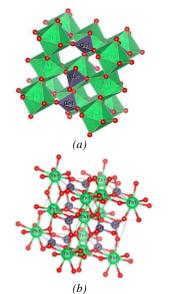

(a)

(b)

Fig. 1. Tetragonal (I41 / amd) ThGeO$_4$ crystal a) Polyhedral View b) General view (color online)
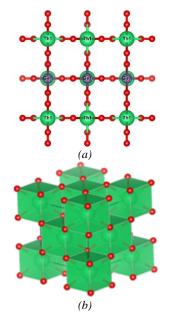

(a)

(b)

Fig. 2. Cubic "Fm-3m" ThO$_2$ crystal a) View from the z-axis b) Polyhedra view (color online)

3. Results and discussions

The XAFS method provides the most valuable data for research on the electronic structure of materials. In this study, account data produced with this important technique were used for analysis. Study L$_3$-edge spectra of thorium atoms in the TGO and ThO$_2$ structures were produced with the code FEFF 8.20. The XANES absorption spectra of Th L$_3$-edge in TGO and ThO$_2$ materials are presented by comparing them in Fig. 3.
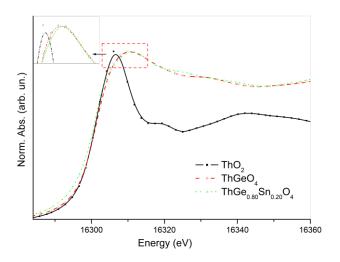

Fig. 3. Th L$_3$-edge XANES spectra comparison of ThO$_2$, ThGeO$_4$ and ThGe$_{0.80}$Sn$_{0.20}$O$_4$ materials (color online)

The high agreement between the spectra of the Th L$_3$-edges of the TGO and Sn-substituted TGO materials indicates similar oxidation states of Th atoms in each material. However, the broader absorption spectra of the TGO materials highlight broader molecular bands that are built with the support of the outer shell levels of

germanium with rich quantum symmetry. Besides, the shift at the peak positions points out a change in the oxidation state of the thorium atoms in the TGO materials, unlike in the ThO_2. Absorption spectra of the Th L_3-edge correspond to the excited $2_{p3/2}$ electrons' transition to the unoccupied levels as a final state. The ground state electronic configuration of the thorium atoms is [Rn] $6d^2$ $7s^2$ and for the Th^{4+} ionic state is [Rn] $6d^0$ $7s^0$. The transition route for the excited p electron is p-->d which obeys the quantum selection rules, i.e., $\Delta l=\pm 1$. Thus, the spectra have a smooth rise at 16284 eV. This rise shows that the bond of Th atoms with oxygen atoms in ThO_2 or $ThGeO_4$ crystal structures does not lead to hybridization with strong overlaps, but Ge atoms are dominant on oxygen bonds than Th atoms and cause the shift. While Th atoms in ThO_2 give a maximum at 16306 eV, it is seen that Th atoms in TGO give a maximum of 16310 eV, and Th atoms in TGOs with 20% Sn substitution at 16311 eV.

Since ThO_2 and TGO have different crystal geometries, their structural differentiation is natural. However, due to the high electronegativity value in the structure where the shift in the energy peaks of the Ge containing material, it is understood that the oxygen above Th affects the bond structures and makes their own oxygen bonds stronger than the Th-O bonds. It is known that ThO_2 material is formed in the tetrahedral structure [12]. As shown in Figure 1, TGO structure is bonded as Th-GeO_4 and Ge-O bonds are seen to have tetrahedral structure and "Isolated" tetravalent germanates have been reported in papers [9]. However, for the SnO_4 structure, which is the second step of the study and substituted for Ge coordinations, formed the octahedral structure by the closest O atoms. There are many supporting papers stating that the links between Sn-O in the literature are octahedral in structure [13].
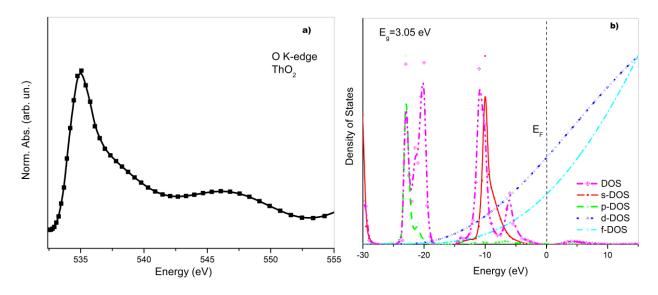

Fig. 4. a) O K-edge XAS spectra of ThO₂ b) DOS calculation in ThO₂ (color online)

One of the best solutions to understand the electronic interplay between metals is to have a look from the other side, i.e., a view from oxygen, where all elements have traces on the bonds. Therefore, O K-edge absorption spectra were calculated and given in figure 4.a. Besides, to make the electronic interactions more visible, calculated density of states (DOS) data of the ThO_2 material is given in Fig. 4.b.

O K-edge is the result of the excited 1s electrons' transitions to the unoccupied $2p$ levels as the final state. The pre-edge structure is the indicator of the hybridization of overlapped outer shell levels of the atoms and it is familiar for oxygen. However, the narrow and edge feature of the ThO_2 addresses weak coupling between outer shell electrons of oxygen and the outer shell levels of Th atoms. To visualize the electronic interplay, the density of states (DOS) data can be a good solution. In Fig. 4.b. DOS data of the ThO_2 material is given with a line showing the Fermi level (E_F), as a guide for eyes. The electronic bandgap for the ThO_2 is determined from the DOS data as 3.05 eV which agrees with the literature [14]. As seen in

Fig. 4.b., d- and f-levels are unoccupied in ThO_2 structure. A powerful peak showing the s-DOS is located at 4 eV below the Fermi level which is an overlapped data of 6s of Th and $2s$ of the O atoms. Empty d- and f-levels of the seems no coupling with the p-level of oxygen. The presence of the d-levels in the region of the p-levels confirms possible hybridization between Th $6d$-O $2p$ levels (for the Th^{4+} has unoccupied d-levels, i.e., [Rn] $6d^0$ $7s^0$). Hybridization between the outer shells of the atoms may occur when two levels have close energies or they overlap when two atoms get closer in distance. Thus, it seems the outer shell levels of both Th and O did not satisfy the conditions. This phenomenon was also confirmed by the Th L_3-edge XANES spectra in Fig. 3, where $2p$-$3d$ transition obeys the selection rules and does not give any pre-edge structure. The absorption peak of the O K-edge at 546 eV is a result of the scattering process of the photoelectrons among its neighboring atoms.

Comparison of the O K-edge spectra for TGO and 20% Sn substituted TGO materials are given in Fig. 5 and their calculated DOS spectra are given in 6.a. and 6.b.,

respectively. In Fig. 5, the O K-edge XANES spectra of the studied materials have a high agreement. However, the main edge has a broader and powerful structure than the ThO^2 material. The pre-edge structure confirms the formation of the hybridized molecular bands between Th, Ge and/or Sn atoms. The pre-edge structure has a narrow band structure with a maximum at 539 eV, which is approximately 4 eV higher than the main edge of the O K-edge in ThO$_2$ material.

Narrow pre-edge but broader and stronger main edge structure points out distortion on the pre-edge due to multiple quantum symmetry presence in the hybridized levels that avoid s electrons to localize in the hybridized levels. In Fig. 6.a., *d*-state from the Th ions seem to preserve its position on the DOS data.
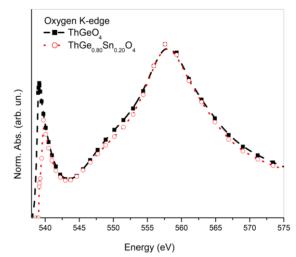

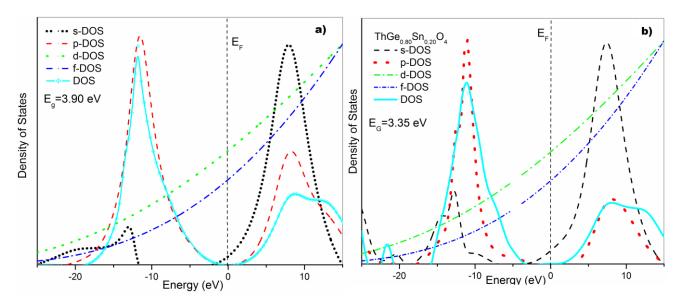*Fig. 5. Comparison of the O K-edge XAS spectra of ThGeO$_4$ (TGO) and ThGe$_{0.80}$Sn$_{0.20}$O$_4$ (color online)*

Fig. 6. Calculated Density of States for a) ThGeO$_4$ (TGO) b) ThGe$_{0.80}$Sn$_{0.20}$O$_4$ (color online)

The ground state electronic configuration of Ge atom is [Ar]$3d^1 4s^2 4p^2$, so Ge^{4+} is [Ar]$3d^1 4s^0 4p^0$, while ground state electronic configuration of Sn atom is [Kr] $4d^1 5s^2 5p^2$, and Sn^{4+} is [Kr] $4d^1 5s^0 5p^0$. In Fig. 6.a, the unoccupied s- and p- states are localized above the Fermi level where s-levels has a tail below E$_F$ as an indicator of *sp* hybridization between O *2p* and Ge *4s* levels. 3p and 6p levels DOS of Ge and Th atoms overlapped and gave a powerful signal at 2 eV below the Fermi level. Above the Fermi level, unoccupied s- and p-levels of Ge and Th atoms are localized and increased the possibility of the hybridization of the Ge *4s* levels with the unoccupied 2p levels of oxygen. In Fig. 6.b, calculated density of state data for the 20% Sn substituted TGO material is given. The electronic configurations of both Ge^{4+} and Sn^{4+} have so similar conduction bands and their both *p* and *s* states are almost unoccupied. The broadening in the main edge spectra is addressed to the hybridized *s* states of the unoccupied Ge atoms and more powerful with the

presence of the unoccupied *s* states of the Sn superposed with *p*-states of oxygen. Besides, *p*-states of oxygen exposed an impulse from the *p*-states of both Ge^{4+} and Sn^{4+}. Thus, *d*- and *s*- symmetry gained due to the hybridization with oxygen p states, excited *s* electrons avoid transition to the *p*-levels of oxygen. However, *p*-levels of both Ge^{4+} and Sn^{4+} seem to become the final state of the excited *s* electrons of oxygen and caused a high energy shift to higher energy with a broader spectrum. The main absorption edge has the maximum at 557.75 eV, which is 11.75 eV higher than ThO$_2$ materials O K-edge.

The effects of the electronic interplays on the atomic environment and the crystal order, EXAFS spectra were extracted from the XAFS spectra.
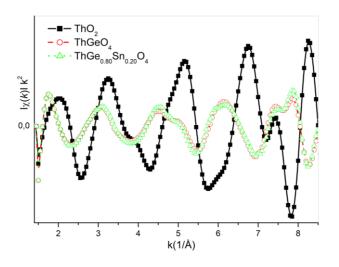
Fig. 7. EXAFS scattering data comparison of in ThO₂, ThGeO₄ and ThGe₀.₈₀Sn₀.₂₀O₄ (color online)

Fig. 8. Radial Distribution Function (RDF) results of ThO₂ and ThGeO₄ materials (color online)

In Fig. 7, the EXAFS scattering intensity (χ(k)) of the photoelectrons emitted from the Th atoms are given in comparison. Scattering peaks of ThGeO₄ and ThGe₀.₈₀Sn₀.₂₀O₄ materials have a high agreement at high k-values pointing out the similar environment of the Th atoms, i.e., the same crystal structure. However, the different crystal structure of the ThO₂ material is clear and the higher scattering intensity is a result of the heavy atoms (Th) in the environment of the thorium atoms. The lower scattering intensities of the ThGeO₄ and ThGe₀.₈₀Sn₀.₂₀O₄ materials are due to the decrease occurred as a result of the light atoms in the environment of the Th atoms, i.e., Ge and Sn. Atoms provide potentials to the interstitial media where photoelectrons move. No quick decay in the energy has determined in the scattering data. This can be explained with the low potential values of oxygen that decreases the interstitial potential that supports the photoelectrons mean free path with longer range.

To shift from the energy space to real space, the Fourier Transform of the scattering data yields the Radial Distribution Function (RDF). RDF data gives the bond lengths (atomic distances) from the source atom (Th) on a one-dimensional axis. With the RDF data atomic types and the coordination numbers can also be determined by the fitting of the scattering paths produced during the EXAFS calculations. Single scattering paths from the closest neighboring atoms can give the exact atomic distance to the source Th atoms that sit in the origin, i.e, at (0, 0, 0). Weak multiplet peak features are results of the overlapped signals of the multiple scattering mechanisms. To determine the exact information from the scattering data, the analysis should be processed with care. As a result of the RDF analysis, the atom types are assigned to the peaks in Fig. 8 and the nearest neighbors and distances are determined as follows.
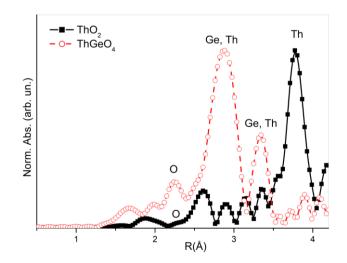
In the ThO₂ material, the closest atom group was determined as oxygen atoms that are located as the nearest neighbors to the source Th atoms at a distance (bond length) of 2.42 Å (Th-O). Nearest Th neighbor of the source Th atoms is determined at a distance of 3.96 Å (Th-Th). The peak structures between two peaks are determined as a result of the multiple scattering paths which do not contain healthy atomic displacements, so they are omitted during the analysis.

For the TGO material, the first row atoms were determined as oxygens and are located at a distance of 2.47 Å (Th-O). Beyond the oxygen atoms, the powerful peak was determined as the overlapped signals from both Ge and Th atoms which are located at the distance of 3.03 Å (Th-Ge and Th-Th), but with different azimuthal angles.

4. Conclusions

In this study, the influence of the Sn substitution in the Ge coordinations is studied via the ThGeO₄ (Thorium germanate) material which is a wide bandgap semiconductor. The studies were conducted by the XAFS technique calculations. Calculations were performed with the commercial code FEFF 8.2 for Th L₃-edge and O K-edge absorption spectroscopy. ThO₂ material was used as a reference material to guide for the difference on the thorium atoms electronic structure in the presence of germanium atoms and also the tin atoms. In the ThO₂ material, oxygen atoms are the only atom surround the thorium atoms as the neighboring atoms. The analyses showed that unoccupied *6d* levels of the Th atoms were coupled with *2p* levels of the oxygen to build up molecular bands. However, in the ThGeO₄ materials, unoccupied *p* levels of both Ge atoms and the substituted Sn atoms were suppressed the oxygen *p*-levels and caused the wide bandgap. Thus, the route for the excited *1s* electrons of the oxygen atoms was determined as the *p*-levels of the neighboring Ge and Sn atoms that are mixed with the *s*-levels.

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