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# Değişen Sıcaklık Koşullarının $LiNi_2Sn$ Malzemesinin Elektronik Seviyeleri Üzerine Etkilerinin Araştırılması: Bir Ab-Initio Çalışması

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**ÖZ**

Bu çalışmada, kararlı kristal yapıya sahip olduğu bildirilen ancak henüz üzerinde bir çalışma yapılmamış olan $LiNi_2Sn$ malzemesinin elektronik ve kristal yapıları farklı sıcaklık koşullarında incelenmiş ve bulgular ışığında termoelektrik özelliğinin izleri araştırılmıştır. Termoelektrik malzemelerin araştırmalarını desteklemek amacıyla, termoelektrik özelliğin elektronik ve kristal yapı üzerindeki izlerine soğurma spektroskopisi yöntemiyle yeni bir bakış açısıyla bir test çalışması yapılmış ve sonuçlar detaylı analizlerle sunulmuştur. $LiNi_2Sn$ malzemesinin elektronik yapısal özellikleri üzerine X-ışını soğurma ince yapı (XAFS) spektroskopik hesaplamaları 300 K, 323 K, 373 K ve 423 K artan sıcaklık koşullarında XAFS kodlu FEFF 8.20 ile hesaplamaları kullanılarak teorik araştırmalar yapılmıştır. Çalışmanın sonuçları literatür verileri ile uyumludur.

# Investigation of the Effects of Varying Temperature Conditions on the Electronic Levels of $LiNi_2Sn$ Material: An Ab-Initio Study

**Research Article**

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**ABSTRACT**

In this study, the electronic and crystal structures of the $LiNi_2Sn$ material reported to have a stable crystal structure but not yet thoroughly studied were examined at various temperatures, and traces of the thermoelectric property were looked for in light of the results. A test research was carried out with a fresh perspective on the thermoelectric property traces on the electrical and crystal structures in order to promote the studies of thermoelectric materials, and the results were provided with complete analysis. Theoretical investigations using X-ray absorption fine structure (XAFS) spectroscopic calculations were made into the electronic structural characteristics of the $LiNi_2Sn$ material. Calculations were made with XAFS code FEFF 8.20 under increasing temperature conditions of 300 K, 323 K, 373 K, and 423 K. Findings from the study included the quantity and potency of the atoms' outer shell electrons, which are where the photoelectrons are directed. The results of the study are compatible with the literature data.

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## 1. Introduction

One of the leading goals of today is to meet the energy needs more cheaply and easily with increasing technological investments, and to support the energy deficit with renewable resources supported by reuse with environmentally friendly investments as much as possible. In this sense, both the conversion of waste heat into benefit and the transformation of disadvantages caused by harsh

conditions into advantages have brought thermoelectric materials to the fore. Increasing the working performance of the thermoelectric materials used today and adding new thermoelectric materials that offer different advantages to the existing materials constitute the essence of the research. In this respect, 3d transition metal structures, which are cheap and easily accessible, are very popular study subjects.

The unoccupied d-shells of transition metals exhibit interesting electronic behaviors that make them an active role player in current technological applications, especially when interacting with different electronic outer shells of neighboring atoms (Eerenstein, 2006; Ozkendir, 2013; Ozkendir, 2020). This situation has placed transition metals at the center of many studies and has made them the most important material building blocks. Due to their abundance in the earth's crust, their cheap and easy supply has clinched their place in technological studies (Ozkendir, 2013; Ozkendir et al., 2018). Some important transition metal behaviors were summarized in the literature: They can be listed with properties as a result of their superior conductivity, magnetic arrangements, and bonding with oxygen (O). The interactions of light elements and empty s levels, which make electronic bonds with their levels difficult due to quantum selection rules, reveal interesting and sought-after electronic and magnetic properties that are frequently used in today's technologies.

In this study, the effects of the variable temperature applied to the triple intermetallic $LiNi_2Sn$ alloy in a Heusler type structure on the crystal and electronic structure were investigated, and its connection with the thermoelectric structure was investigated. The material subject to the study was first studied on the basis of the $LiCo_2Ge$ crystal in the literature, and the interactions of Li atoms with 3d transition metals were questioned. Although the $LiCo_2Ge$ structure contains Li and is formed in the full Heusler structure sought in many technological applications, the interest in these materials has taken place in various research subject. However, the $LiNi_2Sn$ material has not received the same attention, and stable crystal structure of the $LiNi_2Sn$ material allowed us to question its response to variable temperature in terms of electronic interactions and to test its thermoelectric properties theoretically through its electronic structure. Previous studies have revealed that the response of the electronic structure to the effect of temperature is proportional to its thermoelectric properties (Ozkendir, 2022). This situation changes in direct proportion to the electronic conductivity, as can be understood from the formula "$zT= \sigma Z^2T/\kappa$" which defines the thermoelectric efficiency and the conductivity is defined as " $\sigma= ne\mu$". For this purpose, XAFS calculations based on the synchrotron system at different temperatures (300 K, 323 K, 373 K, and 423 K) were made with the commercial code FEFF 8.2, which is one of the most reliable codes for this technique (Ankudinov, 1997; Ozkendir, 2015; Gunaydın, 2020). X-ray Absorption (XAS) spectra of 3d transition metals can provide detailed information about the electronic structure and crystal coordination of atoms. X-ray absorption fine structure (XAFS) spectroscopy is an extended version of the XAS technique and is one of the best techniques for studying the electronic structure of materials. The XAFS technique provides very important data for investigating the electronic structures of atoms, the properties of valence electrons,

bond structures, and atomic configurations within the crystal (Ankudinov, 1997). The XAFS spectrum is divided into two regimes containing electronic and crystal structure information for detailed analysis. These are the extended-XAFS (EXAFS) and x-ray absorption near-edge spectroscopy (XANES) regions. XANES spectroscopy is sensitive to the XAS mechanism's inner shell ionization process and provides detailed information about the electronic structure of atoms in the studied materials. The XANES region in the spectrum starts 20 eV below the main absorption edge and extends to 50~70 eV above it. The high-energy portion of the spectrum, called the Extended XAFS (EXAFS) region, consists of the tail portion, where spectral fluctuations occur as an indication of the continuous scattering of photoelectrons released from the excited atom with high kinetic energy. The EXAFS spectrum is beyond the XANES spectrum and its range can be extended to the energy range of 400~800 eV. The oscillation observed in this region is related to the arrangement of the atoms. The data in this region includes configurations of neighboring atoms, atomic distances, coordination numbers, etc. and contains information about crystal structure (Ozkendir, 2016).

## 2. Material and Methods

The electronic structure properties of $LiNi_2Sn$ material were investigated by using a real-space multi scattering approach the code FEFF8.20, which makes XAFS spectroscopy calculations (Ankudinov, 1997). The FEFF code reads an input file into which instruction cards are written for the computational steps, providing electronic energy details, crystal data, and ambient conditions. The input files used in the calculations were created using the TkATOMS package, which is part of the IFEFFIT Shell interface (Ravel, 2005). For $LiNi_2Sn$ calculations, Ni atoms were chosen as the source atoms and placed at the origin of the real space in the calculations. For the calculations, the lattice parameters for the $LiNi_2Sn$ material with the cubic “F m -3 m” space group given in Figure 1 and the input file for the 10 Å thick cluster (Li, Ni, and Sn) containing 331 atoms were prepared (Mewis, 1977; Momma et al, 2011). Lattice parameters in the input file are; a=b=c: 5.9630 Å, $\alpha=\beta=\gamma=90^o$, and Ni (x, y, z): (0.25, 0.25, 0.25), Li (0.50, 0.50, 0.50), Sn (0.00, 0.00, 0.00), with calculations were made for the temperatures of 300 K, 323 K, 373 K, and 423 K.

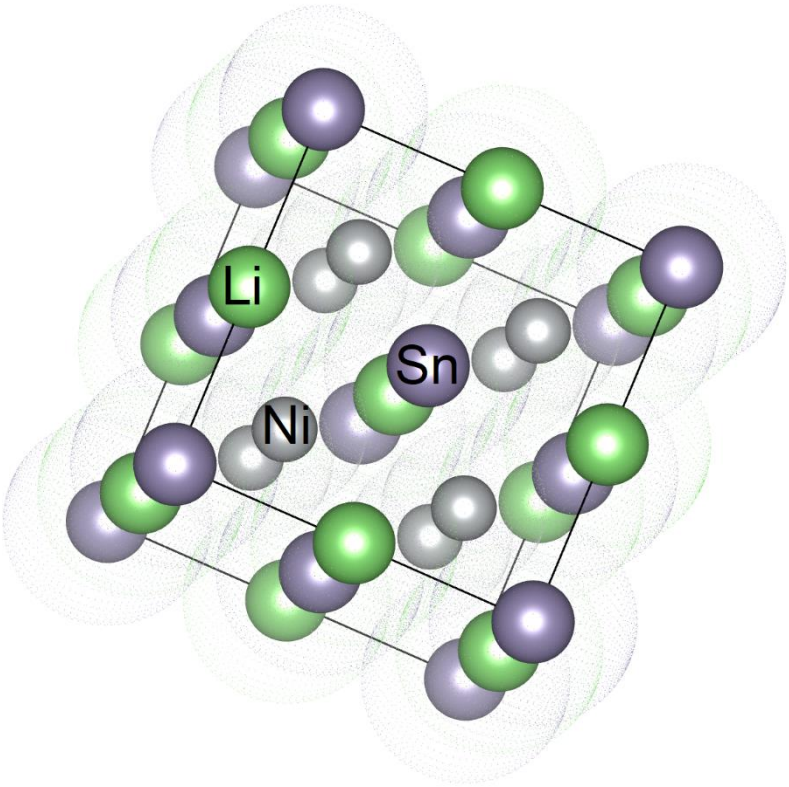


**Figure 1.** Crystal of $LiNi_2Sn$ material drawn in the cubic "F m -3 m" space group.

### 3. Results and Discussion

Observing the interactions between atoms and their results is the most important step in having detailed information about the structure of materials. Electrons in the outer shells of atoms can overlap to form molecular bands with hybrid levels when they get closer and have close energies to the empty levels of neighboring atoms. In order to understand the electronic properties of matter, XAFS calculations were made in our study, and information was collected through Ni metal in the $LiNi_2Sn$ structure. In the K-edge absorption spectrum of the Ni atom given in Figure 2, it has been observed that the absorption starts to increase from the value of 8335 eV. The K-edge absorption spectroscopy of atoms states that the 1s core electrons are excited by photon absorption and reach their final state by relocating to a suitable level above the valence level as a final state. For Ni atoms, the K-edge absorption corresponds to the transition between 1s→4p levels.

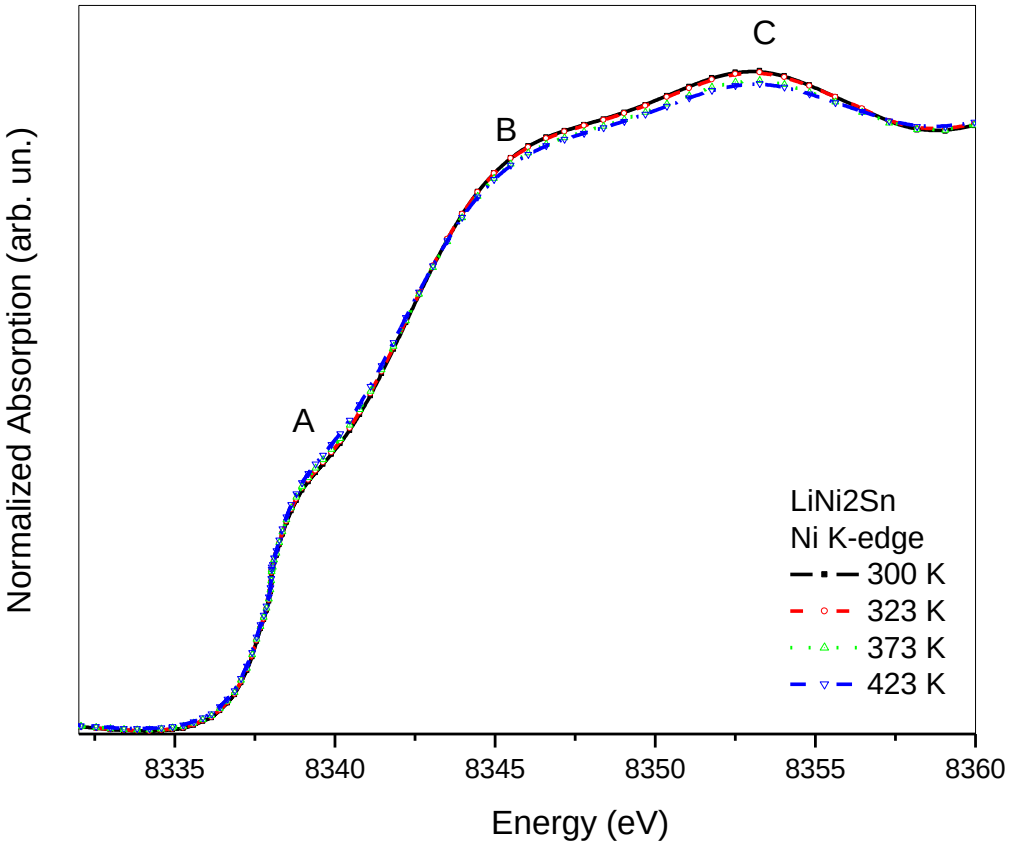


**Figure 2.** Comparison of XAFS spectrum calculations of nickel K-edge under different temperatures.

In Figure 2, a shoulder-like edge structure is clearly visible just above the first rise of the peak. This structure shows the transition of Ni atoms to 3d-5p hybrid levels formed by the coupling of the 3d levels of Ni atoms as a result of the hybridization with the 5p levels of the tin atoms, which are close neighbors, at an energy value of 8338.56 eV (Song, 2007). The 3d levels are just below the 4p level, which is suitable for the 1s electrons to make a transition according to the dipole selection rules, which is assigned as "A". The Ni main absorption edge, which manifests itself with two different peak values, as “B” gave 8345.3 eV, while the main absorption edge at the “C” point peaked at 8353.22 eV. In normal K-edge excitation, although the 1s electrons are not fully charged, they skip the 3d level and switch to the empty and suitable 4p levels, because their transition to the 3d level is forbidden according to the dipole selection rules. In fact, we should see a spectrum of the main absorption edge with no point “B”, but only a level “C” (1s-->4p). The peak “B” is the result of the mixing of nickel 4s levels with low energy 4p levels just below the main absorption that is a result of the ligand field splitting. The 4s level has attracted the lower energy levels of 4p as a result of Coulomb interaction, and the energy difference between these levels reveals the transitions to 4p levels as a separate peak. In addition, Figure 2 gives comparative calculations of the Ni K-edge spectra at different temperature values. It is clearly seen that the compared absorption spectrum structures do not cause any shift or

shape change in the electronic structure with the effect of temperature. In this regard, it can be seen that the $LiNi_2Sn$ material's structure (both crystal and electronic) is unaffected by changes in temperature. However, it is clear that there are small decays in the absorption peak intensities. This suggests that under the influence of temperature, there are less electrons present at the electronic levels, or that weakly bound electrons are released.

The best way to see the response of individual atoms to temperature rise is to walk around the crystal atoms and collect one-on-one data from the atoms. In this sense, the XAFS spectrum provides the researcher with unique data from inside the crystal about the scattering of photoelectrons moving between atoms with their high kinetic energies. In the tail region of the XAFS spectrum, where the data from electronic interactions ceases and fluctuations arise from photoelectron scattering, offers information. Temperature-dependent comparisons of scattering intensity data resulting from scattering from neighboring atoms of photoelectrons released by Ni atoms in $LiNi_2Sn$ material are shown in Figure 3. Absorption spectroscopy is an electron excitation process with a photon energy equal to or higher than the binding energy of the excited electron. An inner-shell excitation process occurs in the XAS data, which can reveal electronic and bonding information, when the photon energy is equal to the binding energy of the core electron. However, when an electron is excited by a photon with energy greater than its binding energy, the excited electron is released from the host atom using energy equal to the binding energy, and the extra energy is given as kinetic energy. The nearby atom repels the photoelectron through its outer shell electrons, preventing it from moving freely and resulting in scattering. Variations in the x-ray data take place when the photoelectrons' entering and outgoing wave functions during the scattering phase coincide. Waves are either constructive (positive peak) or destructive (negative peak) depending on how the wavefunctions interact. The equation $\chi=[\mu(E)-\mu_0(E)]/\delta\mu_0$ is used to extract the data from the EXAFS area. The absorption coefficient is shown here as $\mu$.

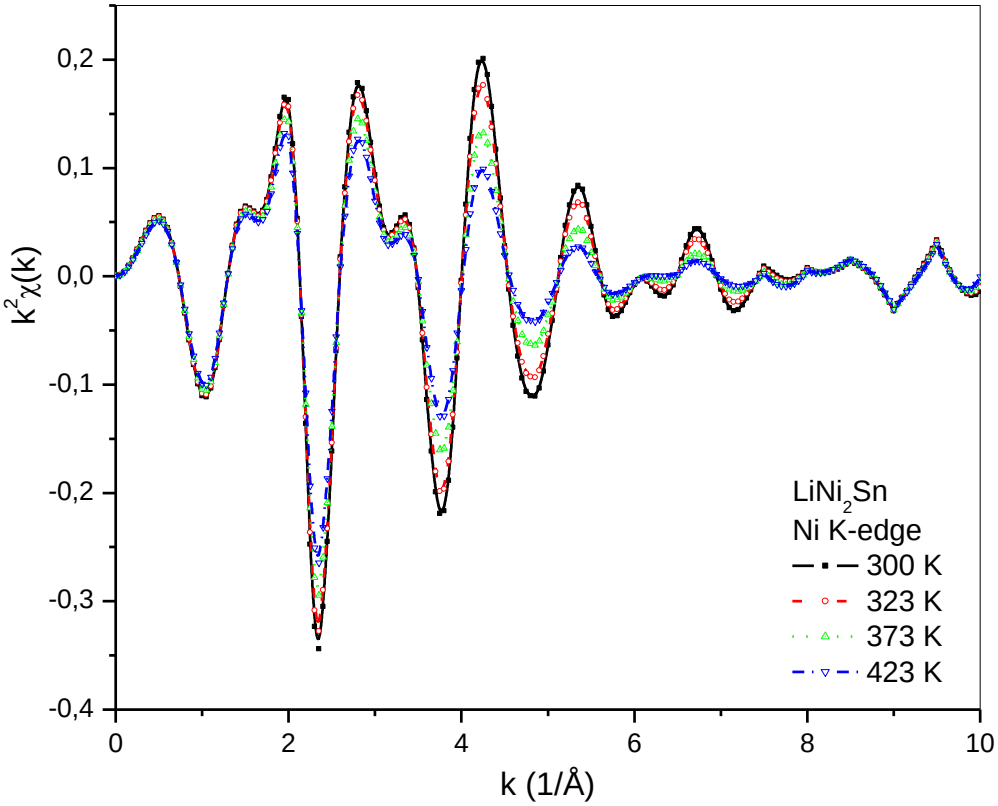


**Figure 3.** Comparison of scattering data from photoelectrons emitted from Ni atoms in $LiNi_2Sn$ material depending on temperature.

The absorption spectra in Figure 2 shows a temperature-dependent loss in intensity, which is more evident in the scattering data. The decline in intensity demonstrates that with each temperature value, less outer shell electrons exert a repulsive force on the moving photoelectrons. The symmetry of the scattering intensity peaks underlines the stable state of the crystal structure against increasing temperature. Furthermore, high decay in the higher k values ($\lambda \sim 1/k$) shows that the light atoms (Li) are farther away from the source Ni atoms while the heavy atoms (Sn) are closer. The emitted photoelectrons move via the potentials between the atoms and can lose a significant amount of energy when they pass through a high heterogeneous potential (Anspok, 2011).

The Fourier transform, which converts data from the energy space to the real-space, is the most crucial step in the processing of photoelectron scattering data. The distances of the atoms to the absorbing atom located in the origin are thus determined in one-dimensional axis in real space from the scattering data. The scattering data in Figure 3 were transformed into real space to create the data in Figure 4.

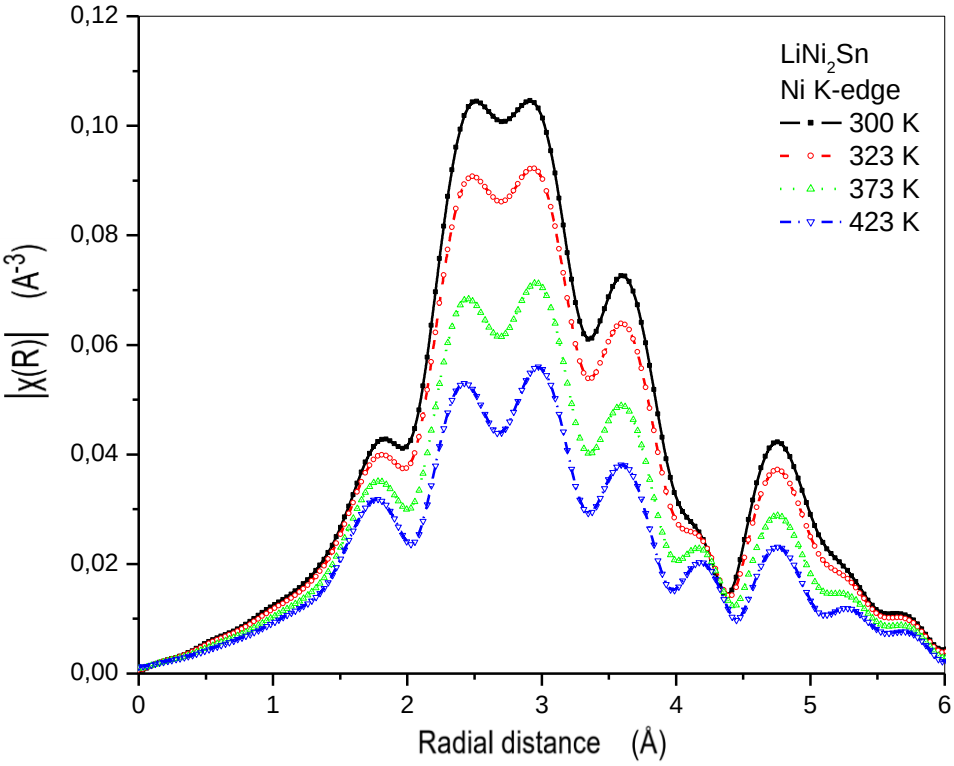


**Figure 4.** In order to compare the scattering data from photoelectrons emitted from nickel atoms in $LiNi_2Sn$ material, Fourier transforms of the data were performed in real space.

The aforementioned figure clearly demonstrates how temperature affects high degredation. Each peak represents an atomic position, and demonstrating the crystal structure temperature stability. Furthermore, it is undeniable that weakly bound, low energy electrons are released by atoms under the influence of temperature, and their outer shell impulse, or intensity, weakens. In the one-dimensional axis system, the nickel atom at position (0,0) has the following neighboring atom distribution. The peak of the four Sn atoms, which are at the same distance as the four Li atoms, 2.58 Å away, are included in the figure as the peak of the first two atomic shells closest to the source atom. The figure includes the peak of the closest first two atomic shells of the four Sn atoms, which are 2.58 Å distant from the the source nickel atom with four Li atoms at the same distance from each other. The fact that Sn atoms and lithium atoms are spaced equally is another significant factor. Although it could initially appear to be unclear, the explanation is really quite straightforward. The distance between the tin and lithium atoms in the lattice arrangement is the same, but their azimuth angles are different. Therefore, the signals overlapped, resulting in a broad gaussian plot. The same is true for other peak structures. The six nickel atoms at a distance of 2.99 Å are responsible for the second intense peak, which is situated directly behind the shell of the closest neighbor atoms. Ni atom shells are followed by another shell formed by nickel atoms, and eight nickel atoms are located at a distance of 4.22 Å.

## 4. Conclusions

In this study, electronic and crystal structure investigations were used to examine the thermoelectric property of cubic $LiNi_2Sn$ material that had been formed into a Heusler type structure at temperatures just above room temperature. According to studies, the outer shell electrons become free with a rise in temperature and give free electrons to the environment, but the $LiNi_2Sn$ structure was unaffected by this process and had a stable structure. This makes it abundantly evident that $LiNi_2Sn$ materials can be assessed in terms of their thermoelectric capabilities at temperatures slightly above room temperature. The results of the study, which were both precise and easy to grasp, have been demonstrated that it is possible to investigate thermoelectric properties using the XAFS approach as a significant method.

## Conflict of Interest

There is no conflict of authors in this work.

## 5. References


Ankudinov AL., Ravel B., Rehr JJ., Conradson SD. Relativistic calculations of spin-dependent x-ray-absorption spectra. Phys. Rev. B. 1997; 56: R1712-R1715.

Anspoks A., Kuzmin A. Interpretation of the Ni K-edge EXAFS in nanocrystalline nickel oxide using molecular dynamics simulations. Journal of Non-Crystalline Solids 2011; 357(14): 2604-2610.

Eerenstein W., Mathur ND., Scott JF. Multiferroic and magnetoelectric materials. Nature 2006; 442: 759-165.

Gunaydin S., Ozkendir OM. Synchrotron facilities for advanced scientific oriented research. Advanced Journal of Science and Engineering 2020; 1(1): 3-6.

Mewis A., Schuster HU. Die struktur der phasen LiCo2Ge und LiNi2Sn, zeitschrift für naturforschung-teil b anorganische chemie. Organische Chemie 1977; 2: 1947-1952.

Momma K., Izumi F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. J. Appl. Crystallography 2011; 44: 1272-1276.

Ozkendir OM. Structural and magnetic study of $Cu_xFeCr_{1-x}O_2$ Oxides under high external magnetic fields. Journal of Electronic Materials 2013; 42(6): 1055-1062.

Ozkendir OM. Electronic and crystal structure study of erbium doped $TiBO_3$ semiconductors. International Journal of Metallurgy and Metal Physics 2015; 1(1): 1-6.

Ozkendir OM. Crystal and electronic study of neodymium-substituted $CuFeO_2$ oxide. Metallurgical and Materials Transactions A 2016; 47(6): 2906-2913.

Ozkendir OM., Yuzer A. Influence of Sm-substitution on the crystal and electronic structure of the FeBO3 oxide. Journal of Optoelectronics and Advanced Materials 2018; 20(3-4): 201-207.

Ozkendir OM. Boron activity in metal containing materials, advanced journal of chemistry. Section B: Natural Products and Medical Chemistry 2020; 2(2): 48-54.

Ozkendir OM., Miyazaki H., Gunaydin S. Traces of thermoelectric properties on XAFS spectra. J. Electron. Mater. 2022; 51: 1740–1751.

Ravel B., Newville M. Athena, Artemis, Hephaestus: data analysis for X-ray absorption spectroscopy using IFEFFIT. Journal of Synchrotron Radiation 2005; 12(4): 537-541.

Song J., Wei Z., Pan Z., Xie Z., Wei S. Effect of phosphorus content on local structures of NiP amorphous alloys. AIP Conf. Proc. 2007; 882: 453–456.