

High Temperature Thermoelectric Properties of W18O49-based Materials

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**High Temperature Thermoelectric Properties of
 $W_{18}O_{49}$ -based Materials**

Kyushu University

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Abstract

This thesis is devoted to the investigations for various properties of $W_{18}O_{49}$ -based materials for high-temperature thermoelectric applications. The study began with the synthesis strategies for acquiring monophasic ceramic $W_{18}O_{49}$, following by attempts on improving thermoelectric properties via oxygen vacancies manipulating. Next, the anisotropic nature of the structures and microstructure morphologies were investigated for the effects on thermoelectric performance. Finally, attempts on carrier concentration control by substitution W^{6+} with lower valance cations were reported with significant improvement in thermoelectric efficiencies.

The Tungsten oxides WO_x ($2 \leq x \leq 3$) are a series of homologous structures, isolating any single structure is difficult via conventional solid state reaction method. Many attempts were made from solid-state reaction in vacuum, to hot-pressing sintering and reactive spark plasma sintering. The $W_{18}O_{49}$ ceramic could be synthesize as a single phase through reactive spark plasma sintering, or pre-reacted in vacuum following by densification via SPS. The former method yields the sample with anisotropic structures and thermoelectric properties, while the later is suitable for doping strategy through thermal diffusion mechanism.

Single phase $W_{18}O_{49}$ sintered polycrystalline samples were successfully synthesized via one-step rapid reactive spark plasma sintering directly from commercially purchased WO_3 and WO_2 powders. Thermoelectric properties of the samples sintered at 15 and 30 MPa showed insignificant anisotropy, while a strong anisotropy was observed for the sample sintered at 50 MPa. The in-situ reaction under a high applied pressure allowed a

preferential grain growth along the direction perpendicular to the pressure axis. The high anisotropy of the sample sintered at 50 MPa yielded the lowest thermal conductivity of $4 \text{ Wm}^{-1}\text{K}^{-1}$, resulting in a ZT value of 0.08 at 1073 K. This study offers the rapid and cost-effective preparation method for $\text{W}_{18}\text{O}_{49}$ materials, which can also be applied for other tungsten suboxide phases, with partially controlled anisotropic properties by the influence of applied pressure for thermoelectric performance enhancement.

The most effective strategy to enhance the thermoelectric properties of $\text{W}_{18}\text{O}_{49}$ -based materials is carrier concentration through doping. High-temperature thermoelectric properties of tungsten-based Magnéli phase oxide $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ ($0 \leq x \leq 0.25$) prepared by solid state reaction followed by densification via spark plasma sintering (SPS) were studied. The Ti substitution increased the Seebeck coefficient, the power factor, and decreased both the electronic and lattice thermal conductivity. The synergistic substitution effect on the electrical and thermal properties and inherently low total thermal conductivity of $1.46 \pm 0.08 \text{ WK}^{-1}\text{m}^{-1}$ originating from the tunnel-like crystal structure of the oxide led to a significantly high ZT of 0.50 ± 0.07 at 1073 K for the sample with $x = 0.2$.

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Chapter 1. Introduction

1.1. Fundamentals of thermoelectricity

1.1.1. Seebeck effect

First discovered by the Estonian German physicist Thomas Johann Seebeck in 1821, the phenomenon is an electric potential built up across a temperature difference in solid materials [1]. It could also be explained as an electromotive force (EMF) generated by a temperature gradient:

$$\mathbf{E}_{\text{emf}} = -S\nabla T \quad (1.1)$$

Where S is the Seebeck coefficient with the unit of VK^{-1} (or also known as the thermopower) and ∇T is the absolute temperature gradient with unit of K. Hence, the Seebeck effect can be applied for electric generation. Since the S value is an internal property of the material, there is no external factor in generating the $\mathbf{E}_{\text{emf}}$. Therefore, the energy conversion by the Seebeck effect is directly from the material itself, without the need for any additional moving parts. The mechanism behind the effect is illustrated by the schematic shown in Fig 1.1. In a thermoelectric (TE) material, when one side become hotter than the other, the charge carrier on that side also become more energetic, so they have the tendency to diffuse to the colder side. The charge carriers accumulate on the colder side, so an internal electrical field is built up due to the unbalance in charge neutrality. Eventually, the equilibrium is reached between the diffusion of charges and a potential difference (voltage) across the material, under the circumstance of remained temperature gradient. When electrons are the main carriers, the accumulated cold side is negatively charged, leaving the hot side lack of electron and hence positively charged. The materials with negative charges as the dominant carriers is considered n -type thermoelectric materials. Thus, there are also p -type thermoelectric materials where the

main carriers is positive charges, and the mechanism is reversed from the n -type counterpart, so is the built up voltage.

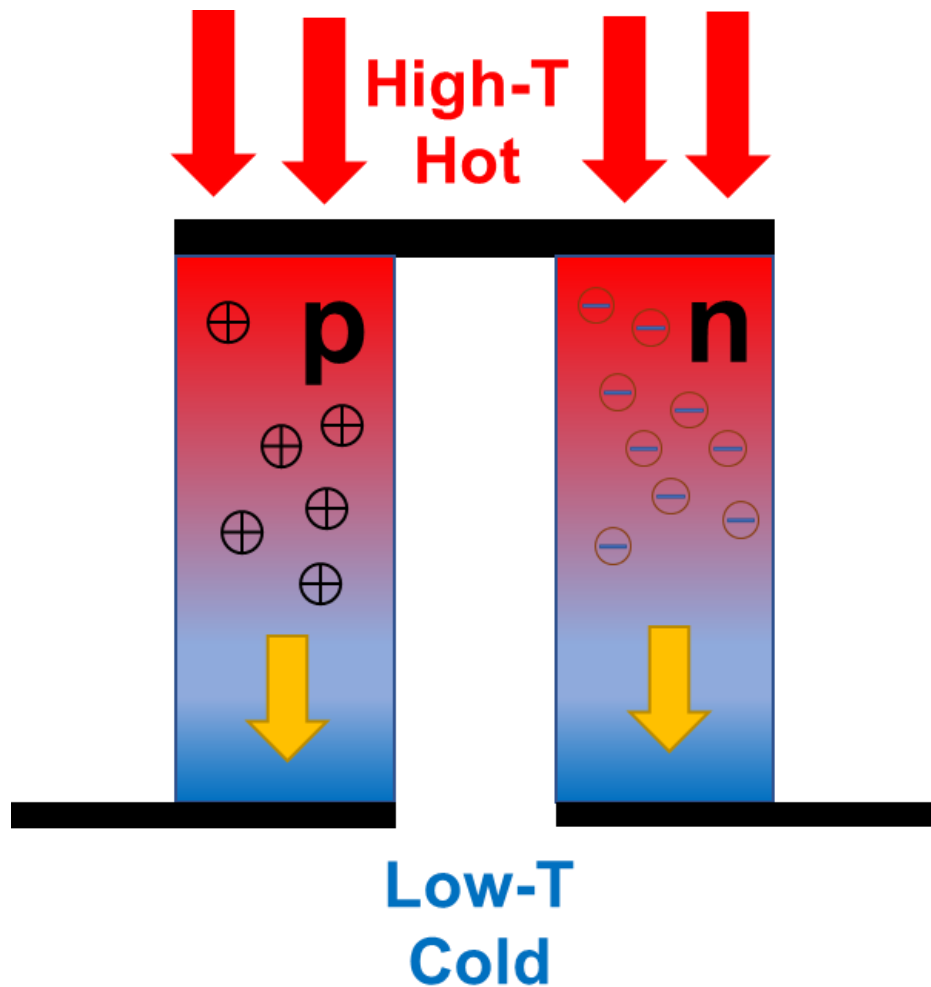


Figure 1.1. Schematics for the mechanism behind the Seebeck Effect.

It is also possible to explain the Seebeck effect via the second law of thermodynamic and the change of entropy [2]. Lord Kelvin stated: “A transformation whose only final result is to transform into work heat extracted from a source which is at the same temperature is impossible”. Because of the temperature gradient, the Seebeck effect converts some of the thermal energy into electromotive force inside the thermoelectric materials, which is not contradicted to the second law. Let’s consider the change in entropy:

$$\Delta S = \frac{Q}{T} \quad (1.2)$$

Where ΔS is the change in entropy, Q is the heat transferred, and T is the temperature at which the changes occurred.

Assuming the heat transfer is only between the heat source and the heat sink, where the TE only play the role of a transfer medium. Consider the change in entropy ΔS_H of the TE material at the heat source (the hotter end):

$$\Delta S_H = \frac{Q_H}{T+\Delta T} < 0, \quad (1.3)$$

Where Q_H is the heat got transferred at the hotter end. ΔS_H is negative for the heat flow direction is from hotter end to the TE materials.

Considering the heat sink (cooler end) and the TE materials. The change in entropy ΔS_L is:

$$\Delta S_L = \frac{Q_L}{T} > 0, \quad (1.4)$$

The Q_L is the heat transfer at the cooler end. Because the heat flows from TE materials into the heat sink, the ΔS_L is positive to indicate the flow direction. Applying the second law of thermodynamics, the total entropy change is $\Delta S = \Delta S_H + \Delta S_L$, and is must be positive for the heat transfer to take place. Hence, $\Delta S_H < \Delta S_L$, which is:

$$\frac{Q_H}{T+\Delta T} < \frac{Q_L}{T}. \quad (1.5)$$

Then with the building up of a potential difference in the TE materials, a portion of the heat flow through got kept back and converted into electrical energy which will not be rejected into the heat sink, hence $Q_H > Q_L$. This is based on the conservation law of energy, and so the ΔT must also be nonzero. Consequently, it can be stated that a temperature difference is an

incentive for the energy conversion in TE material, which agree with the other explanations about Seebeck effect.

So by the law of thermodynamic, the Seebeck coefficient could be viewed as the entropy transferred per charge carrier [3,4], and is described as:

$$S = \frac{1}{e} \frac{\partial S_n}{\partial n} \quad (1.6)$$

Where n is the carrier density and S_n the entropy density of the charge carriers, and e is the electronic charge. So the change in entropy density could also be explained as the total electronic heat capacity over the total number of carrier in the systems. Hence equation 1.6 can be rewritten as:

$$S = \frac{1}{e} \frac{C_{el}}{N} = \frac{1}{eN} \frac{\partial U_{el}}{\partial T} \quad (1.7)$$

Where C_{el} is the total electronic heat capacity of the system, N is the total number of carriers, and U_{el} is the total thermal kinetic energy carried by the charges. It is worth noting that not all charges contribute to the Seebeck coefficient, but those who take part in the conduction process. Consider a non-degenerate semiconductor, charge carriers need to be excited from the valence band (VB) across the bandgap (E_g) to the conduction band (CB), so it can contribute to the Seebeck coefficient. At a certain temperature T , the total number of carriers in the conduction band is:

$$N_c \sim N \frac{E_g}{k_B T} \quad (1.8)$$

Where the k_B is the Boltzmann constant. From equation 1.7 and 1.8:

$$U_{el} \approx \left(N \frac{E_g}{k_B T} \right) k_B T = N E_g \quad (1.9)$$

$$S = \frac{k_B}{e} \left(\frac{E_g}{k_B T} \right) = \frac{1}{e} \frac{E_g}{T} \quad (1.10)$$

We have the k_B/e as the Seebeck coefficient for a classical free electron gas model.

Considering metals or degenerated semiconductors, only the thermally excited electrons contribute to the Seebeck coefficient. Hence the dependency between temperature T and participated number of electron is $N_e = N (T/T_F)$ with T_F being the Fermi temperature [5]. The Fermi temperature can be calculated by Fermi energy through: $T_F = E_F/k_B$. Hence, the Seebeck coefficient for metals or degenerated semiconductors can be expressed as [6]:

$$S = \frac{2}{e} \frac{k_B^2 T}{E_F} = \frac{2k_B}{e} \left(\frac{k_B T}{E_F} \right) \quad (1.11)$$

Employing the parabolic band approximation, the Fermi energy can be calculated as:

$$E_F = \frac{\hbar^2}{2m^*} (3\pi^2 n)^{\frac{2}{3}} \quad (1.12)$$

With $\hbar$ is the Planck constant, m^* is the effective mass, and n is the carrier concentration.

Then the Seebeck coefficient of a degenerate system can be expressed as [7]:

$$S \approx \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}} \quad (1.13)$$

This expression indicates the dependency between S , carrier concentration and effective mass, where S is large when carrier concentration is small or effective mass is large. This also suggests the criteria for acquiring a good TE materials with large S value.

1.1.2. Thermoelectric efficiency and the dimensionless figure of merit ZT

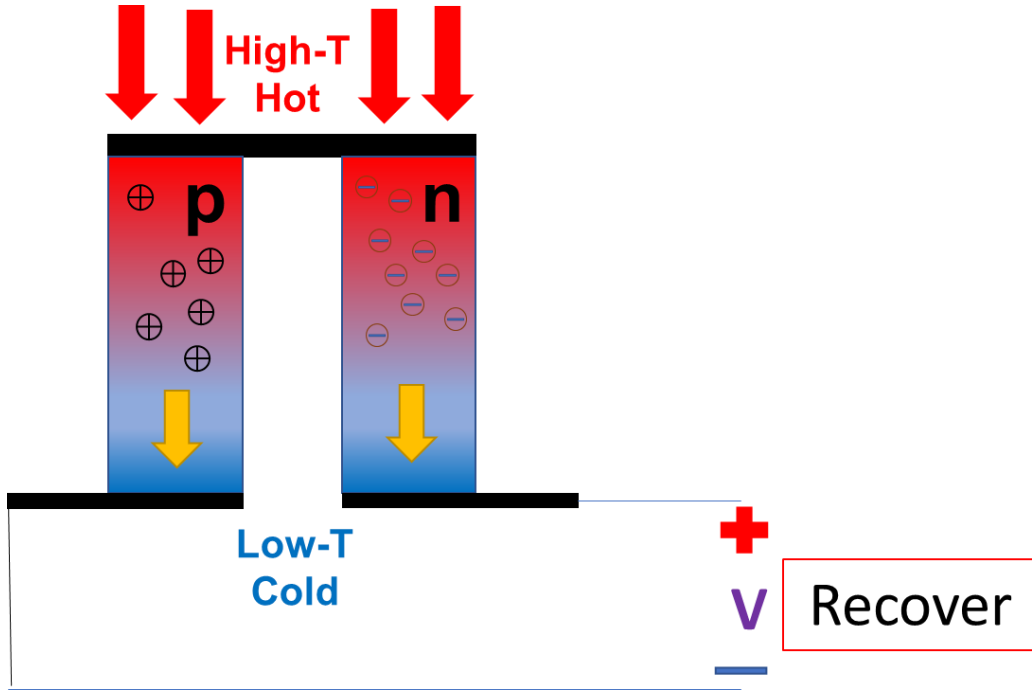


Figure 1.2. Schematic illustration of a thermoelectric uni-couple.

Because the sign of Seebeck coefficient of a TE materials is dependent on the sign of the dominant charge carriers, the EMF generated by p -type and n -type TE materials are of opposite signs. Hence, the EMF can be doubled if we combine a module made of both p -type and n -type like in Figure 1.2. Schematic illustration of a thermoelectric uni-couple. Consequently, an electric generator can be made out of a uni-couple TE material for heat conversion. Consider the uni-couple in Figure 1.2 with R_p , R_n and R_L being the resistance of the p -type, n -type and the load respectively [1]:

$$I = \frac{(S_p - S_n)(T_1 - T_2)}{R_p + R_n + R_L} \quad (1.14)$$

Then the generated power is:

$$W = I^2 R_L = \left[\frac{(S_p - S_n)(T_1 - T_2)}{R_p + R_n + R_L} \right]^2 R_L \quad (1.15)$$

Part of the total power is lost to the medium, which means the TE materials itself. Thus, the total rate of heat flow through to the load is:

$$q_1 = (S_p - S_n)T_1 + (K_p + K_n)(T_1 + T_2) \quad (1.16)$$

With K_p and K_n are the thermal conductance of p -type and n -type materials, respectively. Hence, the efficiency is equal to the ratio of W/q_1 . The maximum useful power is achieved when the load resistance become equal to the generator resistance. Equivalently, assuming no heat loss through the thermal conductance, the maximum efficiency is still 50%. Then the efficiency can be expressed by:

$$\eta = \frac{(T_1 - T_2)(\sqrt{1 + ZT} - 1)}{T_1(\sqrt{1 + ZT} + \frac{T_2}{T_1})} \quad (1.17)$$

With ZT is the dimensionless figure of merit of the material, which is independent of the engineering design. It also indicates that η monotonically increases with ZT , and when ZT becomes very large, η should reach the efficiency of the Carnot cycle. Thus, improving ZT is essential to have a better thermoelectric generator. The efficiency dependent of ZT plot is shown in Figure 1.3., indicating that the higher ZT the higher η . Moreover, η is also higher when the ΔT become large, and the efficiency can be acquired at 1200 K is higher than that of 600 K. Consequently, the generator made of thermoelectric material that can operate at high temperature is desirable for higher energy conversion efficiency.

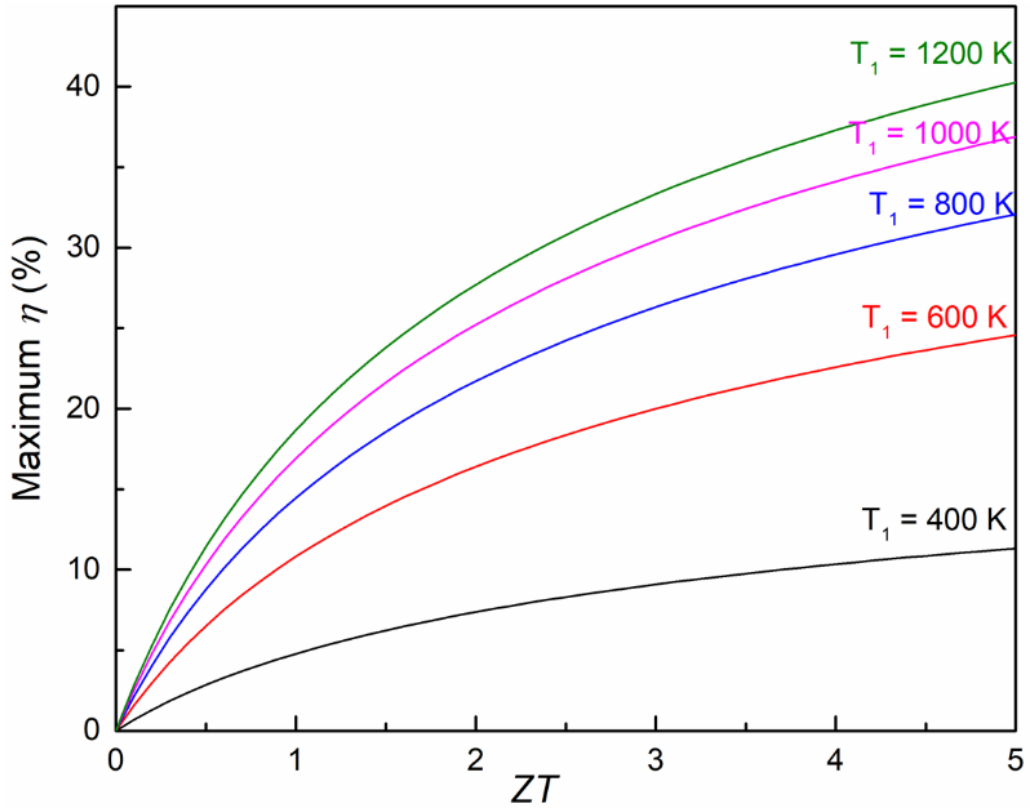


Figure 1.3. Estimation for maximum energy conversion efficiency as a function of ZT .

With T_2 taken to be 300 K

The dimensionless figure of merit ZT is an internal property of materials, and is influenced by the electrical conductivity σ , the Seebeck coefficient S and the total thermal conductivity κ , which is given by the following equation:

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (1.18)$$

With

$$S = -\frac{k}{e} \left[\eta - \left(r + \frac{5}{2} \right) \right] \quad (1.19)$$

$$\sigma = ne\mu \quad (1.20)$$

$$n = N_v \exp(\eta) \quad (1.21)$$

Where η is the reduced Fermi energy, N_v is the effective density of state, k is the Boltzmann constant, r is a constant scattering parameter, e is the electrical charge of electron, μ is the carrier mobility and n is the electron concentration. If the carrier mobility, the density of states, and the conduction mechanism are unchanged regardless of the carrier concentration, the relationship between S and σ can be expressed as $S = -(k/e) \ln \sigma + A$, with A as a constant. It is thereby possible to assume that S is linearly proportional to $\ln \sigma$. Moreover, disregarding the bipolar effect and radiation, the total thermal conductivity is $\kappa = \kappa_{el} + \kappa_{lat}$, where κ_{el} is the electronic thermal conductivity and κ_{lat} is the lattice thermal conductivity. The κ_{lat} is determined by the heat capacity and the phonons mean free path [8], while the κ_{el} is dependent on carrier concentration by the following condition from Wiedemann-Franz law:

$$\kappa_{el} = \sigma LT = ne\mu LT \quad (1.22)$$

With L being the Lorentz number. For degenerate limit materials, the L value is taken from the free electron gas model and approximate $2.45 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$. However, this number was derived disregarding the carrier scattering effects as well as the correlation between electrical conductivity and Seebeck coefficient. In this study, the L value was calculated following the approximation model of Kim et al. [9]

$$L = 1.5 + \exp\left(-\frac{|S|}{116}\right) \quad (1.23)$$

With L being in the unit of $10^{-8} \text{W}\Omega\text{K}^{-2}$ and S in μVK^{-1} . This approximation yields a better estimation for κ_{el} and so the deduced κ_{lat} is also more accurate. Thus, the all the thermoelectric parameters are dependent on the carrier concentration, and can be optimized by the model of dependencies upon the carrier concentration, as plotted in Figure 1.4. Good thermoelectric materials often are heavily doped semiconductors with carrier concentration values between 10^8 and 10^{21}cm^{-3} as predicted in Snyder and Toberer, 2008 [7]. The strategy for improving ZT

would be having a TE material with the optimized carrier concentration. Nevertheless, it is difficult to achieve simultaneous improvements of the three parameters σ , $|S|$ and κ_{el} , because they are all dependent on the carrier concentration in a controversial way. Another straightforward method is reducing κ_{lat} via employing additional phonon scattering mechanisms or structural features for intrinsically low lattice thermal conductivity [10–13], since κ_{lat} independent of the carrier concentration.

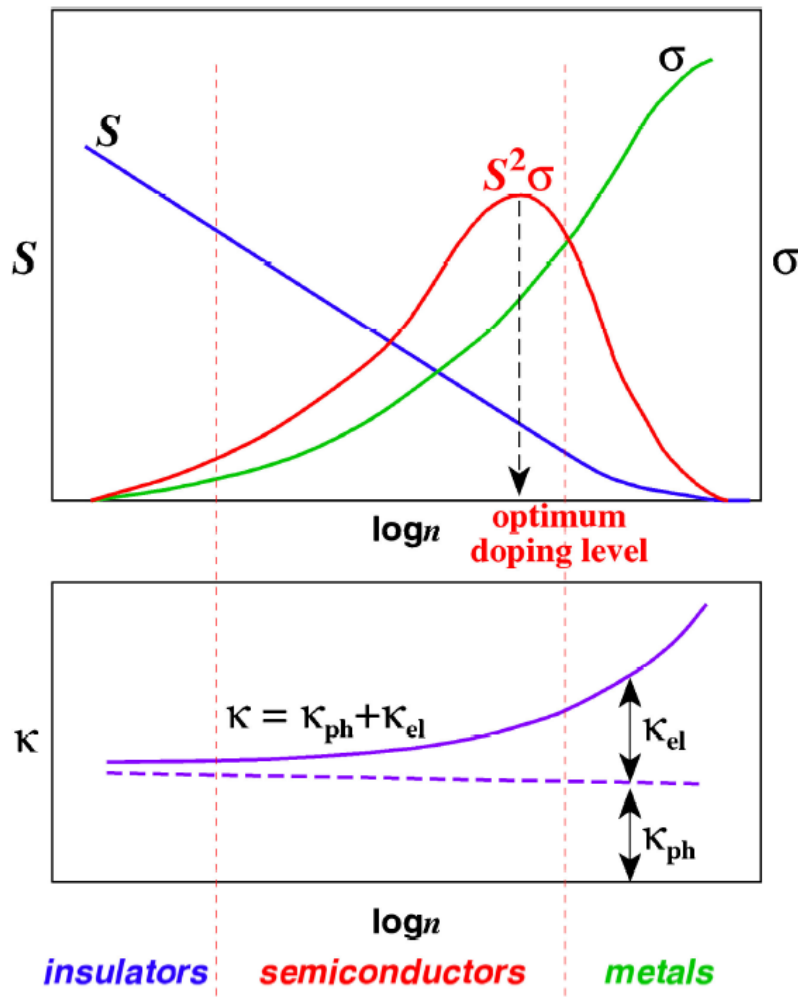


Figure 1.4. The model for dependencies of the S , σ and κ values on the carrier concentration.

The figure was taken from Ohtaki et al, 2011 [14].

1.2. High temperature thermoelectric materials

According to the prediction of energy conversion efficiency above, the higher the operating temperature the higher the efficiency. Hence high ZT materials at high temperature is greatly desired. In this section, a brief introduction on high temperature thermoelectric materials with their corresponding properties and ZT will be given.

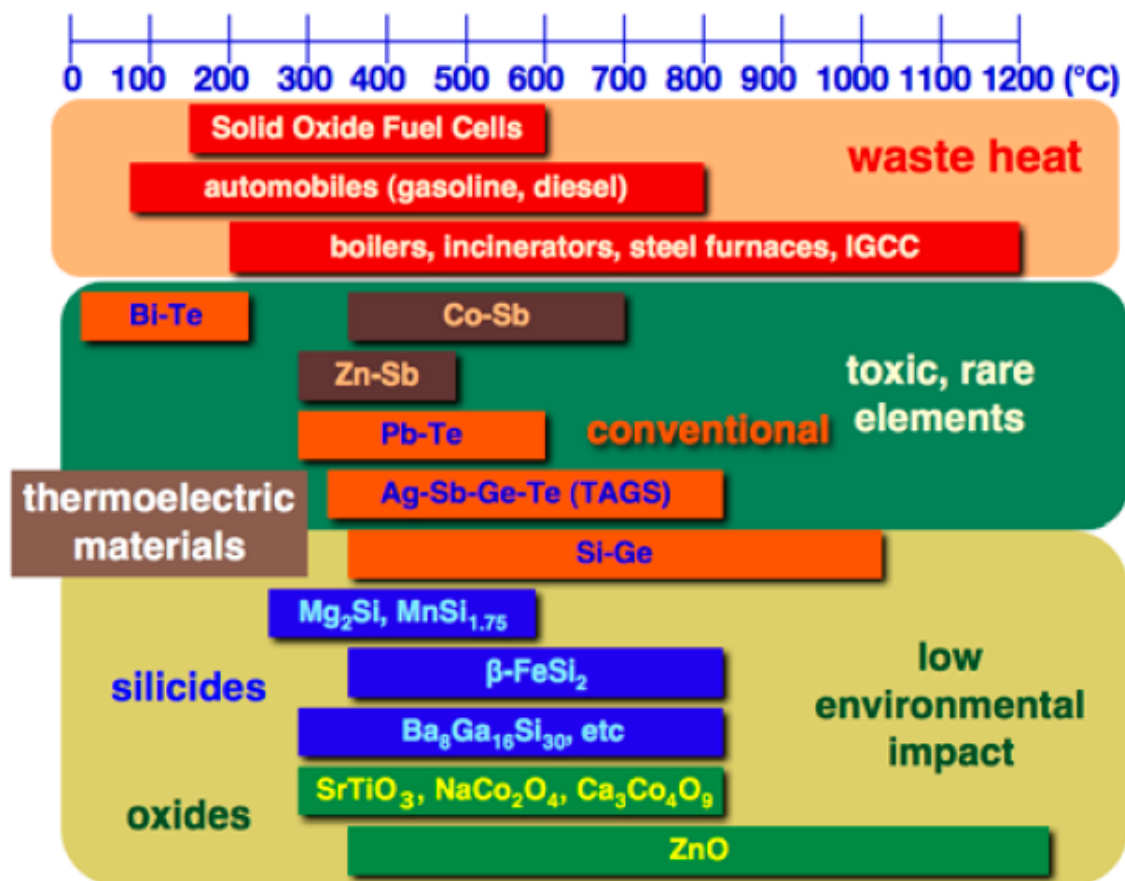


Figure 1.5. Typical waste heat and operating temperature ranges of various thermoelectric materials.

Figure was taken from Ohtaki et al, 2011 [14].

Due to the large variety of chemical properties, resilience and crystal structures, different thermoelectric materials can only operate within a certain range of temperature as shown in Figure 1.5. According to the prediction plot in Figure 1.4, up until the 1990s, conventional

thermoelectric materials have been focused heavily dependent on those criteria, which make the heavies elements such as Bi, Te, and Pb the most suited with their corresponding low κ_{ph} . The exemplars are Bi_2Te_3 for room temperature till 200°C [15], PbTe for $400\text{--}600^\circ\text{C}$ [16,17] and Si-Ge alloy for $400\text{--}1000^\circ\text{C}$ [18,19]. The progressive ZT throughout the years of thermoelectric bulk materials are presented in Figure 1.6. Nevertheless, most of those mentioned materials are not commercialized for industrial purposed due to their poor durability at high temperature in air, expensive for mass production, low on reserves, and often high toxicity.

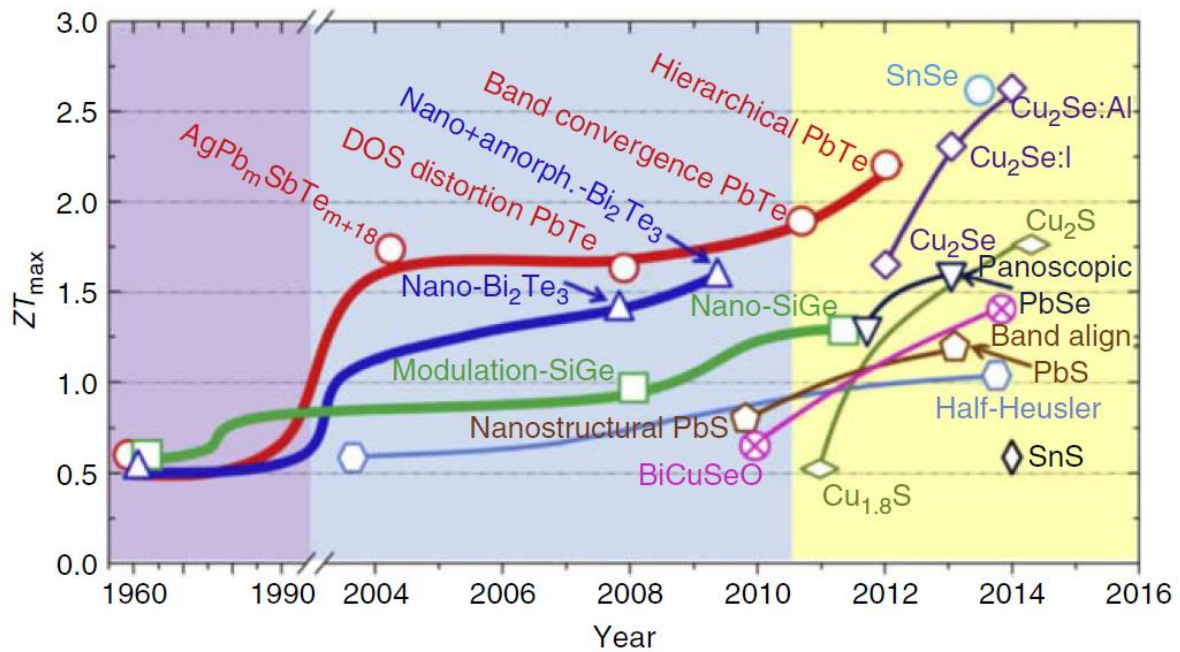


Figure 1.6. The maximum ZT values of the current bulk thermoelectric materials progressing throughout the past decades.

[Source Zhang et al, 2015 \[20\].](#)

To date, many new thermoelectric materials have been developed out of the scope of conventional criteria. Many new promising materials or classes of materials have been being reported and studied such as copper and tin chalcogenides [21], oxide-based materials[22–25],

half-Heusler [26–29], copper sulfides[30–32], intermetallic compounds [33], and last but not least organic polymers [34]. Among those materials, oxides once considered as not suitable for thermoelectric applications, have now been concentrated due to the cost-effective, low-toxicity, highly durable and highly stable in high temperature regime. Initially, most oxides have very high thermal conductivity due to their strongly bound crystal structure. However, the development of nano-structuring has allowed significant reduction in the κ value of oxide, thus practical applications for thermoelectricity of oxide-based materials have become highly promising.

1.2.1. Metal oxides

Metal oxides are compounds made of covalent bonding between metal cations and oxygen anions. The large polarization is also the reason for highly stable and durable of metal oxide, nevertheless, it is also the origin for low charge mobility and high effective mass, leading to overall low ZT value. From the extensive studied of Gaultois et al. [35], most thermoelectric oxide needs to have the electrical resistivity $< 0.1 \text{ } \Omega\text{cm}$. Carrier concentration and bandgap manipulation is often controlled by solid solutions (doping) between oxide and donor or acceptor cations. This method also allowed the forming of p -type and n -type thermoelectric materials based on the respective donors or acceptors for doping. According to equation (1.13) and equation (1.20), both Seebeck coefficient and electrical conductivity of a material are dependent on its carrier concentration. Furthermore, if taken τ as the relaxation time, the electrical conductivity can be rewritten as:

$$\sigma = ne\mu = \frac{ne^2\tau}{m^*} \quad (1.24)$$

Many studies have shown that oxides have narrow bands and equivalently low charge carrier mobility and large effective mass m^* [36–39]. Consequently, to achieve effective electrical resistivity $< 0.1 \text{ } \Omega\text{cm}$, a large carrier concentration in oxides materials is needed due

to the respective large effective masses m^* , short scattering length and low mobility, for example in TiO_2 and cobaltites [40–43]. In addition, the larger carrier concentration is accompanied by larger electrical thermal conductivity, which is destructive to the maximum ZT . Furthermore, the Seebeck coefficient is also inversely proportional to $n^{2/3}$, which in turn, as the carrier concentration becomes larger, the corresponding Seebeck coefficient becomes smaller. Hence, this presents the large obstacle for thermoelectric applications for oxide materials.

Moreover, manipulating carrier concentration through doping is limited by the solubility limits of the dopants, and the forming of thermodynamically favored compounds as elevated temperature. Disorder may also appear due to doping effect on the stoichiometry of metal oxides. It can be taken advantage of to manipulate the vibrational properties of the crystal structure and decrease the thermal transport speed by implementing additional phonon scattering sites. The phonon velocity in the crystal is linked to the bonding energy, the forces constants, the group velocity and atomic masses [8]. So similar to ideal gas model, the average distance in travelling between two scattering events of phonon can be defined the phonon mean free path. The phonon mean free path is affected by scattering occurrences by defects, grain boundaries, or other phonons. Thus, this can be used for manipulating the phonon speed and in turn lowering the κ_{lat} , which eventually improved the ZT value [13,44–46].

1.2.2. Nanostructuring in metal oxides.

The set back of thermoelectric metal oxides is their high κ value, which is even larger due to the coupling of the electronic and thermal transport. One solution for this issue is the nanostructuring of the periodic crystal arrangement, with functionalized structures for enhancing thermoelectric properties in several methodologies. The ideal structure for thermoelectric application would be allowing high mobility of carriers while affecting phonon

movement by scattering mechanism. Normally, the mean free path for electron in metal oxide crystal is about angstrom to several nano-meters, while the mean free path of phonon ranging from nano-meters to few hundreds micro-meters depending on the crystal structure and the microstructure of the materials. So, should the scattering origins have dimensions larger than few nanometers, it would not affect carrier movement but effectively blocking and scattering phonons with comparable mean free path. Employing these occurrences promises a good methodology to improve thermoelectric performance in materials. Correspondingly, Dresselhaus et al, has theoretically predicted and experimentally proven the superior ZT value in 1D quantum wires and 2D quantum well structures over polycrystalline and single crystal monolithic materials [47–52].

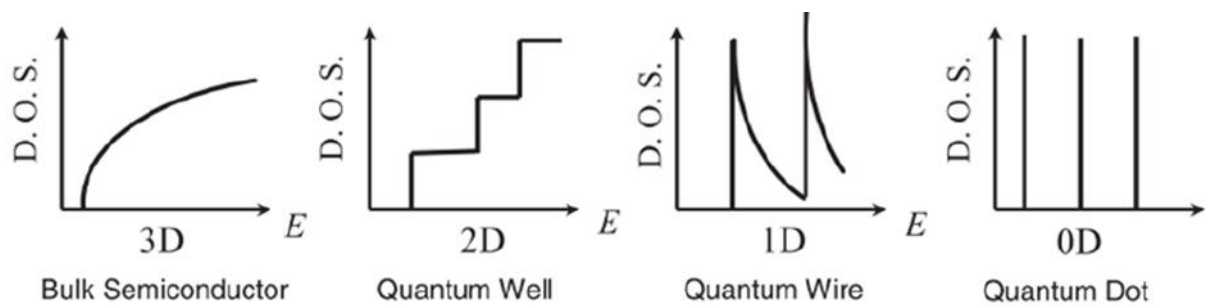


Figure 1.7. Illustration of the electronic density of states (DOS) of low-dimensional semiconductors.

Figure taken from Dresselhaus's work [49].

As shown in **Figure 1.7**, taken from Dresselhaus work in 2007, the density of states (DOS) of materials varied depending on their system dimensions, allowing the manipulation of the S , σ , and κ , in particular, when the length scale falls within the quantum-confinement effects threshold. The effect of nanostructuring on κ value has also been reported intensively over past decades. Nano scaled scattering sites and a great number of interfaces preferentially scattered phonons could lead to a significant reduction in thermal conductivity, as shown in Figure 1.8. for SiGe-base materials, which is much lower than the theoretically calculated possible

minimum κ value of SiGe alloy [53]. Consequently, the highest ZT values has been achieved over 2 through nanostructuring [54] and from materials with intrinsic 2D supper lattice structure [55].

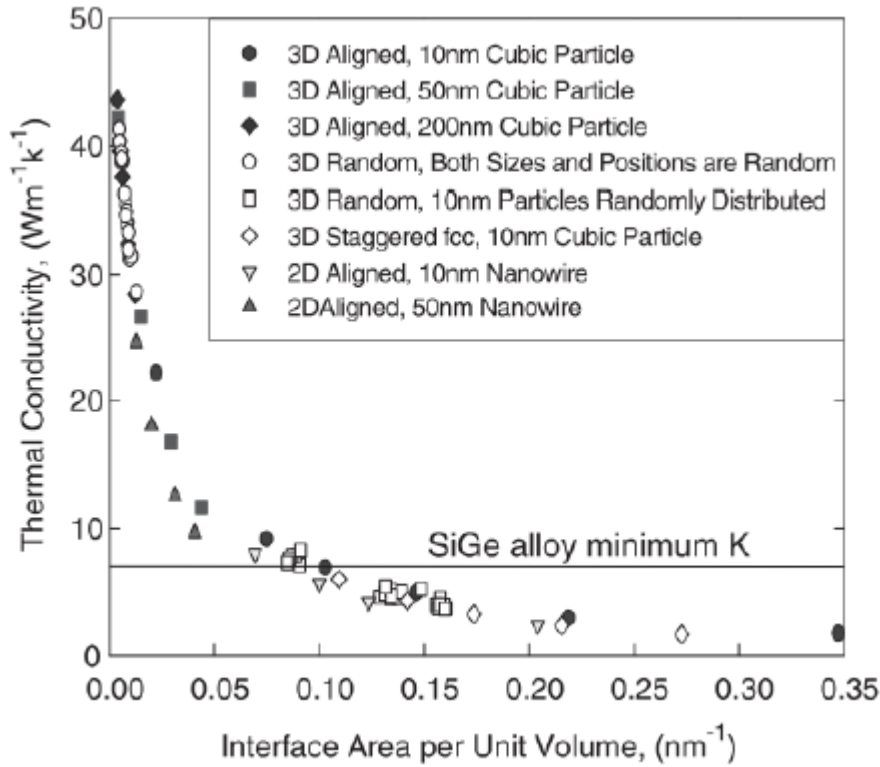


Figure 1.8. Effects of interfacial scattering on the reduction of the thermal conductivity by adding Si nanoparticles and nanowires into SiGe host material.

Figure taken from Dresselhaus's work [49].

1.2.3. *p*-type Layered Cobaltites.

It was first discovered in Na_xCoO_2 systems have analogous structures with layered of cobaltites. This type of structures has allowed high conductivity as found in some cuprates system for superconducting with high- T_c . In addition, it is also expected that the thermal conductivity of such layered structure is significantly low due to phonon scattering at the boundaries (interfaces) between layers. It has been predicted for possible quantum-well structures with remarkably high DOS (about 100 to 1000 times larger than normal values)

leading to extraordinarily high S value [47]. It was reported that the layered cobaltites possess exceptionally high ZT for p -type thermoelectric applications.

The thermoelectric performance of the layered cobaltites are highly dependent on the stoichiometry of the compound. The amount of Na plays very important role in Na_xCoO_2 , forming the disordered phonon glass layers and influencing the phonon scattering and electronic properties [56,57]. The CoO_2 layers and Na layers are alternatively stacking along the c -axis, where the CoO_2 acts as the conduction path, and the Na layers being largely nonstoichiometric and deficient, contributing to the large thermopower for its high carrier concentrations. Another type of layered cobaltites is $\text{Bi}_2\text{A}_2\text{Co}_2\text{O}_9$ where A are alkaline-earth metal. These cobaltites thermoelectric performance are significantly influenced by the amount of Co [58,59]. A strong electron correlation due to spin fluctuation was proposed to explain the large thermopower in these systems. Accordingly, the specific heat measured was $40 - 50 \text{ mJ/mol K}^{-2}$, comparable to the “heavy fermion” systems [60]. There are many debates under the electronic properties of cobaltites, and the Heikes formula has closely depict its values with reasonable approximation [61]. The formula describes the entropy per charge carrier in high temperature limit and is applicable for polaron hopping, while the cobaltites show metallic conducting [61]. A better model for the cobaltites was developed by Koshibae, 2000, by modifying the Heikes formula with the degeneracy of ions in polaron conduction taken into account [62]. The highest thermopower and ZT values were found in Na_xCoO_2 -based materials, however the high volatility and hygroscopicity of the compounds limit is real application.

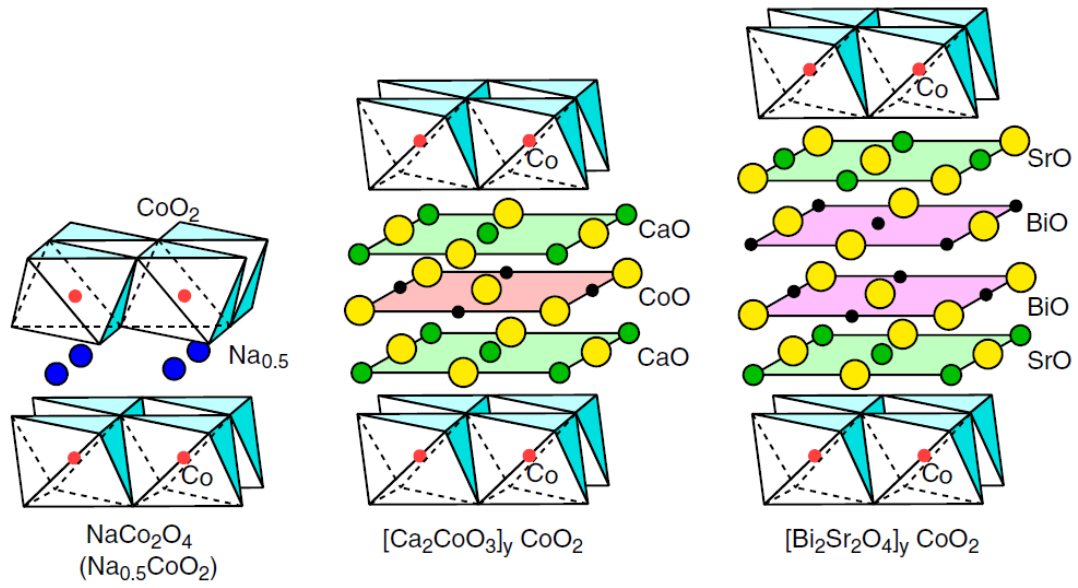


Figure 1.9. Crystal structures of layered cobalt oxides.

[Figure taken from Ohtaki et al, 2011 \[14\].](#)

The later developed Ca₃Co₄O₉ is more stable and have been intensively focused for high temperature applications. In this system, the triple rock salt structure sandwiched by the CoO₂ layers, which is very anisotropic as well as more stable than the disordered Na-based cobaltites. Another worth mentioned cobaltites is the Bi₂Sr₂Co₂O₉ as shown in Figure 1.9. In these oxides, alternate stacking of hexagonal CoO₂ layers and rectangular rock salt layers causes a peculiar lattice misfit, in which only the b-axis length is incommensurate between the adjacent layers. The thermoelectric properties of these oxides measured on whiskers (ribbon-like single crystals) of 50-200 μm width along the in-plane direction revealed the largest ZT = 1.2-2.7 for Ca-349 at 873 K [63] and ZT ≥ 1.1 for BC-222 at 1000 K [64]. Doping to manipulate the thermoelectric properties of cobaltites has also been studied with various successful results. Some recent developed thermopower and ZT values of various cobaltites are listed in the table below.

Table 1.1. Dimensionless figure of merit ZT and power factor $S^2\sigma$ of *p*-type Ca₃Co₄O₉, Na_xCoO₂ and Bi₂Ca₂Co₂O₉ with different dopants [65].

Material	Dopant	T/K	ZT	$S^2\sigma/\mu Wcm^{-1}K^{-2}$
Ca ₃ Co ₄ O ₉	Cr [66]	1000	0.16	3.5
	Sm [67]	1000	0.15	2.4
	Tb [68]	1000	0.73	11.5
	K [69]	1000	0.22	2.85
	Cd [70]	1000	0.35	5.25
	Sr [71]	1000	0.22	3.95
	Na, W codoping [72]	1000	0.21	2.7
	La, Fe cooping [73]	1000	0.32	4.15
	NCO, BCCO nano composites [74]	1100	0.34	6.08
Na _x CoO ₂	Ag, Au [75]	1000	0.4-0.5	13-15
	Ni [76]	1073	N/A	10.8
	Cu [77]	1000	N/A	15.5
	K, Sr, Y, Nd, Sm, Yb [78]	1000	0.36-0.5	6.8-7.3
Bi ₂ Ca ₂ Co ₂ O ₉	Na [79]	900	N/A	2.1
	K [80]	1000	0.305	1.92
	Pb, La [81]	1000	N/A	1.6-2.2

1.2.4. *n*-type metal oxides

Along the discovery of *p*-type cobaltites, *n*-type oxides materials are also being developed to suit the uni-couple for thermoelectric generators. Many promising candidates have been introduced with the most dominant being ZnO-based, SrTiO₃ based and CaMnO₃-based. Each of those materials have their unique advantages and disadvantages, which are going to be briefly introduced in the following parts.

a. Ruddlesden-Popper phases and the SrTiO₃-based materials.

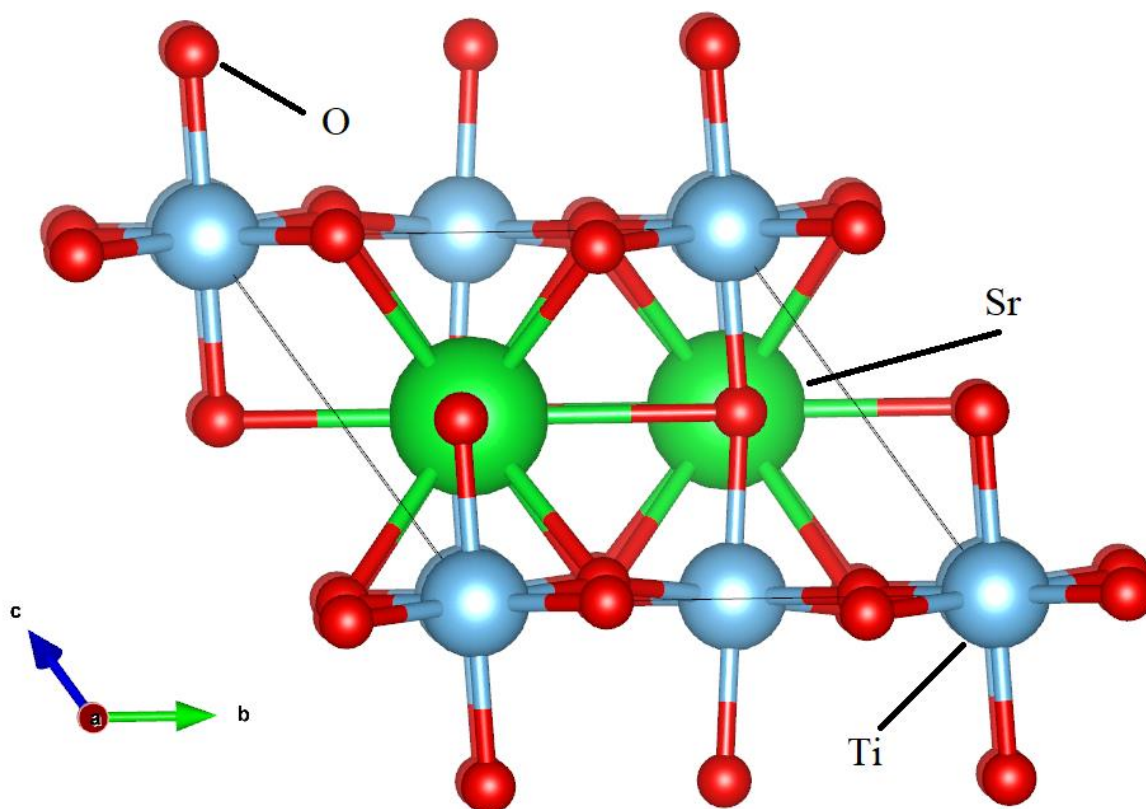


Figure 1.10. The unit cell of Ruddlesden-Popper phase SrTiO₃

The Ruddlesden-Popper (RP) phases are the type of perovskite structure with two-dimensional perovskite-like slabs interleaved with cations as shown in Figure 1.10 for the SrTiO₃. The general formula of RP phases is $A_{n+1}B_nX_{3n+1}$, where A and B are cations, X is an anion (such as oxygen, etc.) and n is the number of the layers of octahedra in the perovskite-like stacks [82]. The parent compound strontium titanate (SrTiO₃) shows a strong structural tolerance with respect to substitutional doping [83]. The oxide is essentially a band insulator with an empty conduction band consisting mainly of Ti3d orbitals and the filled valence band consisting of O2p orbitals. However, heat treatment in reducing atmosphere can form oxygen vacancy and thereby inject electrons into the conduction band, resulting in high electrical conductivity. Since the bottom of the conduction band consists of 3-fold degenerated narrow Ti3d- t_{2g} orbitals [84] the conduction electrons were expected to have relatively large effective

mass, due to its d band nature the effective mass of the carriers is quite large, resulting in a large Seebeck coefficient S . In its pure form, SrTiO_3 is insulating, but it can be tuned to be semiconducting or metallic by substitutional doping with La^{3+} or Nb^{5+} [83]. Intensive electron doping under the reducing conditions resulted in the power factor values of approximately $0.1 \text{ mWm}^{-1}\text{K}^{-2}$ for polycrystalline samples [83], and $0.2\text{-}0.3 \text{ mWm}^{-1}\text{K}^{-2}$ for single crystal [85,86]. The highest ZT for a La^{3+} and Nb^{5+} -doped SrTiO_3 single crystal is 0.1 at room temperature and 0.27 at 1000K [85,86].

The ZT values of SrTiO_3 are limited by the high thermal conductivity, because even in the presence of dopant cations phonon scattering by point defects is low. the thermal conductivity of the oxide is as high as $6\text{-}10 \text{ Wm}^{-1}\text{K}^{-2}$ at room temperature due to its simple crystal structure and the light constituting elements, limiting the figure of-merit of the oxide as $ZT = 0.1\text{-}0.2$. Ohta et al. [83,86] obtained $ZT = 0.27$ on Nb-doped ($3.3 \times 10^{20} \text{ cm}^{-3}$) SrTiO_3 single crystal [87], and $ZT = 0.37$ (1000 K) on 20% Nb-doped ($4.0 \times 10^{21} \text{ cm}^{-3}$) SrTiO_3 epitaxial thin film [88]. Moreover, polycrystalline samples were confirmed to show a good performance of $ZT = 0.35$ at 1000 K [86], comparable to that of high-quality thin films. While grain boundaries in the polycrystalline samples strongly deteriorate the performance at low temperature, the influence is considered to become negligible at high temperature $\geq 700 \text{ K}$. The Nb doping to SrTiO_3 expands the crystal lattice and extends the Ti-Ti interatomic distance, leading to larger effective mass due to increased localization of the carrier electrons. This influence may compensate a decrease in the Seebeck coefficient due to the carrier doping, and thereby relatively large thermopower would be maintained even at high carrier concentrations. Recently, Shinji and Ohtaki have successfully acquired ZT of 0.8 at 800°C by significant suppression of phonon thermal conduction by synergetic effects of introduced pores and metallic nanoparticles in the crystal matrix of Nb-doped SrTiO_3 , leading to the simultaneous

enhancement in the Electrical Conductivity and Reduction in the Lattice Thermal Conductivity [13].

b. ZnO-based oxides

ZnO is considered as a cheap, abundant, and promising high temperature thermoelectric material. ZnO is a wide bandgap semiconductor with a direct bandgap of 3.2-2.5 eV. Pure ZnO shows at room temperature a power factor of $800 \mu\text{Wm}^{-1}\text{K}^{-2}$, but also a high relatively large thermal conductivity ($\kappa = 40 \text{ Wm}^{-1}\text{K}^{-1}$), which reduces at higher temperatures to $5 \text{ Wm}^{-1}\text{K}^{-1}$ (at 1000 K). This has been attributed to increased phonon scattering due a large and anisotropic thermal expansion [23,46]. Although it is possible to reach κ values of $2\text{--}3 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature for nanograined ZnO [89] it still maintains a low electrical conductivity σ . Therefore, ZT does not improve; defects at grain boundaries are major contributors to the low conductivity.

Al doped ZnO has been widely studied for the high ZT values from 0.3 to 0.45, which is the most suitable dopant for ZnO so far [45,46,89,90]. Defect engineering for phonon scattering has been proven effective to improve ZnO-based performance significantly, and as shown by Tsubota and Ohtaki [45], ZnO with Al doping has reduction in κ value as the dopant concentration increases. In addition, the morphology and synthesis condition also greatly affect the performance of ZnO-based materials, as shown by Han et al. works [4], the ZT values of ZnO synthesized from nanoparticles is 1.5 times higher than that synthesized from platelet-shaped particles. The carrier mobility of ZnO at room temperature was reported as $200 \text{ cm}^2/\text{Vs}$ for single crystal [14] and $80 \text{ cm}^2/\text{Vs}$ for Al-doped ceramic sample [45]. Co-doping ZnO with Al and Ga successfully reduced the κ value and enhance ZT values to 0.47 at 1000 K and 0.65 at 1273 K, which is by far one the highest ever reported ZT values for bulk n -type oxides [22].

Table 1.2. Figure of merit ZT and power factor $S^2\sigma$ of various significant candidates for n -type oxide TE materials.

Material	Dopant	T/K	ZT	$S^2\sigma/\mu Wcm^{-1}K^{-2}$
ZnO	Al [45,46,89,91]	1273	0.3-0.45	5-8
	Ni [92]	1073	0.09	5.8
	Al,Ga co-doped [22]	1273	0.65	23
	Ga [93]	973	0.25	12
SrTiO ₃	La, Nb, Sm, Gd, Dy [86]	1073	0.2-0.28	5.5-9
	La [87]	973	0.365	11.6
	Gd [94]	1023	0.37	10.9
	Nb [88]	1023	0.39	11.3
	Nb.Nd co-doped [95]	1073	0.315	8.8
CaMnO ₃	Nb [96]	1073	0.325	1.9
	Dy, Ho, Er, Yb [97]	1000	0.15-0.2	2-3.5
	W [98]	1073	0.16	3.2
	Y, Dy co-doped	800	0.18	3.1
	Pr, Yb co-doped [99]	973	0.24	3.3
In ₂ O ₃	Sn, Al [100]	1200	0.08	7.1
	Ge, Mn, Zn [100]	1200	0.15	3.6

1.2.5. Oxides with adaptive structures.

Lately, a series of corresponding in crystal structures of reduced early titanium oxides in the form of Ti_nO_{2n-1} ($4 \leq n \leq 11$), have shown promising thermoelectric properties as a new economic and environment-friendly high temperature TE n -type materials [101–105]. This so-called Magnéli phases titanium oxides adopt the ReO_3 parent structures, and has been attracted

attention due to the charge density waves, and high electrical conductivity, as was first discovered by Ange Magnéli in the 50s, hence they were named after him [23,106,107]. Due to the oxygen deficiency, the crystal structure is distorted, resulting in the formation of crystallographic shear planes, which has been reported to facilitate the phonon scattering process to lower the lattice thermal conductivity. This provide a new concept in designing a new oxide thermoelectric materials based on manipulating the crystal distortions, phonon scattering effects and carrier concentrations by controlling the oxidation states of the mother phases [108].

Initially the compounds of early transitional metal oxides such as $\text{TiO}_{1.90}$, $\text{MoO}_{2.75}$, and $\text{WO}_{2.90}$ was thought to be nonstoichiometric with a wide homogeneity range [109]. However, observed by A. Magneli via electron imaging and diffraction techniques, the concept of homologous structures with crystallographic shear planes was confirmed and also found in other structures [23]. The reduction in the structures lead to the formation of planes where the octahedra MO_6 are corner shares instead of edge shares as shown in Figure 1.11 for $\text{WO}_{2.90}$ compound. Such planes are called crystallographic shear planes, introduced by Wadsley [110] through mathematic calculation of the periodic planar defects, and can be viewed as intrinsic nanostructure.

Tsuyomoto et al. [111] reported that TiO_x ($x = 1.94 \sim \text{Ti}_8\text{O}_{15}$) exhibits a Seebeck coefficient S of $-518 \mu\text{VK}^{-1}$ and σ of $2 \times 10^3 \text{Sm}^{-1}$ at 350 K. They demonstrated that both S and σ increase as temperature elevates, resulting in a power factor PF of $540 \mu\text{Wm}^{-1} \text{K}^{-2}$ at 343 K. Single crystal rutile TiO_2 reduced to TiO_{2-x} (phase not specified) by heating under hydrogen at elevated 1050 K shows high PFs at low cryogenic temperatures. The thermal conductivity of TiO_{2-x} is low ($0.83 \text{Wm}^{-1} \text{K}^{-1}$) due to enhanced phonon scattering by the defect planes. The Seebeck coefficient of TiO_{2-x} can be as large as $6 \times 10^4 \mu\text{VK}^{-1}$, leading to a ZT of 0.1 at 1073K

[112]. Another study showed that non-stoichiometric TiO_{2-x} (derived from rutile) formed after annealing and reduction with carbon at 1373K has a power factor of $100 \mu\text{Wm}^{-1} \text{K}^{-2}$ up to 550 K [113]. The formation of oxygen vacancies in TiO_2 leads to enhanced electrical conductivity due to an increased carrier concentration. Although TiO_2 is a classical-type wide band semiconductor, conduction is reported for slightly reduced TiO_2 . Calculations using Heikes formula suggests temperature activated polaron conduction, at least in the high temperature regime [114]. In combination with a thermal conductivity of $2\text{--}3\text{Wm}^{-1} \text{K}^{-1}$, the ZT value of 0.13 could be achieved at 800 K. Calculations of the charge carrier mobility as a function of the reduction suggests that crystallographic shear planes are effective scattering centers for phonons without disrupting the electronic transport properties. This underlines the role of the CS planes. TiO_2 nanoparticles doped with Nb on the metal position and N on the oxygen site so far show the best performance of Magneli oxides and related systems [115]. Although these nanoparticles do not belong strictly to the Magneli phases, defects and metal cations with different valences may induce the formation of Wadsley defects.

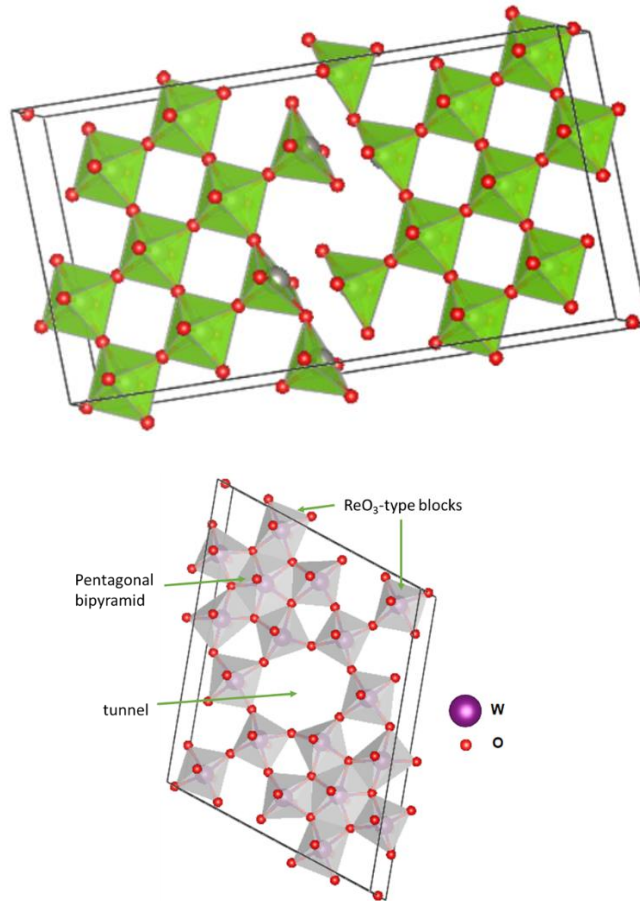


Figure 1.11. Crystal structures of $W_{20}O_{59}$ ($WO_{2.90}$)-CS left, and $W_{18}O_{49}$ -PC right.

Other material with adaptive structures similar to the Magnéli phase can be found in the series of tungsten bronze (TTB) compounds such as $Nb_{8-x}W_{9+x}O_{47}$, which also show very promising thermoelectric performances [116–118]. The Magnéli phases was also found in other transitional metal oxides compound such as Tungsten, Molybdenum, Niobium and Vanadium, however, except for the compound with tungsten, other materials show much less optimistic TE results. Another worth mentioned candidate would be the Penta-columns structure (PC) of Tungsten sub oxide $W_{18}O_{49}$ which possess a very high powerfactor $S^2\sigma$ of $1 \text{ mWm}^{-1}\text{K}^{-1}$ at room temperature, however, the high carrier concentration hinder the TE application for the low S value and hence low overall ZT .

1.3. Tungsten sub-oxide phases WO_{3-x}

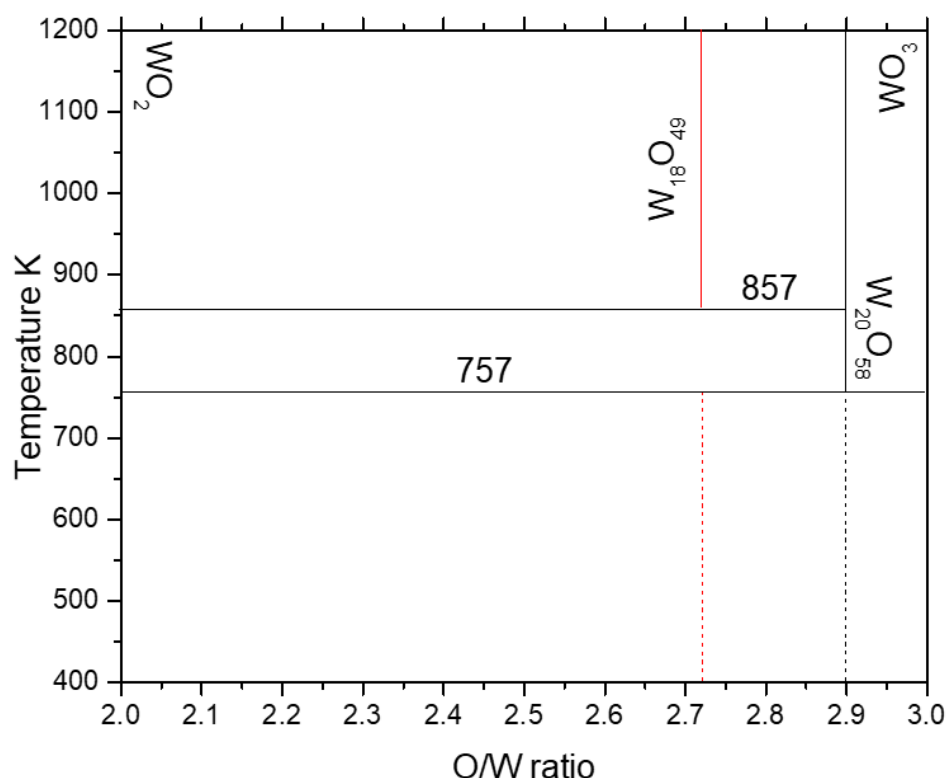


Figure 1.12. **Binary phase diagram of Tungsten and oxygen.**

As shown in Figure 1.12, the binary phase diagram of tungsten and oxygen, between WO_3 and WO_2 there are a series of homologous systems of structure with the most dominant motifs being the $\text{W}_{18}\text{O}_{49}$ structures with pentagonal columns (PC) and the $\text{W}_{20}\text{O}_{58}$ with crystallographic shear (CS) planes. Other phases with different ratio of O/W are the derivatives from the former two main phase, with the increase and decrease number of penta-columns or shear planes density.

1.3.1. Crystallographic shear planes $\text{W}_{20}\text{O}_{58}$

The oxides with CS adaptive structures are quite common in metal oxide, especially in Niobium oxide, Titanium oxide and Tungsten oxide. Moreover, some studies also reported the CS structure in Vanadium oxides and Molybdenum oxides. The crystal structure of the

$W_{20}O_{58}$ is shown in Figure 1.11. Other close family of the $W_{20}O_{58}$ is the $W_{25}O_{73}$ structure, which is almost similar with less frequency of the CS planes.

Emerged since 2013, the Tungsten oxides CS phase has shown promising thermoelectric properties due to the intrinsic good electrical conductivity and low thermal conductivity. Kieslich et al [119] reported that the crystallographic shears in the structure can act as the native phonon scatterings centers, hence, the thermal conductivity is significantly inhibited. This is a desired character of a good thermoelectric material. Many following studies have reported improvements in the phonon scattering resulting in the enhancements of thermo-conversion efficiency. However, the thermodynamic instability of the CS phase has become a major obstacle for further development, not only for Tungsten oxide, but also for other oxide with CS structure such as Titanium oxide. It has almost been decades since the first CS phase structure was considered for thermoelectric application, however, few advancements have been met.

1.3.2. Penta-columns $W_{18}O_{49}$

The Tungsten oxide with penta-columns structure is quite unique for Tungsten, since it has not been found to exist in other transitional metal oxide phases. Moreover, the PC structure is similar to that of superconducting Tungsten bronze compound, with very large electrical conductivity. Nevertheless, $W_{18}O_{49}$ phase has also been extensively studied in the fields of gas sensor, catalysis, and electrodes for lithium ion battery because of its mesoporous nature and the ability of growing nano rod, needle or nanotubes out of it. In addition, the PC phase of Tungsten oxide is stable and unique that it could be the only tungsten oxide with large oxygen vacancies can be isolated as a single crystal phase. Despite many advantages of this PC phase, the early studies on its thermoelectric properties revealed that it is not suitable due to very small Seebeck coefficient with extremely large thermal conductivity.

However, in 2010, Migas et al [120] with their theoretical study on the metallic behavior of the tungsten suboxide phases has revealed the electronic band structure of the phases with the ability to manipulate the carrier density through oxygen atoms variation. It was predicted that the metallic behavior could be switched to semiconducting through adding more oxygen atoms into the structure. Moreover, the PC $W_{18}O_{49}$ was reported to be mesoporous by its nature, which would associate to the low lattice thermal conductivity, a desired property of thermoelectric materials. All of those reason should point out that $W_{18}O_{49}$ -based materials could be a promising candidate for thermoelectric application, however, the obstacles to be overcome are the high carrier density and low Seebeck coefficient.

Therefore, in this study, a series of attempts on enhancement the thermoelectric performance of $W_{18}O_{49}$ -based materials by manipulating the carrier concentration through the substitution a portion of W^{6+} with lower valance cation. Moreover, it was found that the polycrystalline bulk type ceramic of $W_{18}O_{49}$ could have anisotropic electrical properties due to the preferential orientations of the grains, leading to the ability to control thermoelectric performance according to it anisotropy nature. Theoretically, the single crystal of $W_{18}O_{49}$ could be growth as a 1D material in the form of nano rod or nano tube, which could be extremely promising for reducing thermal conductivity while preserving the good electrical properties of the materials.

Chapter 2. Rapid synthesis of $W_{18}O_{49}$ via reactive spark plasma sintering with enhanced anisotropic phonon scattering.

Abstract

We successfully synthesized single phase $W_{18}O_{49}$ sintered polycrystalline samples via one-step rapid reactive spark plasma sintering directly from commercially purchased WO_3 and WO_2 powders. Thermoelectric properties of the samples sintered under 15 and 30 MPa showed insignificant anisotropy, while a strong anisotropy was observed for the sample sintered under 50 MPa. The in-situ reaction under a high applied pressure allowed a preferential grain growth along the direction perpendicular to the pressure axis. The high anisotropy of the sample sintered under 50 MPa yielded the lowest κ value of $4 \text{ Wm}^{-1}\text{K}^{-1}$, resulting in a ZT value of 0.08 at 1073 K. This study offers the rapid and cost-effective preparation method for $W_{18}O_{49}$ materials, which can also be applied for other tungsten suboxide phases, with partially controlled anisotropic properties by the influence of applied pressure for thermoelectric performance enhancement.

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2.1. Introduction

Spark plasma sintering (SPS) has become one of the critical techniques for the past decades to synthesize modern advanced materials [121]. The ability to control high heating rate with a simultaneously applied uniaxial pressure allows SPS to perform rapid densification (less than 1 hour) at lower sintering temperatures (hundreds of degrees lower) compared to conventional hot-pressing [122,123]. Particularly, the swift densification enables the minimized grain growth, which is highly desired for thermoelectric materials for the enhanced grain boundary phonon scattering effects [123,124]. Furthermore, under the influence of uniaxial pressure, grain orientation is likely to occur, which could yield extraordinary result for anisotropic structured materials [89,90].

Tungsten suboxide $W_{18}O_{49}$ has attracted much interests lately, for the mesoporous property, large electrical conductivity and can be isolated as a stable single phase due to its special crystal structure [125–129]. The crystal structure of $W_{18}O_{49}$ (Figure 2.1 (a)) comprises of loosely connected [WO6] octahedra with pseudo hexagonal void tunnels running along the crystallographic *b*-axis (Figure 2.1(b)) sandwiched by large penta-columns (made of five [WO6] octahedra, each sharing one edge with a bipyramid [WO7]) [106]. The naturally formed orderly empty tunnels could act as phonon scattering centers with similar mechanism to the nano-void embedded materials without its electrical properties being affected [10,14,91]. In addition, the bulky crystal cell, with large number of atoms also contributes to the reduction of the lattice thermal conductivity κ_{lat} due to the low group velocity of optical phonon modes [35,130,131]. Overall, despite its metallic behavior, which is tunable by manipulating the carrier concentration [120], $W_{18}O_{49}$ could be a promising new type of thermoelectric materials. Hence, fast and simple synthesis technique for $W_{18}O_{49}$ synthesis is highly desired.

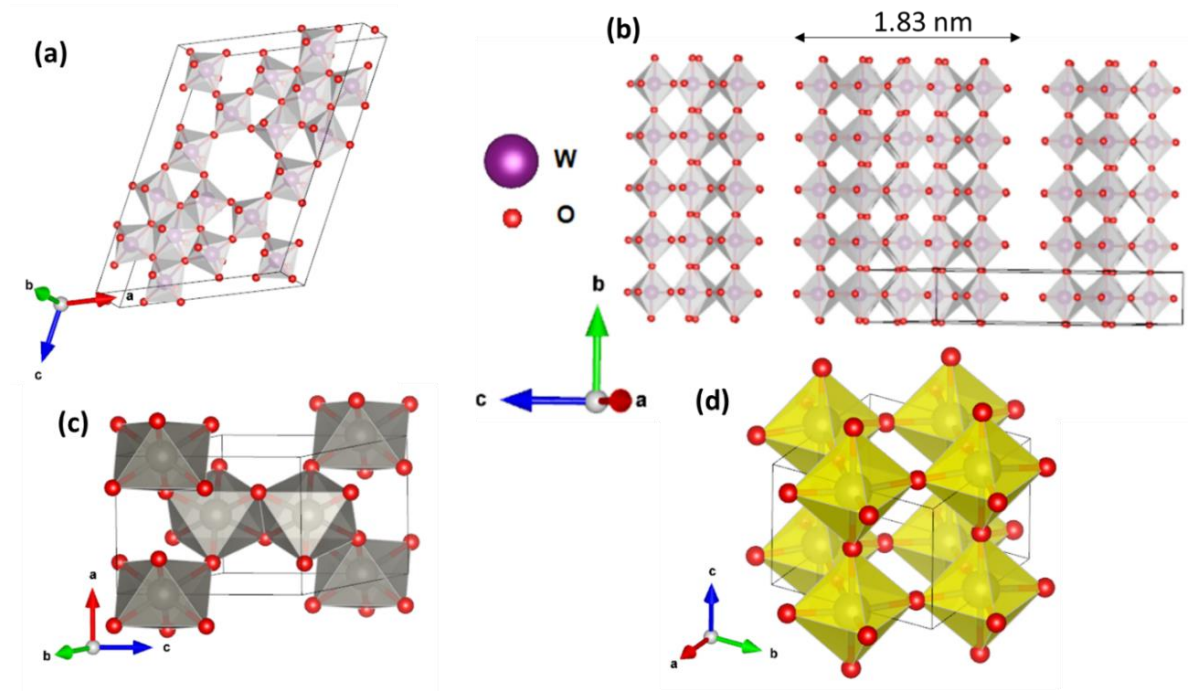


Figure 2.1. Crystal structure of $W_{18}O_{49}$ (a), view along $[010]$ and $[001]$ with intergrowth structure showing void tunnels running along $[010]$ directions (b), of WO_2 (c), of WO_3 (d).

It has been reported that the dc pulses current during SPS is highly suitable for initiating and facilitating the reaction of precursors, eventually yield nanograined synthesized product [132]. This so-called reactive SPS can also synthesize material under much faster reaction time comparing to conventional methods [132–134]. Thus, we propose a study on one-step direct synthesis and simultaneous consolidation of $W_{18}O_{49}$ from commercially acquired precursors via reactive SPS. The precursors were chosen to be WO_3 and WO_2 powders for the similarities in their crystals building blocks. Most of the Tungsten oxide and suboxide WO_{3-x} crystal structures can be described by the different stacking orders of the octahedra $[WO_6]$. As shown in Figure 2.1 (c) and (d), the WO_2 crystal is formed by loosely connecting octahedra with some octahedra sharing edges together, while the WO_3 crystal is made of orderly sharing corners octahedra. Theoretically, this similarity could allow a straightforward in-situ reaction during SPS to form $W_{18}O_{49}$. Moreover, the highly anisotropic nature of $W_{18}O_{49}$ could be preserved

and enhanced during rapid reactive SPS, yielding unexpected anisotropic thermoelectric properties.

2.2. Experimental details

Commercially available materials WO_3 (Kishida Chemical, 99.9%), WO_2 (Wako, 99.9%) were weighed according to the reaction $13\text{WO}_3 + 5\text{WO}_2 = \text{W}_{18}\text{O}_{49}$, and well mixed in an agate mortar. Following the synthesis process in Fig. 2, the mixture was loaded into graphite dies of 10 mm diameter and 60 mm height, lined with carbon paper. The die was placed in the SPS furnace PLASMAN CSP-KIT-02121 (S. S. Alloy), and the furnace chamber was evacuated to the pressure of ≤ 10 Pa. Different pressures ($P = 15, 30$ and 50 MPa) were applied for the study on anisotropic thermoelectric properties. For the reactive SPS, first the sample was heated up to 1423 K at a heating rate of 100 K min^{-1} under respective uniaxial pressure, maintained at 1423 K for 15 mins and the pressure was then released, and cooling rate was controlled at 20 K min^{-1} to room temperature. The pellet was removed from the graphite die, and its surface was polished with SiC abrasive papers to remove all possible carbon contamination. Sample sintered under 15 MPa applied pressure showed 96% relative density, while the others showed the relative density approximately 100% of the theoretical density of $\text{W}_{18}\text{O}_{49}$.

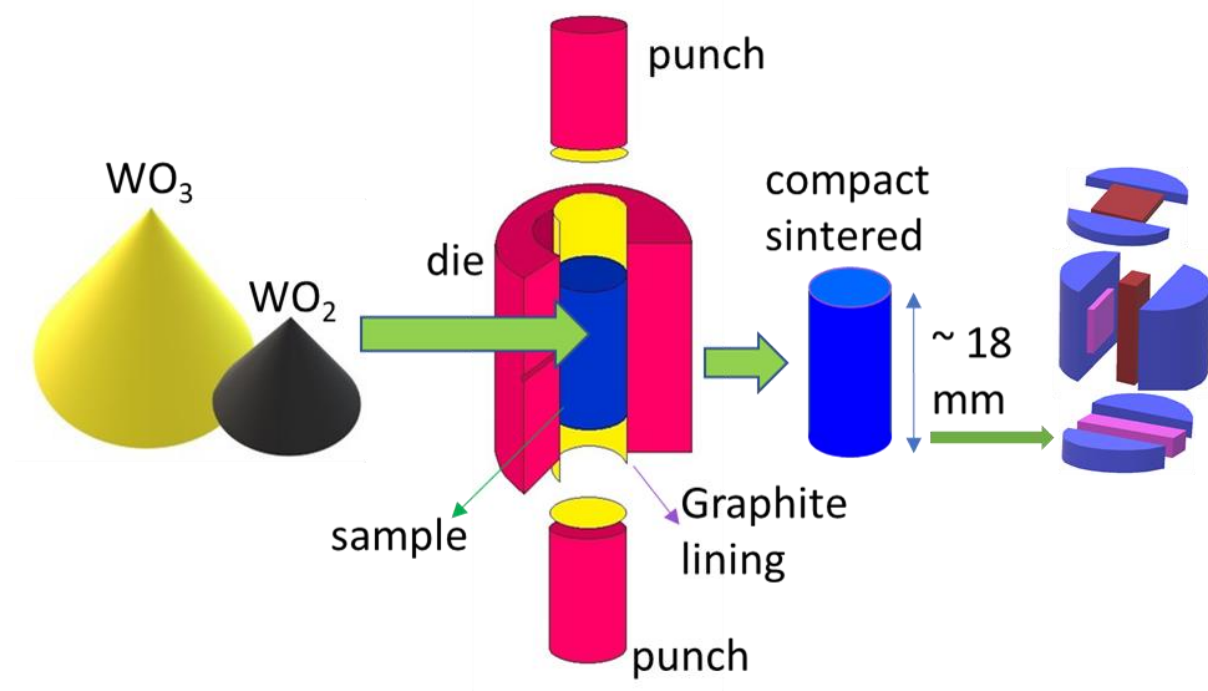


Figure 2.2. Schematic of synthesis procedure and preparation process for TE characterizations of $W_{18}O_{49}$ by direct reactive SPS from WO_3 and WO_2 as starting materials.

For characterization, bar-shaped and disc shaped samples were cut along the direction parallel $\parallel$ and perpendicular $\perp$ to the applied pressure axis P (Figure 2.2). X-ray diffraction (XRD) data were collected using a Rigaku MiniFlex 600 diffractometer with $Cu\ K\alpha$ radiation, within the range of $6^\circ \leq 2\theta \leq 50^\circ$, $\Delta 2\theta = 0.01^\circ$. Disc shaped samples were used for XRD, with observed plane parallel $\parallel$ and perpendicular $\perp$ to P , respectively. Surface morphologies were studied on a JEOL JCM-600Plus NeoScope scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS). The electrical resistivity ρ and Seebeck coefficient S were measured under Ar atmosphere simultaneously by dc four-probe method and temperature differential method, respectively, on a RZ2001i apparatus of Ozawa Science. The thermal diffusivity α and specific heat C_p at 300 – 1073 K were measured simultaneously on a Kyoto electronics LFA-502 by laser-flash method under vacuum. The absolute values of C_p were derived from a comparative method between the measured values and standard C_p values

of reference molybdenum sample. The C_p values of all samples, measured from 300K to 1073 K was $0.31 - 0.40 \text{ J g}^{-1} \text{ K}^{-1}$, being equivalent to $1269 - 1639 \text{ J mol}^{-1} \text{ K}^{-1}$, reasonably agreed with the specific heat of $1668 \text{ J mol}^{-1} \text{ K}^{-1}$ calculated by Dulong-Petit law. The thermal conductivity was calculated using the relation $\kappa = \alpha C_p d_s$, where d_s is the sample density. The measurements were performed for bar and disc samples according to their orientations with respect to the applied pressure axis. The reproducibility of measured data was confirmed by cycling measurement of both heating and cooling from 300 – 1073 K.

2.3. Results and discussion

XRD patterns for the synthesized $\text{W}_{18}\text{O}_{49}$ samples are shown in Figure 2.3 (a). The data was acquired from planes // and $\perp$ to P . All the samples showed peak positions well agreed with the simulated pattern of $\text{W}_{18}\text{O}_{49}$ crystal. It suggested that single phase $\text{W}_{18}\text{O}_{49}$ can be straightforwardly isolated by reaction of WO_3 and WO_2 during the reactive SPS. This is remarkable, since other reports regarding the synthesis of monolith ceramic $\text{W}_{18}\text{O}_{49}$ would involve multiple complicated steps [129,135,136].

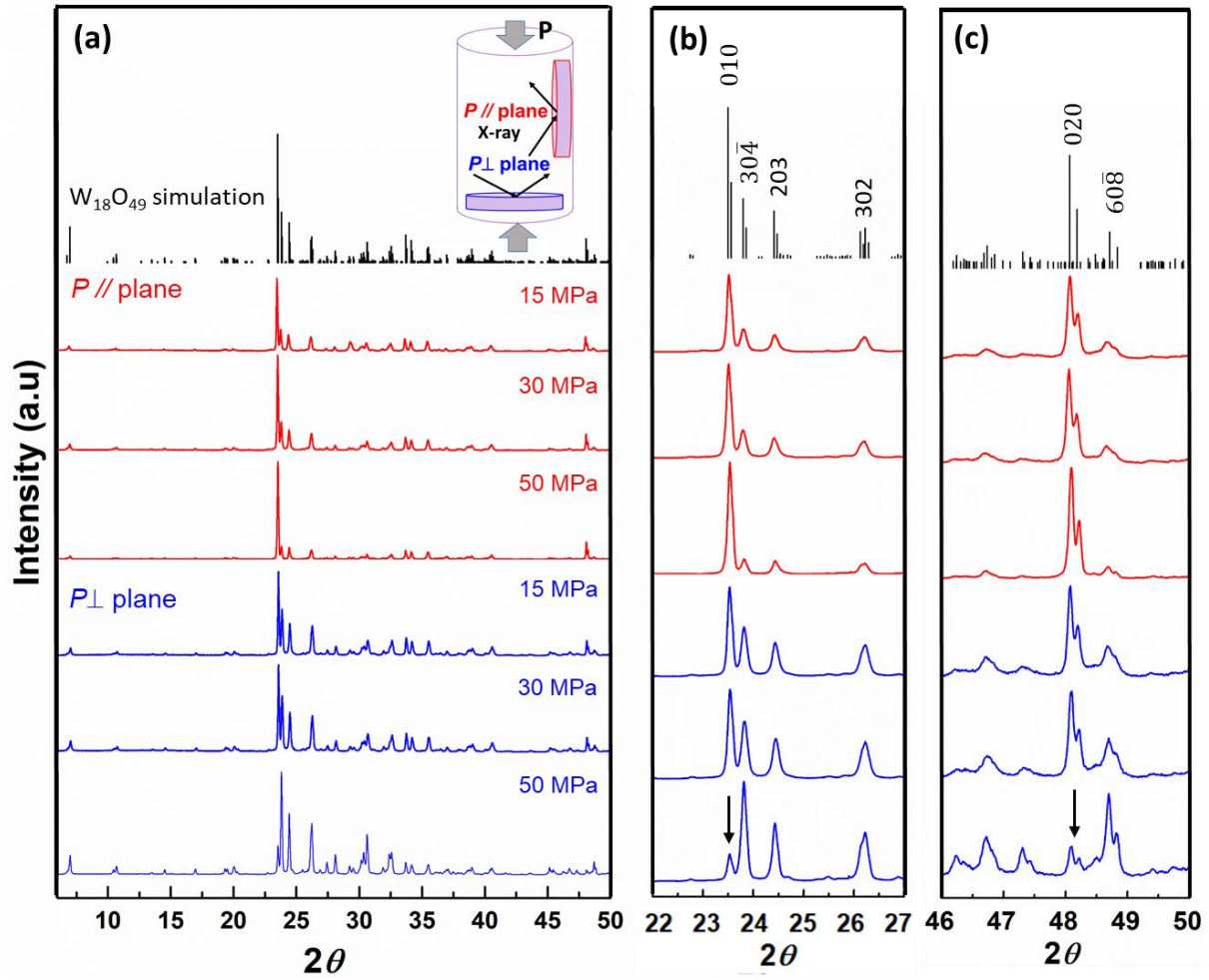


Figure 2.3. X-ray diffraction patterns for planes of SPS sintered $W_{18}O_{49}$ samples with different applied pressure 15, 30 and 50 MPa. The planes are parallel ($//$) and perpendicular ($\perp$) to the applied pressure axis during SPS (a), expanded 2θ scale from 22° to 27° (b), and from 46° to 50° (c). The arrows denote the suppressed of [010] and [020] peaks due to crystal axis orientation.

In order to elucidate the anisotropic orientations, XRD patterns are shown in expanded 2θ sections, from 22° to 27° (Figure 2.3(b)), and 46° to 50° (Figure 2.3 (c)). The arrows in the figures annotated the peaks with repressed intensity, corresponding to the less favored oriented directions of the crystal. Samples sintered under applied pressure of 15 MPa and 30 MPa did not show noteworthy anisotropy. However, the sample sintered under 50MPa showed very

strong anisotropic patterns, similar to those reported patterns of $W_{18}O_{49}$ 1D structures [125,137]. Completely dominance of peak (010) was observed for plane // to P , and highly suppressed for both (010) and (020) peaks was detected on plane $\perp$ to P . This implies that during the reaction under high pressure of 50 MPa, the crystal grain b axis favored the grain growth along the direction $\perp$ to P . This was distinct from conventional method, where SPS was used for densification purpose only, no significant anisotropy was detected. It is possible that the already formed polycrystalline $W_{18}O_{49}$ powder is not easily re-oriented during the densification. Nevertheless, during reactive SPS and under high influence of uniaxial pressure, the growth of newly formed $W_{18}O_{49}$ lattice would follow the minimum formation energy route, thus the perpendicular direction to the applied pressure P .

Table 2.1. Pressures dependence of the relative peak intensity ratios for (010)/(30 $\bar{4}$) and (30 $\bar{4}$)/(203)

SPS pressure	(010)/(30 $\bar{4}$) ratio		(30 $\bar{4}$)/(203) ratio	
	P//plane	P $\perp$ plane	P//plane	P $\perp$ plane
15 MPa	3.31	1.72	1.24	1.19
30 MPa	3.47	1.54	1.26	1.21
50 MPa	8.69	0.28	1.28	1.26

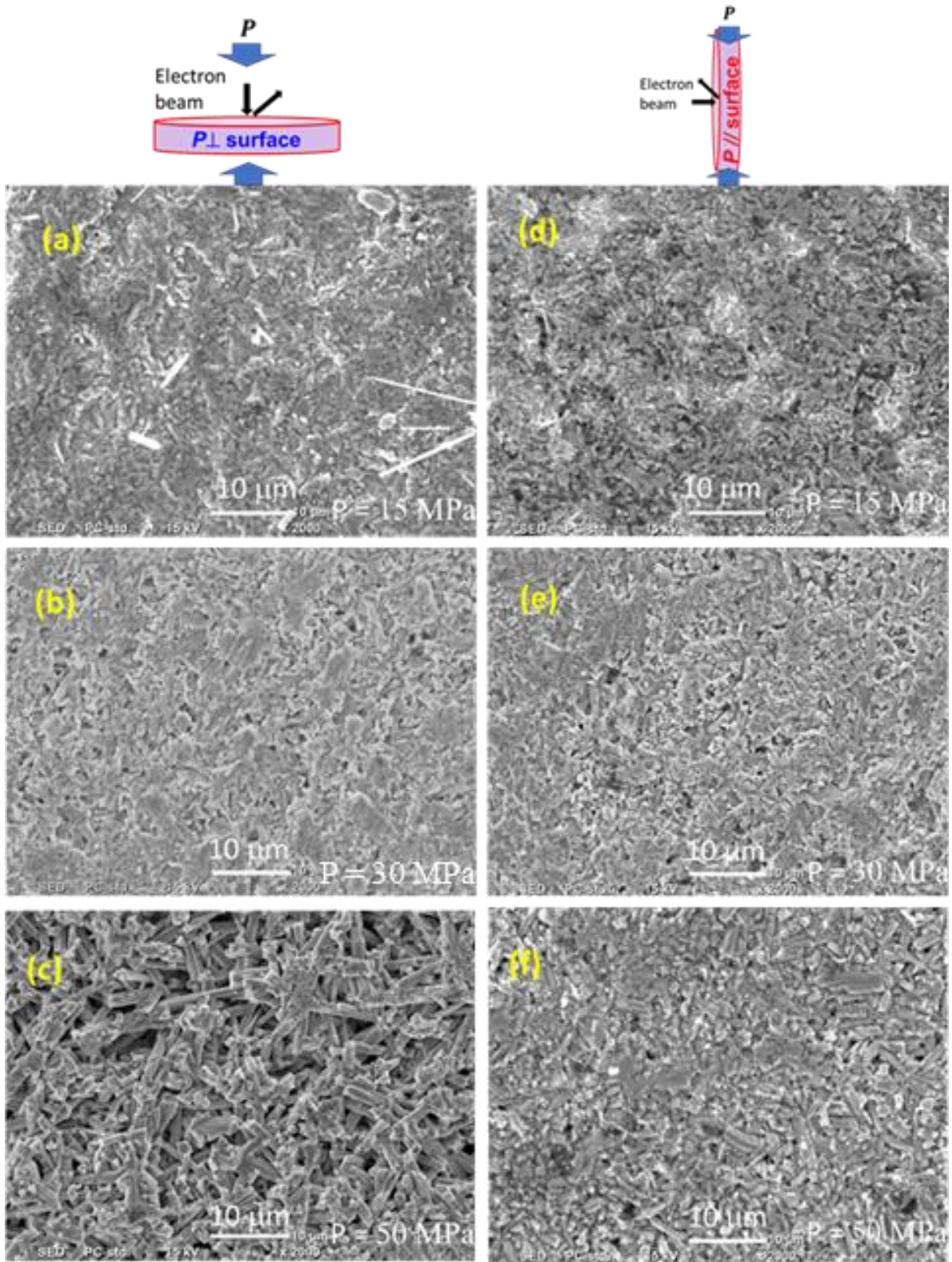


Figure 2.4 Scanning electron microscope images of $W_{18}O_{49}$ sample synthesized by direct SPS. Views of $\perp P$ fractured surface (a, b, c), views of $// P$ fractured surface (e, d, f) of samples synthesized under different applied pressure of 15, 30 and 50 MPa respectively.

Error! Reference source not found.4 shows the SEM images of $W_{18}O_{49}$ sample synthesized by direct SPS with views of fractured surface $\perp P$ (a, b, c), views of fractured surface $\parallel P$ (e, d, f) under different applied pressure of 15, 30 and 50 MPa respectively. Sample synthesized under 15 MPa pressure was dense without visible crystallite or preferential grain orientation for both directions. Small needle-like crystallites are observed in SEM images of sample synthesized under 30 MPa, indicating the possibility of anisotropic thermoelectric properties due to the shape of the grains. However, there is no distinction observed in the images of fractured surfaces between both directions regarding the applied pressure, so the anisotropy is expected to be weak. For sample synthesized under 50 MPa, many rod- and column- shaped crystallites could be identified lying on the plane of observed fractured surface $\perp P$ (Figure 2.4 (c)). Those crystallites are of similar shapes to those of reported $W_{18}O_{49}$ nanowires and nano-rods [125,138], which is elongated along b -axis. While the crystallites are also visible in the fractured surface $\parallel$ to P , there are distinct differences between two observed surfaces regarding to the elongation and orientation of the crystallites. The sample exhibited a strong anisotropic nature with the preferential grain growth along the plane $\perp$ to P . We attempted to estimate the average diffraction domain dimensions via Scherrer equation [139], thus crystallite size for $[100]$ are 31.4 nm and 29.2 nm, for $[010]$ are 72.7 nm and 71.9 nm, for $[001]$ are 45.2 nm and 48.4 nm with respect to observed plane $\perp$ and $\parallel$ to the applied pressure P . Consequently, the size of the observed microstructure crystallites is much larger than that of diffraction domains, indicating their polycrystalline characters.

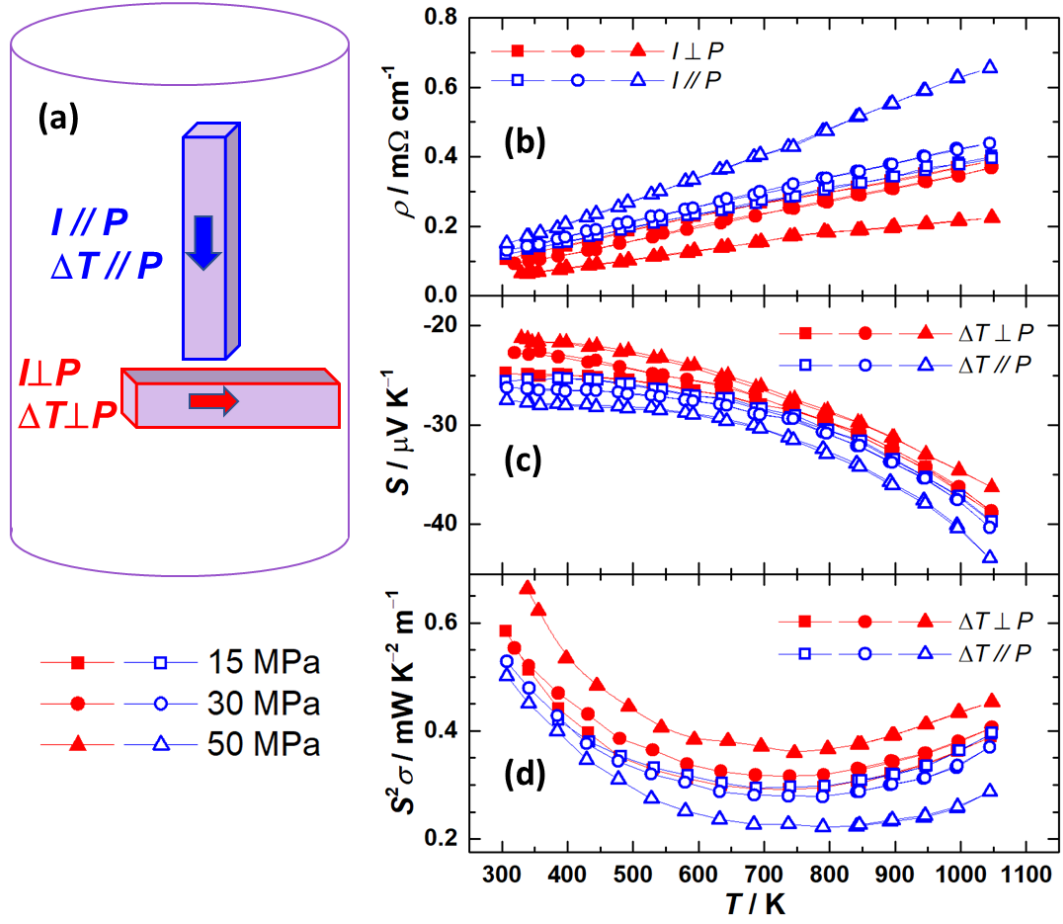


Figure 2.5. (a) Schematic of prepared samples for the σ and S values characterization. ρ , S were measured from bar-shaped samples through an applied current I and a temperature difference ΔT , κ was measured from disc-shaped samples through a heat transfer Q from laser pulses. The measurement directions, parallel $//$ and perpendicular $\perp$ to the applied pressure P axis, were denoted by the respective arrows. Temperature dependence of the resistivity ρ (b), the Seebeck coefficient S (c), the power factor $S^2 \rho^{-1}$ (d), for samples with different SPS applied pressures ($P = 15, 30, 50$ MPa). Data measured for $P //$ and $\perp$ directions are designated by closed and open symbols, respectively.

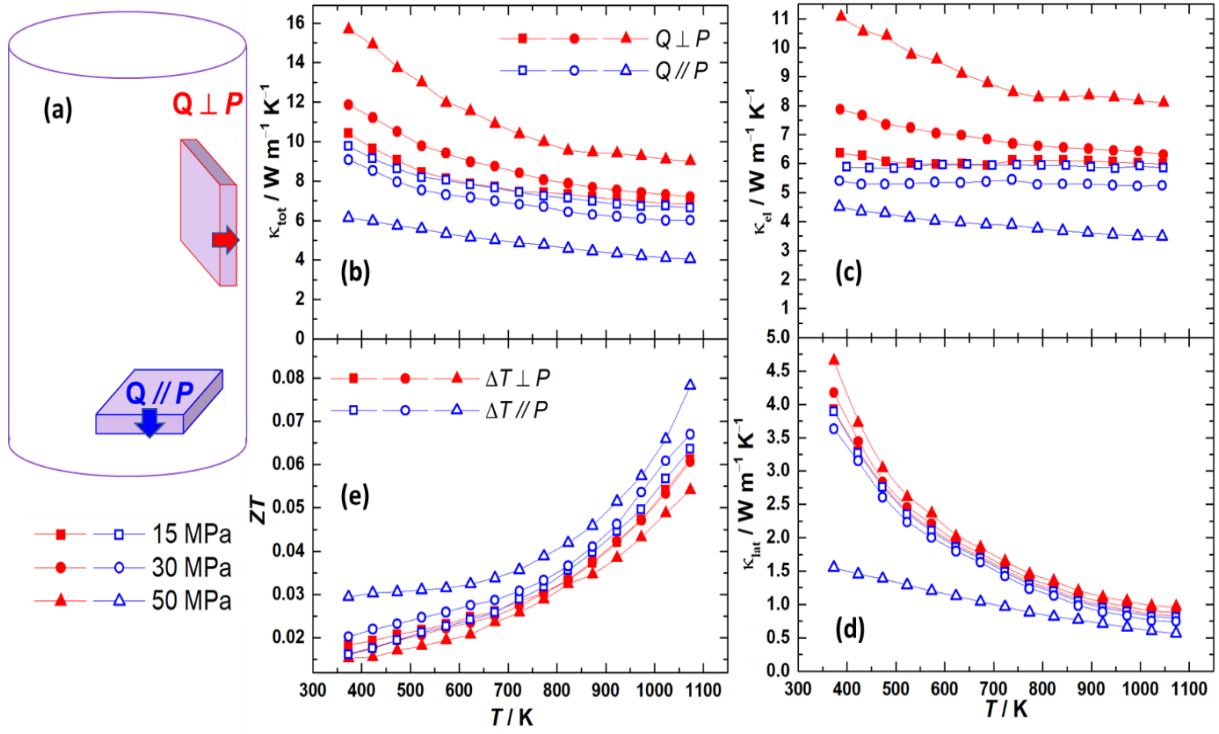


Figure 2.6. (a) Schematic of prepared samples for the κ values characterization. κ was measured from disc-shaped samples through a heat transfer Q from laser pulses. The measurement directions, parallel $//$ and perpendicular $\perp$ to the applied pressure P axis, were denoted by the respective arrows. Temperature dependence of the total thermal conductivity κ_{tot} (b), the electronic thermal conductivity κ_{el} (c), the lattice thermal conductivity κ_{lat} (d) and the dimensionless figure of merit ZT (e) for samples with different SPS applied pressures ($P = 15, 30, 50$ MPa). Data measured for $P //$ and $\perp$ directions are designated by closed and open symbols, respectively.

The temperature dependence of resistivity ρ , Seebeck coefficient S and thermal conductivity κ are presented in Figure 2.5(b), (c) and (e). To study the anisotropic property, characterizations of thermoelectric parameters were conducted with corresponding variations I , ΔT and thermal flux Q generated along the designated directions of $\perp$ and $//$ to P respectively, as shown in the illustration in Figure 2.5(a). Weak anisotropic ρ was found in sample synthesized under applied pressure of 15 and 30 MPa, with slightly larger ρ values along

direction // (P) and smaller ρ values along direction $\perp P$, but not very significant. The resistivity of the two samples bears similarities to reported values of conventional synthesized bulk $W_{18}O_{49}$, in which it shows metallic behavior with electron being the dominant charge carriers [120]. Nevertheless, high level of anisotropy was recorded for sample synthesized under 50 MPa uniaxial pressure, with significant reduction in resistivity ρ value of $0.06 \text{ m}\Omega \text{ cm}^{-1}$ along $\perp$ direction to P , and the increase in ρ value of 0.17 along // direction to P at 330 K. The better ordered grain alignment could have enhanced the mobility of electron along the $\perp P$ direction, while restricting electron movements in the // P direction. Correspondingly, the S values of sample sintered under 15 and 30 MPa samples are closely matched and comparable to the reported values of conventional prepared $W_{18}O_{49}$, hence so is the power factor $S^2\rho^{-1}$. Distinct anisotropy of the S value was found in sample sintered under 50 MPa, where $|S|$ is larger along the direction // P and smaller along the $\perp P$ in comparison with data from other samples. Altogether, the sample 50 MPa got the highest $S^2\rho^{-1}$ of $0.5 \text{ mW K}^{-2} \text{ m}^{-1}$ and the lowest of $0.28 \text{ mW K}^{-2} \text{ m}^{-1}$ with respect to direction $\perp$ and // to P .

The anisotropy of measured κ (Figure 2.5 (e)) was noteworthy, where it was enlarged along the // to P and lessen along the $\perp$ to P direction, comparing to conventional synthesized samples [129]. The increment and reduction became more significant, influenced by the strengthen applied pressure P . κ was both lowest and largest for sample sintered under 50 MPa along its two different orientations. Assuming the total $\kappa = \kappa_{\text{lat}} + \kappa_{\text{el}}$, Wiedemann Franz law $\kappa_{\text{el}} = LT\rho^{-1}$ was used to estimate κ_{el} , then extrapolate the value of κ_{lat} . First, we attempted to use the constant Lorenz number L of $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, accepting the metallic state of the materials. However, at high temperature reaching 1073 K, κ_{el} became larger than the total κ , so the approximation was not reliable. The modified equation $L(T) = 1.5 + \exp(-|S|/116) [10^{-8} \text{ W } \Omega \text{ K}^{-2}]$ was used, in consideration of the correlation between S and L [140]. The temperature

dependence κ_{lat} and κ_{el} are presented in Figure 2.5(f). The high value of κ is mostly built up by its electronic part, resulting in the impressive low κ_{lat} . Remarkably, the κ_{lat} values of all samples along all directions is very closely matched, except for the sample sintered under 50 MPa along its $\perp$ to P direction with significantly smaller value. The low κ_{lat} , in particularly along $\perp$ to P , could be attributed to the phonon scattering effect by intrinsically formed empty pseudo hexagonal tunnels along the b -axis of the $\text{W}_{18}\text{O}_{49}$ crystal. Furthermore, the orderly orientation of the grains and the nanometer grain sizes also contribute additionally to the reduction of the κ_{lat} by grain boundary scattering of phonons. Overall, the weak anisotropic properties of sample sintered under 15 and 30 MPa resulted in quite similar dimensionless figure of merit ZT (presented in Figure 2.5(g)), with comparable behavior and magnitude to those reported for conventional synthesized samples. Nonetheless, because of the large deviation in the anisotropic κ values of sample sintered under 50 MPa along the two different orientations, its ZT value was smallest along the $\perp$ direction to P , despite the largest corresponding power factor. On the other hand, being compensated by the considerably low κ , ZT value along the $\parallel$ to P direction was enhanced to approximate 0.08 at 1073 K. Importantly, the conditions were yet optimized, and ZT can be further boosted with higher applied anisotropy. Last but not least, the thermal tendency of ZT values is still increasing at 1073, indicating the better performance at higher temperatures.

2.4. Conclusions

We have successfully isolated single phase $\text{W}_{18}\text{O}_{49}$ via rapid reactive SPS directly from the starting materials of WO_3 and WO_2 , where the whole synthesis took less than 2 hours totally. This process is a significant improvement from conventional method, often involved complicated heating and cooling cycles in evacuated environments. In addition, the reaction between WO_3 and WO_2 starting materials to form tungsten suboxide WO_{3-x} ($0 < x \leq 1$), could

be more suitable than the reaction between WO_3 and metal W powder, due to the similarities in their $[\text{WO}_6]$ octahedra building blocks.

Furthermore, by reactive SPS, anisotropic thermoelectric properties of $\text{W}_{18}\text{O}_{49}$ could be partially influenced by the increment of applied pressure. The ordered orientation of crystallite under high pressure offers an intrinsically low thermal conductivity materials, despite its metallic nature. Theoretically, anisotropy could even be significantly strengthened by applying even higher uniaxial pressure, thus, ZT was enhanced by employing this technique to 0.08 at 1073 K under sintered pressure of 50 MPa in comparison with the ZT of 0.06 of the less oriented samples. It was reported that that electronic properties of $\text{W}_{18}\text{O}_{49}$ is tunable to become semi-conductive, hence, combining with the manipulatable κ and anisotropy, this compound promises a new potential cost-effective n -type thermoelectric materials.

Chapter 3. Attempts on carrier concentration manipulation via Ni doping.

3.1. Introduction

To ensure good quality thermoelectric materials, the following criteria need to be met (1) High electrical conductivity: this variable depends on the choice of element in used, the nano structure of the material, etc. (2) Low thermal conductivity in order to raise the temperature gradient between the hot and cold sources: this property also depends on choice of elements, doping concentration, nano structure, etc. (3) Large Seebeck coefficient: to gain high voltage output (4) The stability and durability of the material over the range temperature, especially at temperature higher than 1000 K and the repeating circles of operation: to make use of the highest waste heat production areas, the industrial plants.

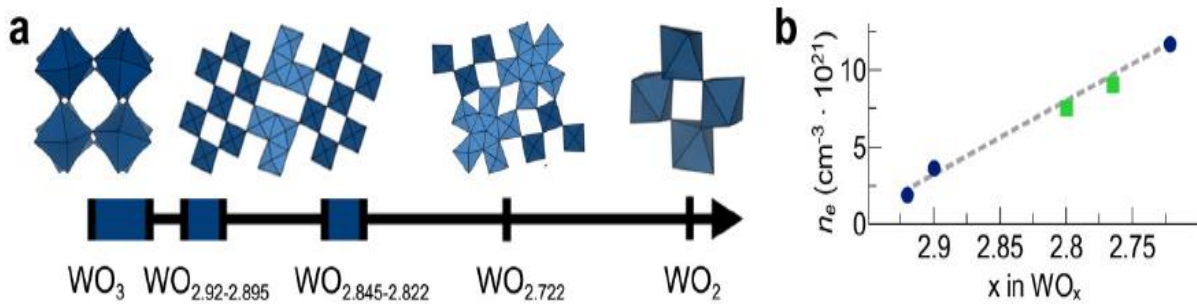


Figure 3.1. (a) changing patterns of crystal structure in the quasi ternary system $WO_3 - WO_2$, and (b) corresponding carrier concentration w.r.t the crystal structure (rounds are experimental data and squares are theoretical ones) [141]. With amount of reduction oxygen lies from 0.005 to 0.155, crystallographic shear planes observed on plane $\{102\}$ and plane $\{103\}$. At higher amount of oxygen deficiencies, pentagonal columns dominate the structure pattern, evidences observed in $WO_{2.833}$ ($W_{24}O_{68}$) and $WO_{2.722}$ ($W_{18}O_{49}$).

Figure taken from Kieslich (2013)

(1) **Increasing charge concentration:** Kieslich et al 2013 has shown that by reducing oxygen in tungsten oxide, the charge carrier concentration would be improved, respectively [141]. Migas et al 2010 has predicted that altering the amount of oxygen in a

tungsten oxide compound can either shift the fermi level toward conducting band or valence band, giving it possibility to be either p-type or n-type materials. Furthermore, reducing ratios of O/W in the compound from 2.92 to 2.625, would increase carrier concentration from 2.90×10^{21} to 1.62×10^{22} , almost 10 times higher than the stoichiometric one [142]. The similar results are being reported for Titanium compounds, as in Yunlu et al 2012, electrical resistivity of $\text{TiO}_2\text{-Ti}$, with an increasing of 8% titanium in total volume, is at $10^{-2} \Omega\text{.mm}$, and is stable across a wide range of temperature from 400 K to 1000 K [143]. Mulenko et al 2014 has reported that a chromium compound of $\text{Cr}_{3-x}\text{O}_{3-y}$ (with $0 \leq x \leq 2$, $0 \leq y \leq 2$) possesses electrical conductivity ranging from 350 to 550 $(\Omega\text{.cm})^{-1}$ as temperature increase from 280 K to 330 K [144].

(2) **Low thermal conductivity while having high electrical conductivity:** another work of Kieslich et al 2013 reported that crystallographic shear planes in $\text{WO}_{2.90}$ significantly lower the thermal conductivity of the material [145]. While the more oxygen vacancies in tungsten oxide compound, the higher carrier concentration, it does not always work in lowering thermal conductivity. However, an appropriate reduction of oxygen would give crystallographic shear planes, effectively reducing thermal conductivity and enhancing ZT value [119]. Many other reports have also published similar tendencies in titanium oxide compounds [146–149]. Mikami et al 2012 has reported that Ti_7O_{13} has ZT of 0.4 at 1150 K [150], almost equivalent to state of the art ZnO-based n-type thermoelectric materials synthesized by Ohtaki's group [151].

(3) **Stable at high temperature:** All magnéli phase materials synthesized from transitional metals have been reported to have good temperature durability. Most of them retained good properties even at temperature higher than 1000 K, since the synthesis process had already involved rapid sintering and cooling at temperature around 1400 K [146,152]. This

is a promising sign for developing good *n*-type thermoelectric materials for industrial applications.

Studying sub-stoichiometry transition metal oxides materials for thermoelectric applications is relatively new area. Oldest reports regarding thermoelectric properties of titanium oxide date back to only around the 2010s [142,143]. There are currently very few publications regarding this type of materials' applications in thermoelectricity, hence, plenty room for quality ideas, researches and publications. Most of the reports concerns bulk Tungsten oxide – based and titanium oxides based materials, synthesized through the spark plasma sintering process [142,146,153–155]. There has yet many studies about thin-film 2D materials, except for one on chromium oxide, synthesized by pulse laser deposition [144], leaving room for researching 2D sub-stoichiometry tungsten oxide and titanium oxide. No one has ever reported on the fabrication of thermoelectric devices utilizing magnéli phase materials, consequently, this part is left opened for future discoveries.

3.2. Experimental details

Samples of $\text{WO}_{2.90}$, $\text{WO}_{2.84}$, $\text{WO}_{2.72}$ were synthesized by direct reaction of single metal oxides as starting materials. WO_3 (Kishida Chemical, 99.9%), WO_2 (Wako, 99.9%) were weighed according to the target elemental compositions including oxygen, and mixed by ball milling at 300 rpm for 1 h. The mixtures were then molded into pellets by applying a uniaxial pressure of 100 MPa, sealed in evacuated quartz ampules, and heated to 1073 K taking a period of 8 h, maintained at this temperature for 24 h, cooled to room temperature taking 8h. After the first heating cycle, the pellets were thoroughly ground, pelletized at 100 MPa and annealed again for an additional 24 h at 1073 K to improve the homogeneity. Subsequently, the pellets were reground and loaded into graphite dies with an inner diameter of 10 mm. The dies were placed in the spark plasma sintering furnace (SPS) PLASMAN CPS-I-03121 (S. S. Alloy). For SPS treatment, the furnace chamber was evacuated to the pressure of ≤ 10 Pa, and the sample was heated up to 1423 K at a heating rate of 100 K min^{-1} under uniaxial pressure of 50 MPa, maintained for 15 min and the pressure was released, and cooling rate was controlled at 20 K min^{-1} to room temperature. The pellet was detached from the graphite die, the lining carbon paper was peeled off, and the surface of the pellet was polished with SiC abrasive papers to remove all possible carbon contamination.

Powder X-ray diffraction (PXRD) data were collected using a Rigaku MiniFlex 600 diffractometer with $\text{Cu K}\alpha$ radiation within the range of $5^\circ \leq 2\theta \leq 90^\circ$, $\Delta 2\theta = 0.01^\circ$. Surface morphologies and elemental compositions of the sample were studied on a JEOL JCM-6000Plus NeoScope scanning electron microscope (SEM) equipped with energy-dispersive spectroscope (EDS). The electrical conductivity σ and Seebeck coefficient S were measured under Ar atmosphere simultaneously by dc four-probe method and temperature differential method, respectively, on an Ozawa Science RZ2001i. The reproducibility of the σ and the S

measurements was confirmed by well overlapped results on heating and cooling paths in the range of 300 – 1073K. The thermal diffusivity α and specific heat C_p at 300 – 1073 K were measured simultaneously on Kyoto electronics LFA-502 by laser-flash method under vacuum. The absolute values of C_p were obtained from a comparative method using a molybdenum. The thermal conductivity was calculated using the relation $\kappa = \alpha C_p d_s$, where d_s is the sample density.

3.3. Results and discussions

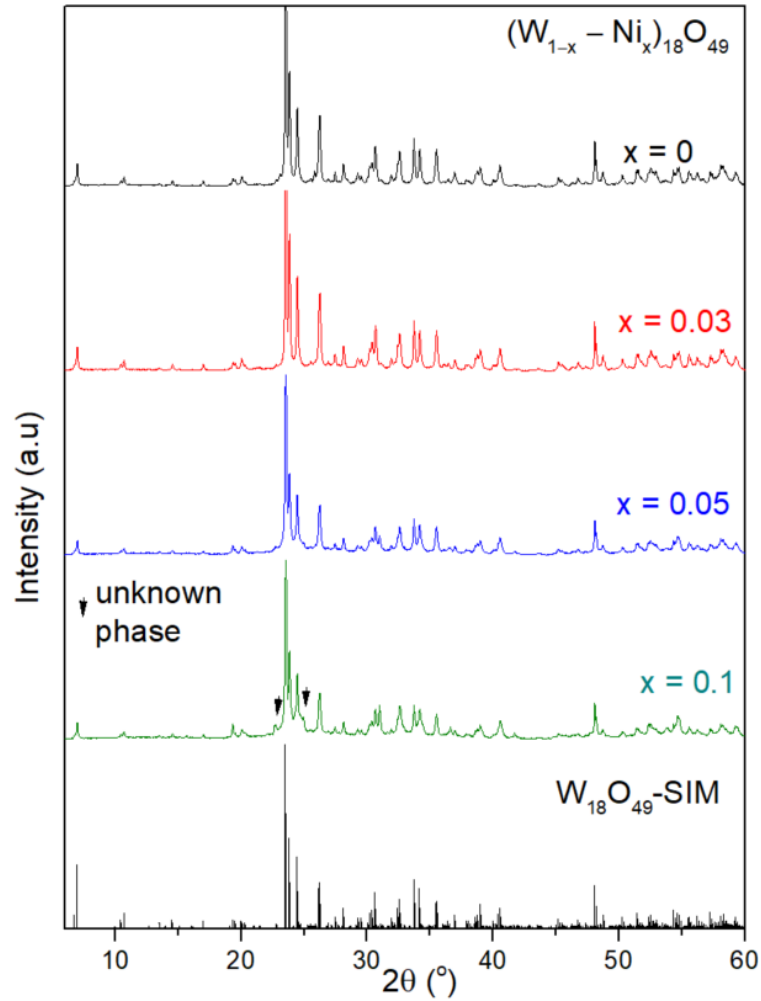


Figure 3.2. PXRD patterns of $(W_{1-x}Ni_x)_{18}O_{48}$ samples ($0 \leq x \leq 0.1$)

The thermoelectric properties of Ni-doped samples showed enhancement in Seebeck coefficient, power factor, reduction in total thermal conductivity, and eventually improved ZT values (Figure 3.3). However, the sample doped with Ni has proven to be not thermodynamically stable, where at high temperature the more favorable phase of NiWO_4 was formed upon the initial phase of $\text{W}_{18}\text{O}_{49}$, which interfered the Seebeck coefficient measurement of the materials and resulted in unreliable large S values as shown in Figure 3.3. The images in Fig 4.6 was acquired after several round of thermoelectric measurement from room temperature up to 800°C under Ar environment. The individual electrical properties measurement of NiWO_4 revealed the materials to be completely insulated with positive Seebeck coefficient value. In addition, the NiWO_4 layer was quite passive, thin, and can be removed by a simple polished with SiC abrasive paper. However, even in complete oxygen isolated environment, the formation of NiWO_4 layer still occurred, however in much less degree as shown in the measurement in Figure 3.3. The thermoelectric properties of the materials were significantly enhanced, but due to the unstable thermodynamic nature, doping Ni was not a good choice.

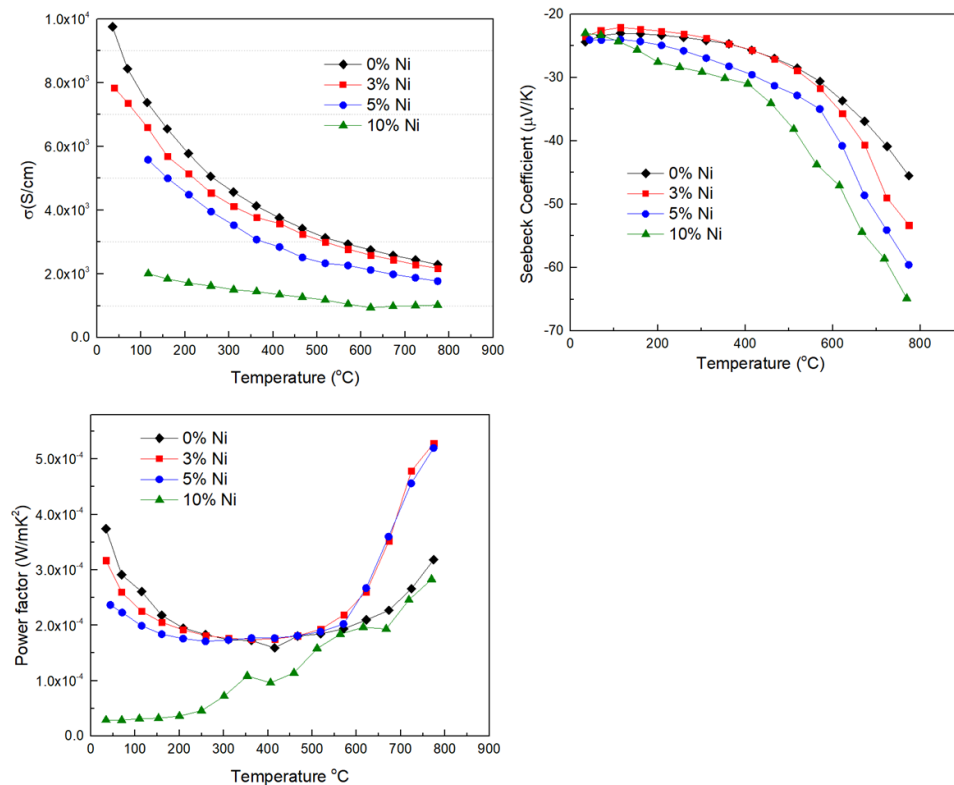


Figure 3.3. S , σ and Power factor of samples $(W_{1-x}Ni_x)_{18}O_{49}$ ($x = 0, 0.03, 0.05, 0.1$)

prepared by SPS.

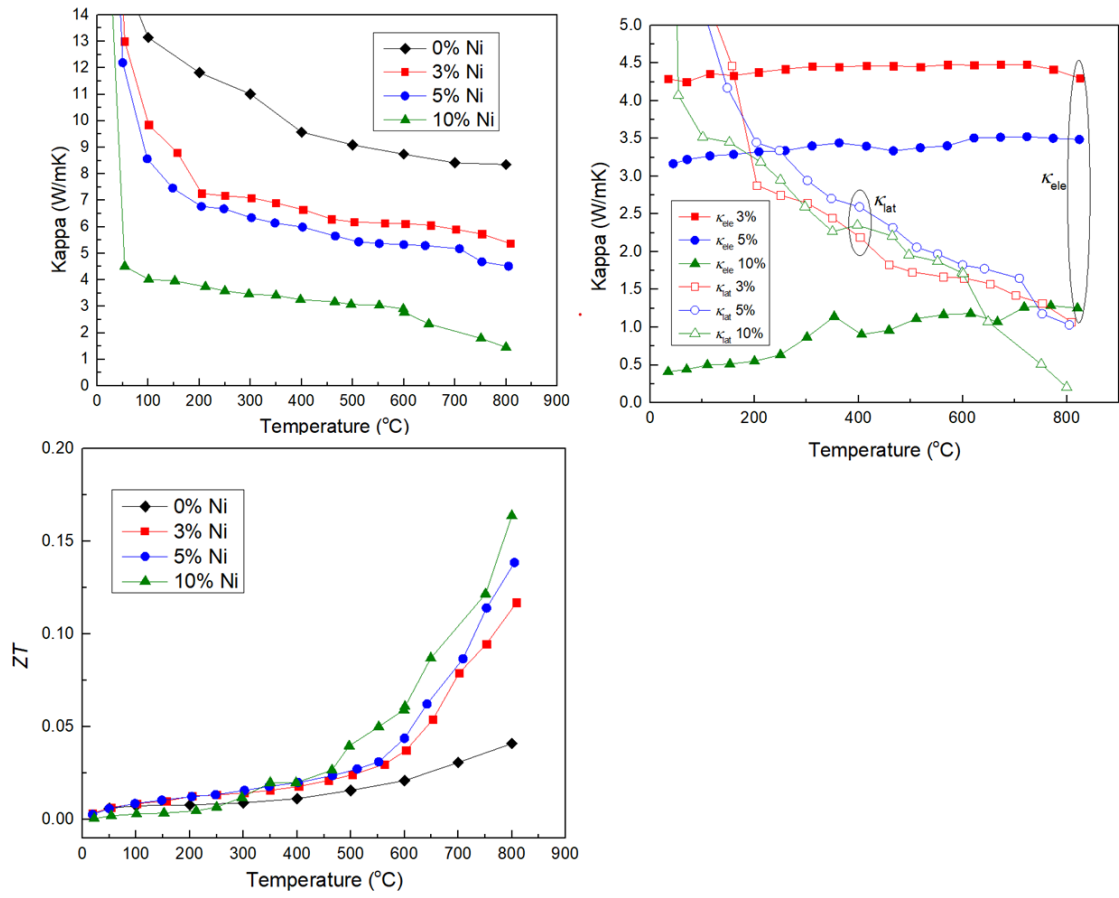


Figure 3.4 κ and ZT values of samples $(W_{1-x}Ni_x)_{18}O_{49}$ ($x = 0, 0.03, 0.05, 0.1$) prepared by

SPS

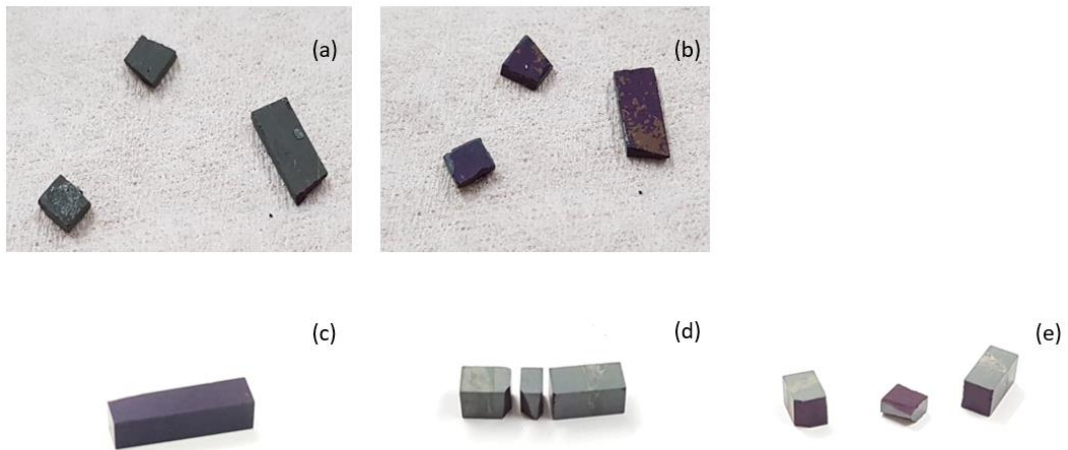


Figure 3.5. Images of 1% Ni-doped sample after thermoelectric measurement at high temperature.

After the unsuccessful attempts with Ni doping, other dopants were employed such as Ta, Ti, and V. The PXRD patterns of sample with different dopants were shown in Fig 4.7. V doped samples were not stable in air and were very volatile.

3.4. Conclusion

This chapter is the foundation of this study with the initial attempts on various synthesis route, different method to improve the thermoelectric performance of Tungsten oxide with adaptive crystal structures, and eventually the successful attempts on manipulation the electrical properties of the $W_{18}O_{49}$ -based materials via doping with lower valance cation of Ni. Ni doping was not a suitable choice due to the thermodynamic instability at high temperature and the favorable formation of $NiWO_4$ phase. Other dopants should be investigated.

Chapter 4. High temperature Thermoelectric Performance of

$(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$

Abstract

Magnéli sub-oxide materials have attracted attention for thermoelectric applications because of their intrinsically good electrical conductivity and low thermal conductivity. Here we report the high-temperature thermoelectric properties of $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ ($0 \leq x \leq 0.25$) prepared by solid state reaction in vacuum followed by densification via spark plasma sintering method. The Ti substitution increased the Seebeck coefficient, the power factor, and decreased both the electronic and lattice thermal conductivity. The synergistic substitution effect on the electrical and thermal properties and inherently low total thermal conductivity of $1.46 \pm 0.1 \text{ W K}^{-1} \text{ m}^{-1}$ originating from the tunnels structure led to the ZT of 0.5 ± 0.08 at 1073 K ($x = 0.2$).

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4.1. Introduction

Thermoelectricity has become of great interest due to its capability of direct conversion of thermal energy into electrical energy, and such conversion is particularly important in the industrial sectors for waste-heat energy recovery. The energy conversion is governed by the Seebeck effect in solid materials, where the efficiency can be evaluated by the dimensionless figure of merit $ZT = S^2 \sigma T \kappa^{-1}$, with the Seebeck coefficient S , the electrical conductivity σ , absolute temperature T , and the total thermal conductivity κ_{tot} . A good thermoelectric material with high ZT should have high σ , large $|S|$, and low κ_{tot} . In addition, other characters such as low toxicity as well as scalable and cost-effective manufacturing capability are also desired. Ignoring bipolar effect and radiation, the total thermal conductivity $\kappa_{\text{tot}} = \kappa_{\text{el}} + \kappa_{\text{lat}}$, where κ_{el} is the electronic component of thermal conductivity and κ_{lat} is the lattice component of thermal conductivity. To enhance ZT , a straightforward method is to reduce κ_{lat} via employing additional phonon scattering mechanisms or structural features for intrinsically low lattice thermal conductivity [157–161]. Another approach is tuning other thermoelectric parameters; however, because σ , $|S|$, and κ_{el} are all dependent on the carrier concentration in a controversial way, it is difficult to achieve simultaneous improvements of all these three parameters.

Transition metal oxides have been attracting significant attention over the last two decades as promising materials for high-temperature thermoelectric applications [162–164]. The advantages of oxides are high thermal stability and environmentally friendly characteristics, and often inexpensive starting materials. The earth-abundant tungsten oxide Magnéli phase $\text{W}_{18}\text{O}_{49}$ with a structural motif of pentagonal columns [165] emerged as a thermoelectric candidate in 2013 [166]. However, the oxide was soon disregarded due to its apparently very high σ , small $|S|$, and high κ . Nevertheless, Migas *et al.* mentioned that the metallic properties

of $W_{18}O_{49}$ is switchable to semiconducting, by manipulating additional oxygen atoms [167]. The band structure of $W_{18}O_{49}$ has the Fermi level crossing into the conduction band (CB) at 1 eV higher than the bottom of the CB. As proposed by Migas *et al*, addition of one oxygen atom shifts the Fermi level toward the band gap, reducing the initial carrier concentration $n \approx 1.1 \times 10^{22}$ to 8.79×10^{21} , and suggests a possibility for improving thermoelectric performance [167].

Due to high σ , the high κ values of $W_{18}O_{49}$ might mostly be built up by the κ_{el} part, while it is highly possible that κ_{lat} is low. In addition, the large unit cell with large number of atoms would associate with a low group velocity of optical phonon modes, and low κ_{lat} shows the crystal structure of $W_{18}O_{49}$, the large void tunnels running in between of the bulky penta-columns, forming from five octahedra stacking together via sharing edges with one pentagonal bipyramid. The void tunnels, expected to act as the naturally formed phonon scattering centers together with the bulky penta-columns, would lead to an intrinsically low κ_{lat} . Moreover, this structure has been reported to be stable to allow $W_{18}O_{49}$ be the only largest oxygen deficient compound that can be isolated as a single phase in all the tungsten Magnéli WO_{3-y} ($0 \leq y \leq 1$) region [169,170]. This stability of the $W_{18}O_{49}$ phase would enable the possibility of tuning the carrier concentration by substitution W^{6+} with the lower valence cation without severely affecting its crystal structure.

In this study, we present the high temperature thermoelectric properties of $(W_{1-x}Ti_x)_{18}O_{49}$ with $0 \leq x \leq 0.25$. In this system, the substitution of W^{6+} with Ti^{4+} at the center of the WO_6 octahedra reduced the electron carrier concentration, reduced κ_{el} and enhanced $|S|$ and thus $S^2\sigma$. Furthermore, the Ti-substitution also gave additional contributions to the reduction of κ_{lat} . Consequently, the ZT was boosted from 0.05 ± 0.01 of the pristine sample to 0.5 ± 0.08 for the sample with $x = 0.2$ at 1073 K.

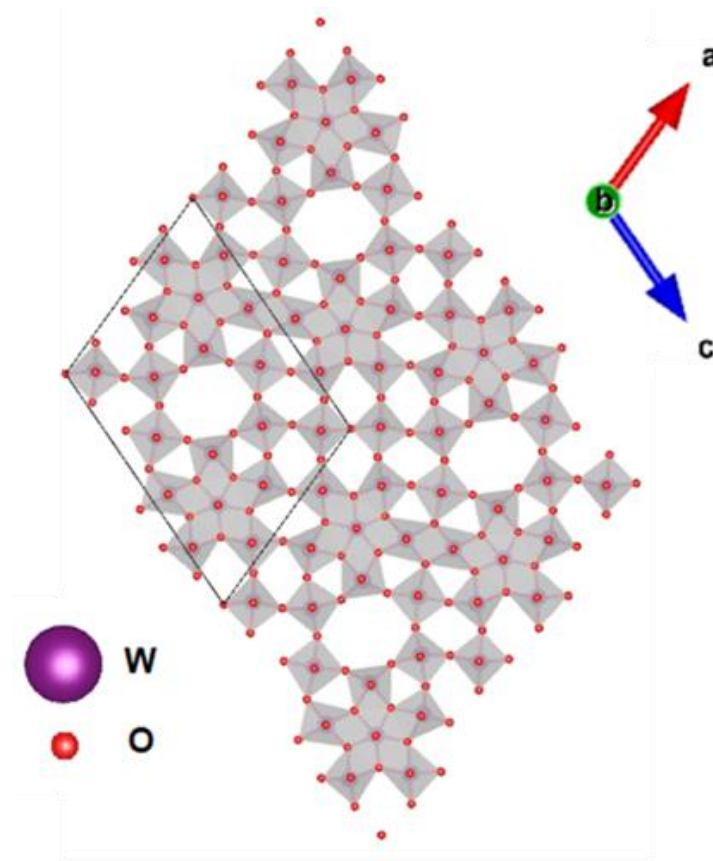


Figure 4.1. Crystal structure of $\text{W}_{18}\text{O}_{49}$

4.2. Experimental details

Samples of $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ ($x = 0, 0.03, 0.05, 0.1, 0.15, 0.2, 0.25$) were synthesized by direct reaction of single metal oxides as starting materials. WO_3 (Kishida Chemical, 99.9%), WO_2 (Wako, 99.9%), and TiO_2 rutile form (Kanto Chemical, 99.9%), were weighed according to the target elemental compositions including oxygen, and mixed by ball milling at 300 rpm for 1 h. The mixtures were then molded into pellets by applying a uniaxial pressure of 100 MPa, sealed in evacuated quartz ampules, and heated to 1073 K taking a period of 8 h, maintained at this temperature for 24 h, cooled to room temperature taking 8h. After the first heating cycle, the pellets were thoroughly ground, pelletized at 100 MPa and annealed again for an additional 24 h at 1073 K to improve the homogeneity. Subsequently, the pellets were reground and loaded into graphite dies with an inner diameter of 10 mm. The dies were placed in the spark

plasma sintering furnace (SPS) PLASMAN CPS-I-03121 (S. S. Alloy). For the SPS treatment, the furnace chamber was evacuated to the pressure of ≤ 10 Pa, and the sample was heated up to 1423 K at a heating rate of 100 K min^{-1} under uniaxial pressure of 50 MPa, maintained for 15 min and the pressure was released, and cooling rate was controlled at 20 K min^{-1} to room temperature. The pellet was detached from the graphite die, the lining carbon paper was peeled off, and the surface of the pellet was polished with SiC abrasive papers to remove all possible carbon contamination. All the samples showed the relative density of approximately 100% of the theoretical density of $\text{W}_{18}\text{O}_{49}$ ($d_{\text{th}} \approx 7.21 \text{ g cm}^{-3}$).

Powder X-ray diffraction (PXRD) data were collected using a Rigaku MiniFlex 600 diffractometer with $\text{Cu K}\alpha$ radiation within the range of $5^\circ \leq 2\theta \leq 90^\circ$, $\Delta 2\theta = 0.01^\circ$. Surface morphologies and elemental compositions of the sample were studied on a JEOL JCM-6000Plus NeoScope scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS). The electrical conductivity σ and Seebeck coefficient S were measured under Ar atmosphere simultaneously by dc four-probe method and temperature differential method, respectively, on an Ozawa Science RZ2001i. The reproducibility of the σ and the S measurements was confirmed by well overlapped results on heating and cooling paths in the range of 300 – 1073 K. The thermal diffusivity α and specific heat C_p at 300 – 1073 K were measured simultaneously on Kyoto electronics LFA-502 by laser-flash method under vacuum. The absolute values of C_p were obtained from a comparative method using a molybdenum. The total thermal conductivity was calculated using the relation $\kappa_{\text{tot}} = \alpha C_p d_s$, where d_s is the sample density.

For microstructure observation, all samples (of size approximate 0.25 cm^2 and thickness from 2 – 3 mm) were polished by abrasive SiC papers with grit size gradually increasing from 320 to 2000. Then the samples were polished by $3 \mu\text{m}$ diamond suspension to achieve finer

condition and remove any damage from the previous polishing steps. The samples were then sonicated in acetone and deionized water for 15 mins each to discard any diamond and contamination residue. After the polishing process, the samples underwent thermal etching process, for grain boundary revealing, in Ar atmosphere at 1000°C within 1 hour with heating and cooling rate of 100°C/h.

4.3. Results and discussion

One of the reasons of employing SPS for densification of the samples is to minimize the loss of oxygen at high temperature via fast heating and cooling process; the short processing time (<1 h) limits the spread of carbon contamination only within the surface of the pellet, and it can easily be removed by polishing. As shown in PXRD data (Fig 5.2 (a)), no secondary phase was observed for the samples with Ti content $x = 0, 0.03, 0.05$ and 0.1 , and the peak positions and relative intensities of the patterns agreed with those of the simulated $W_{18}O_{49}$ pattern. Sample with Ti content $x = 0.15$ shows small signals of unknown phase or phases with the broadening at the base of (010) and (203) peaks. Sample $x = 0.2$ shows significant enhancement of secondary phase signals while the main peaks of $W_{18}O_{49}$ motif are still dominant. The sample $x = 0.25$ has completely different XRD pattern with new dominant unknown phase and little sign of the original $W_{18}O_{49}$ phase. In addition, there are also observable peaks from TiO_2 -rutile phase, suggesting the agglomeration of some undissolved TiO_2 .

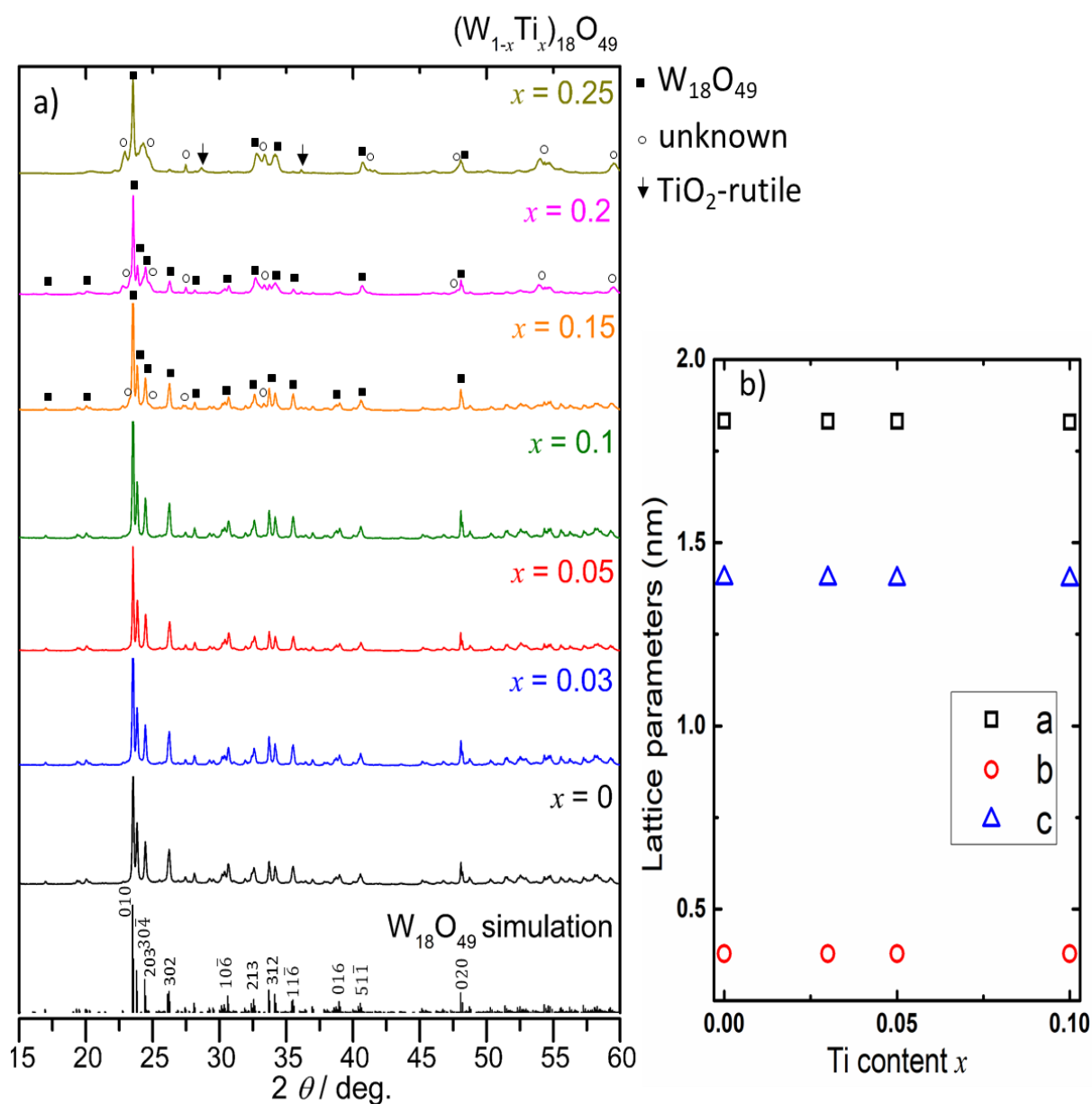


Figure 4.2. Powder XRD patterns for sintered $(W_{1-x}Ti_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.25$) (a), and the lattice parameters of the samples ($x = 0, 0.03, 0.05, 0.1$) obtained by the Rietveld refinement of the XRD patterns (b). The closed square, the open circle and the arrow represent, $W_{18}O_{49}$ phase, unknown phase and TiO_2 -rutile phase.

Since the unknown phase was not identified, Rietveld refinement was only performed on sample $0 \leq x \leq 0.1$, the lattice parameters of those sample are shown in Fig 5.2. (b). The lattice parameters of the non-substituted sample are $a = 1.803$ nm, $b = 1.433$ nm and $c = 0.378$ nm,

which are in good agreement with previously reported values [10]. The lattice parameters of Ti-substituted samples are within 0.1% difference from those of the pure sample. Since the ionic radii of Ti^{4+} (0.605 Å) and W^{6+} (0.600 Å) are almost the same, it is expected that Ti^{4+} can substitute W^{6+} at the center of WO_6 octahedra without considerable distortion [171].

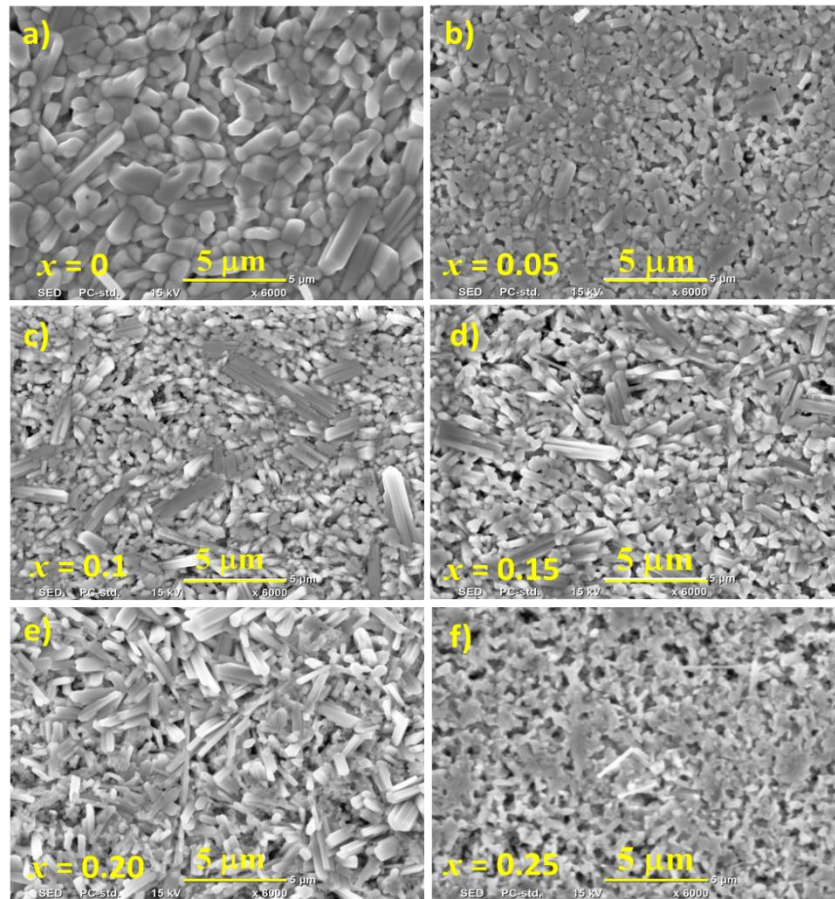


Figure 4.3. Scanning electron microscope images (a, b, c, d, e, f, g) for $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ samples ($0 \leq x \leq 0.25$).

To further elucidate the microstructure properties, SEM observation was carried out on the thermal etching surfaces of the $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ samples with $0 \leq x \leq 0.25$ (Fig. 3.). SEM images of sample with $x = 0, 0.03, 0.05, 0.1$ show well-sintered nature with observable closely packed grains. Grain structures of sample $x = 0$ and $x = 0.03$ (Fig. 3 a, b) have column-like shape, typical of $\text{W}_{18}\text{O}_{49}$ phase. The columnar cross sections have dimension of less than $1 \mu\text{m}^2$

with column's length as long as 5 μm . As Ti x content increase to 0.05 and 0.1, samples SEM images show more diverse grains sizes of similar column-like structures. Larger gain of similar size to those of sample $x = 0, 0.03$ are observed to be mixed with much smaller grains, suggesting that Ti doping might inhibit the growth of $\text{W}_{18}\text{O}_{49}$ grain size. Sample $x = 0.1$ and $x = 0.15$ (Fig. 3 d, e) shows coarser and more disorder grain boundary structure than lesser level doped samples, indicating the disorders originate from higher level of Ti doping. Sample $x = 0.2$ (Fig. 3 f) has secondary grain structures apart from the column-like structure of $\text{W}_{18}\text{O}_{49}$ motif, revealing the growing population of unknown secondary phases in the sample, which agrees with the XRD pattern from Fig. 2. SEM image of sample $x = 0.25$ show complete domination of unknown phases grains with much fewer observable column-like grains.

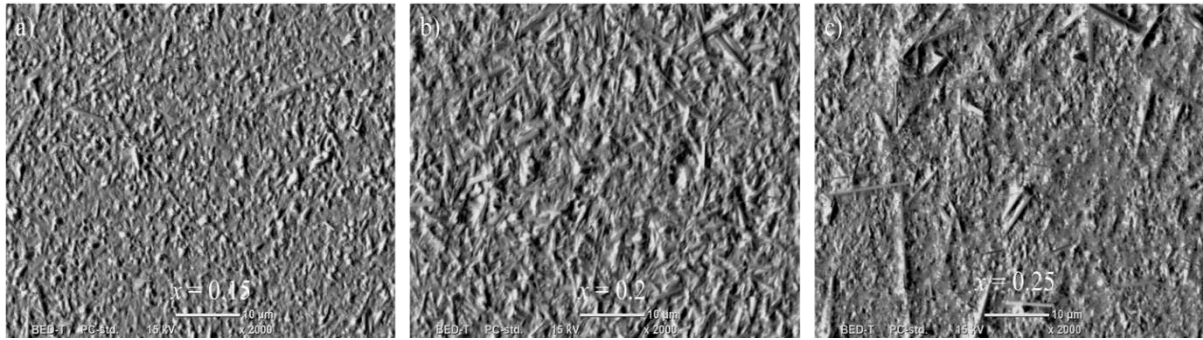
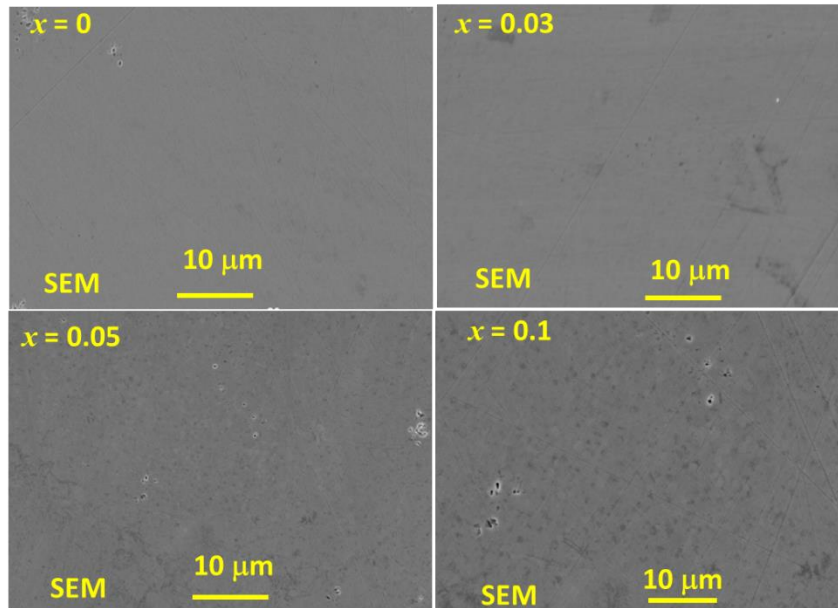
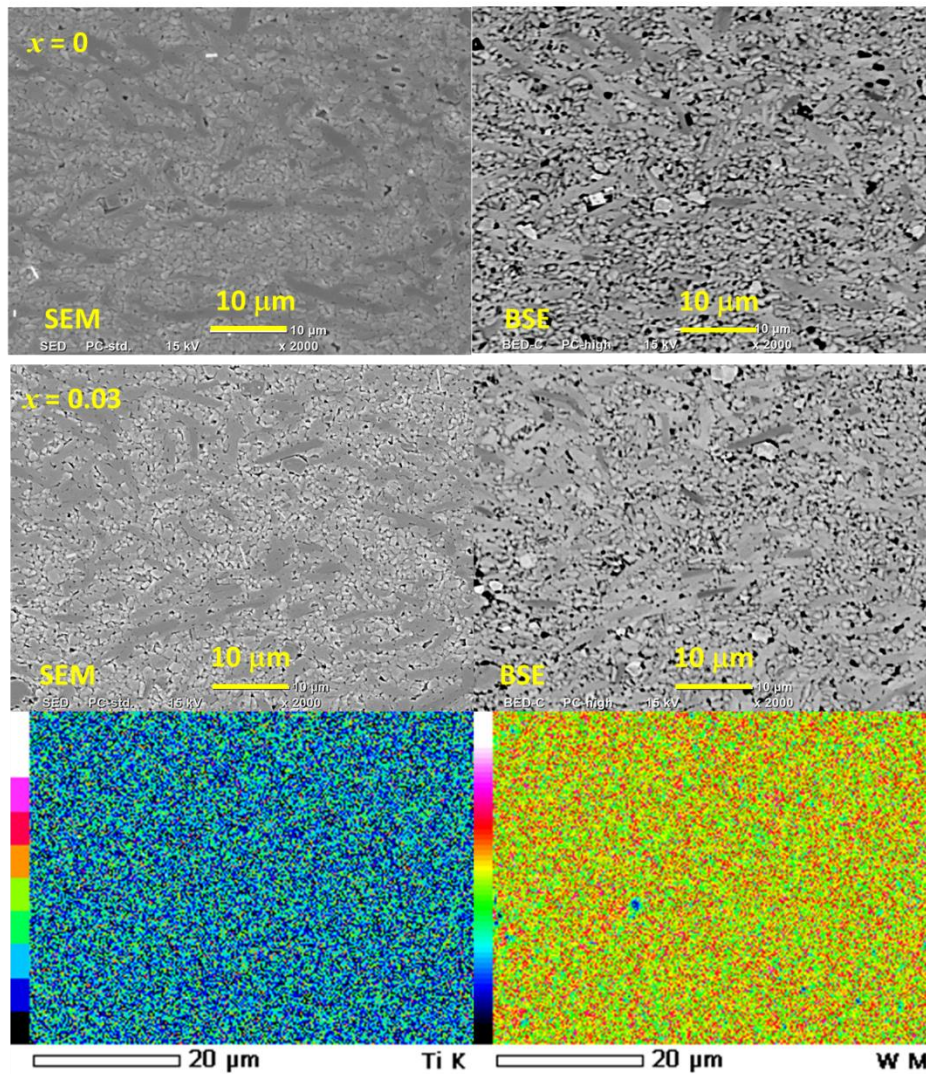
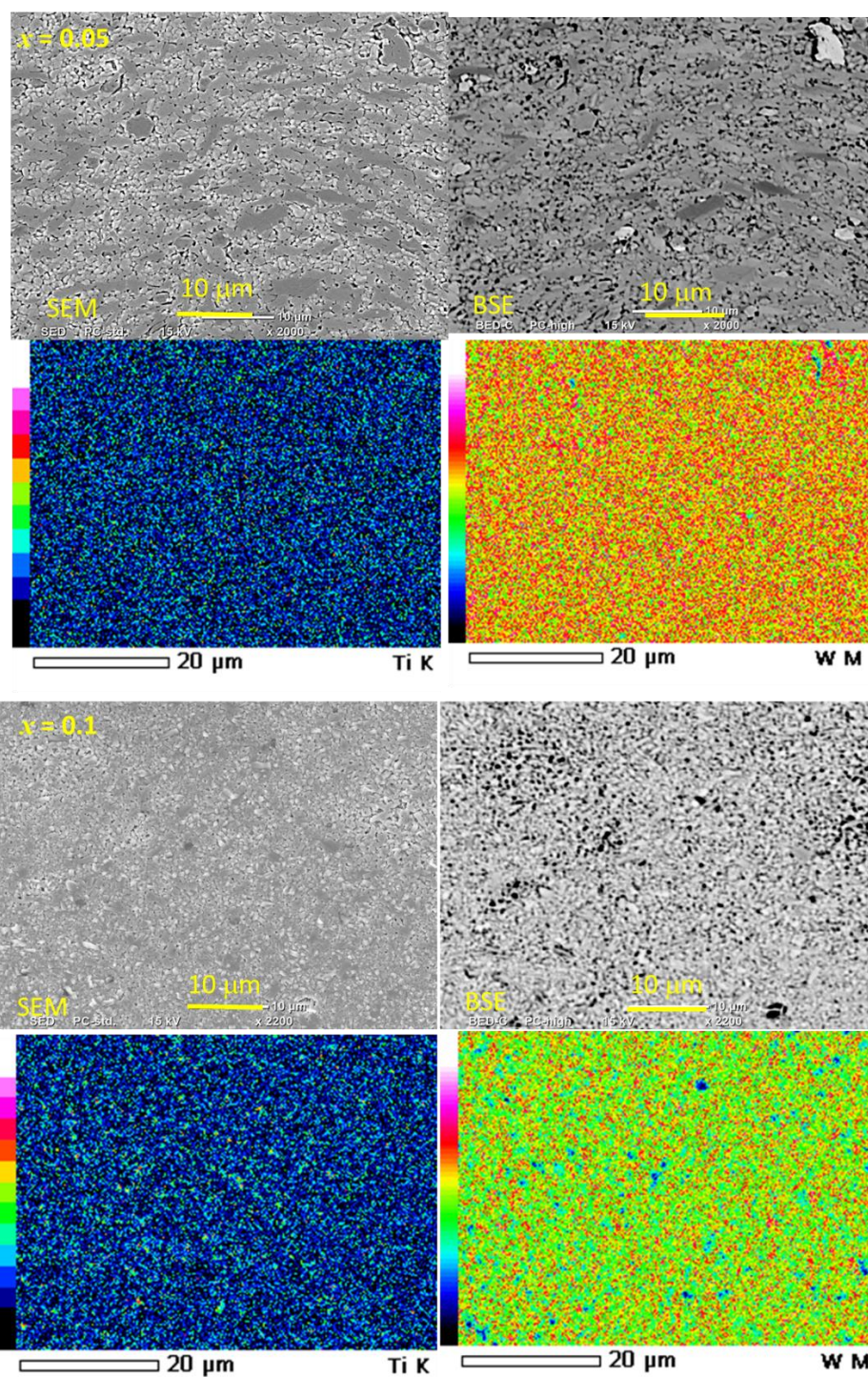


Figure 4.4. Backscattered electron topology images of $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ samples $x = 0.15$, 0.2, 0.25 (a, b, c).



SEM images of polished unetched surfaces of sample with Ti content $0 \leq x \leq 0.1$





The SEM secondary electron images Backscattered electron images, EDS mapping of thermally etched cross sections for for the $(W_{1-x}Ti_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.1$) .

Figure 4.5. Scanning electron microscope images, Backscattered electron images, EDS mapping for the thermally etched cross sections of $(W_{1-x}Ti_x)_{18}O_{49}$ samples ($x = 0.03, 0.05, 0.1$).

Even though the micrographs of samples $x = 0.15, 0.2, 0.25$ suggest the high level of porosity, the Backscattered electron - topology images (Fig. 5.4) of corresponding samples suggest dense natures, which is not contradicted to the measured relative densities. EDS elemental mapping of sample $x = 0.03, 0.05$ and 0.1 (Fig. 5.5) showed random distributions of Ti and W without any segregation, suggesting a good homogeneity of the elemental compositions of the samples. EDS mappings of sample $x = 0.15, 0.2$ and 0.25 (Fig. 5.6) show segregation of unknown WO_y phases mixing among the $(W_{1-x}Ti_x)_{18}O_{49}$ phase. Trace of TiO_2 isolation is also found in sample $x = 0.25$, which is in confirmation with XRD pattern data from Fig 5.2. Chemical compositions of the samples (Table 5.1) with $0 \leq x \leq 0.15$ are close to the stoichiometric composition. The segregation areas in sample $x = 0.2$ and 0.25 had very diverse values for O contents with large variances, implying the existence of multiple suboxide WO_y secondary phases.

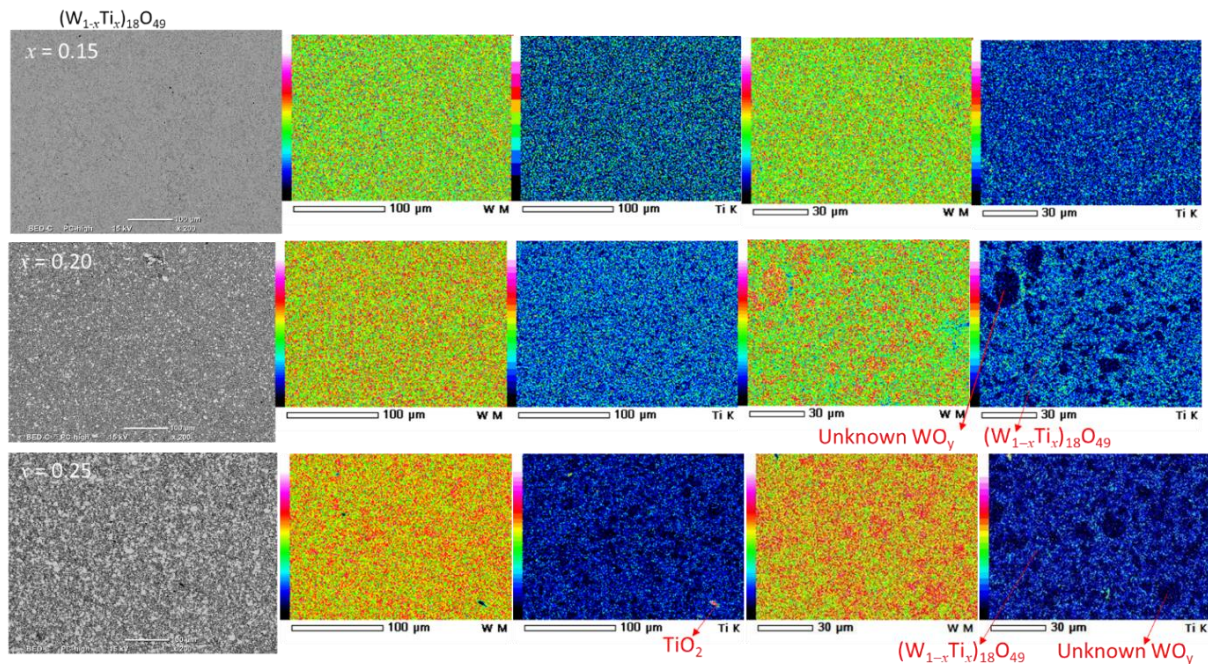


Figure 4.6. Backscattered electron images and EDS mapping for $(W_{1-x}Ti_x)_{18}O_{49}$ samples ($x = 0.15, 0.2, 0.25$).

Table 4.1. Chemical compositions of $(W_{1-x}Ti_x)_{18}O_{49}$ ($0 \leq x \leq 0.25$). The chemical compositions were calculated by assuming the sum of W and Ti being 18, and O being 49. The standard deviation of the composition is given in the parentheses.

$(W_{1-x}Ti_x)_{18}O_{49}$	Ti	W	O
$x = 0$	—	17.8(3)	48.2 (5)
$x = 0.03$	0.5(3)	17.3(5)	48.1 (6)
$x = 0.05$	0.8(4)	16.9(4)	47.9 (7)
$x = 0.1$	1.7(6)	16.0(6)	48.1(7)
$x = 0.15$	2.7(7)	15.5(7)	46.8 (9)
$x = 0.2$ Light areas	4.24 (9)	13.64(8)	47.2 (8)
	Dark Areas	0.1(1)	16.77(5) 50.6 (12)
$x =$ Light Areas	4.9(8)	12.9(8)	44.6 (14)
0.25 Dark areas	0.1(1)	16.89(6)	52.2 (12)

The temperature dependence of the electrical conductivity σ and the Seebeck coefficient S are presented in Fig. 5.7 (a) and (b), respectively. The standard deviation of the electrical conductivity was calculated via Gaussian error propagation method from the standard deviation of the electrical resistivity. The method to determine standard deviation of electrical resistivity and Seebeck coefficient was referred to the work of Wang *et al.*, 2015 on thermoelectric transport properties of n-type compound [172]. The σ values of the sample with $x = 0$

monotonically decreased from $9.2 \times 10^3 \pm 644 \text{ Scm}^{-1}$ to $2.3 \times 10^3 \pm 167 \text{ Scm}^{-1}$ as temperature increased from 300 to 1073 K, showing the metallic behavior. The Seebeck coefficient S was as low as $-22 \pm 1.3 \mu\text{VK}^{-1}$ at room temperature, suggesting the dominating electron carriers, which is consistent with the predicted behavior from Migas *et al* [167]. Focusing on the sample $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ ($0.3 \leq x \leq 0.25$), as shown in Fig 5.7 (a) and (b), σ decreased and $|S|$ increased with increasing x content from 0 to 0.25 both at low and high temperature regions, indicating the reduction in carrier concentration due to the Ti-substitution. $|S|$ was exceptionally enhanced for sample $x = 0.2, 0.25$ being $-128 \pm 7.1 \mu\text{VK}^{-1}$ and $-178.4 \pm 10.5 \mu\text{VK}^{-1}$ at 1073 K respectively. Power factor σS^2 of samples at 323 K constantly decrease as x content increase from $0.43 \pm 0.06 \text{ mWK}^{-2}\text{m}^{-1}$ ($x = 0$) to $0.03 \pm 0.01 \text{ mWK}^{-2}\text{m}^{-1}$ ($x = 0.25$). The uncertainty of σS^2 was calculated referred to Wang., *et al*, 2015 [172] methodology. Due to the compensating relationship between $|S|$ and σ , the σS^2 of sample was improved at higher temperature regime as x content increase from 0 to 0.2 reaching the highest of $0.72 \pm 0.09 \text{ mWK}^{-2}\text{m}^{-1}$ at 1073 K ($x = 0.2$). For sample $x = 0.25$, its exceptionally low σ resulted in overall small σS^2 , insinuating that the domination of unknown phases inhibits its thermoelectric performance. It is worth noting that the measurement did not reach the maximum operation temperature of $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ sample, so the materials will have larger σS^2 at higher temperature. In addition, it was expected that the crystal structure of $\text{W}_{18}\text{O}_{49}$ might result in an anisotropic electrical conductivity due to structural sensitive carrier mobility μ . Nevertheless, the samples prepared with different orientations showed closely matched σ results, suggesting negligible anisotropic effects in sintered polycrystalline samples from the pre-prepare $\text{W}_{18}\text{O}_{49}$ powder in this study.

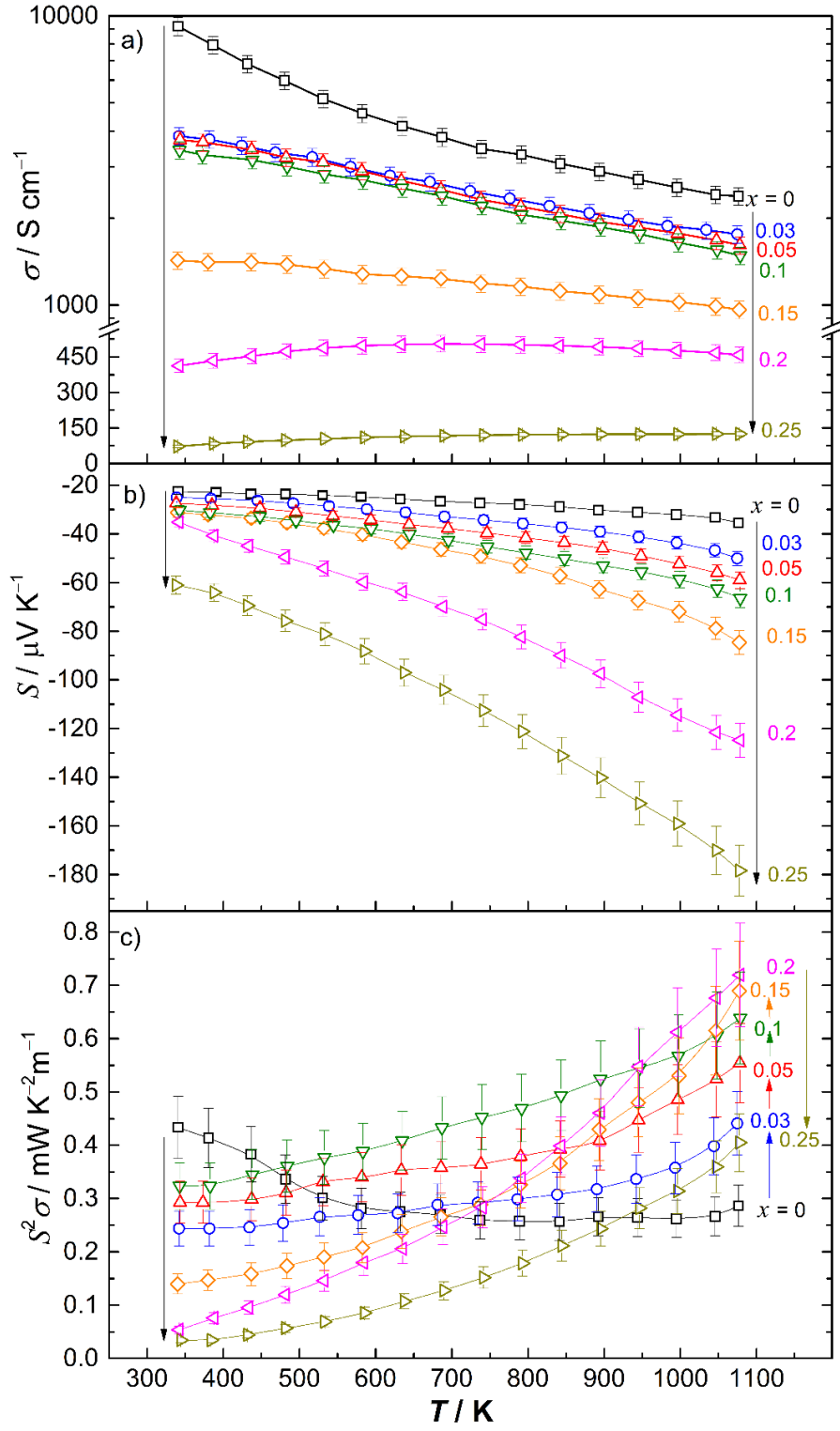


Figure 4.7. Temperature dependence of (a) the electrical conductivity σ , (b) the Seebeck coefficient S , (c) the power factor $S^2\sigma$ of $(W_{1-x}Ti_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.25$).

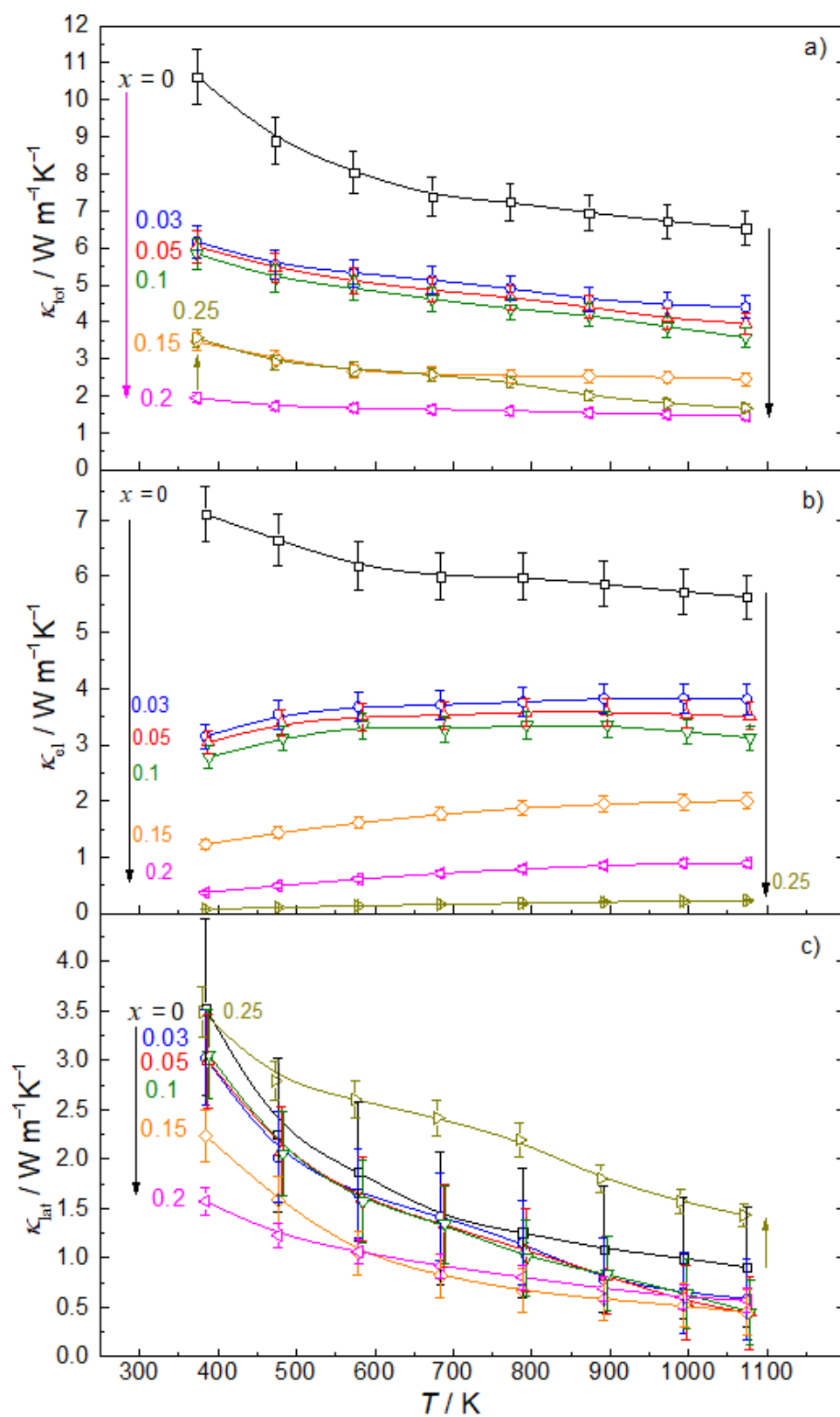


Figure 4.8. Temperature dependence of (a) the total thermal conductivity κ_{tot} , (b) the electronic component of thermal conductivity κ_{el} , and the lattice component of thermal conductivity κ_{lat} for $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ samples ($0 \leq x \leq 0.25$).

The total temperature dependence of the thermal conductivity of $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$ ($0 \leq x \leq 0.25$) is shown in Figure 4.8 (a). The C_p values measured from 300 K to 1073 K was $0.33 - 0.40 \text{ J g}^{-1} \text{ K}^{-1}$, being equivalent to $1351 - 1639 \text{ J mol}^{-1} \text{ K}^{-1}$, reasonably agreed with the specific heat of $1668 \text{ J mol}^{-1} \text{ K}^{-1}$ calculated by the Dulong-Petit law. The uncertainty of thermal diffusivity α and C_p are 2% and 3% respectively, by our instrument's specification, leading to the uncertainty of calculated κ_{tot} being 5%, already taken into account the uncertainty of density value to be 0.4%. The high κ_{tot} value of $10.63 \pm 0.64 \text{ WK}^{-1}\text{m}^{-1}$ for the sample with $x = 0$ reflects its metallic character, with a large contribution from the electronic part κ_{el} . Hence, the κ_{tot} values of the Ti-substituted samples decreased drastically to $1.94 \pm 0.14 \text{ WK}^{-1}\text{m}^{-1}$ ($x = 0.2$) at 373 K, due to the reduction in the carrier concentration. κ_{tot} of $x = 0.25$ sample at 373 K was $3.56 \pm 0.25 \text{ WK}^{-1}\text{m}^{-1}$ higher than those of $x = 0.15$ and 0.2 samples, implying the higher intrinsic thermal conductivity of the unknown phase comparing to those of the base $\text{W}_{18}\text{O}_{49}$ phases.

The lattice component of thermal conductivity was calculated by the equation $\kappa_{\text{lat}} = \kappa_{\text{tot}} - \kappa_{\text{el}}$, with the estimation of electronic component of thermal conductivity $\kappa_{\text{el}} = LT\sigma$ from the Wiedemann-Franz law, and was presented in Fig. 5.8 (b, c). The Lorenz number L was acquired from the equation $L = 1.5 + \exp(-|S|/116) [10^{-8} \text{ W } \Omega \text{ K}^{-2}]$, not the universal value of $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, in consideration of the correlation between L and the increase of the Seebeck coefficient {Formatting Citation}. Uncertainty of κ_{el} was derived from σ , and uncertainty for κ_{lat} was taken as the combine from κ_{tot} and κ_{el} . For the sample with $x = 0$, κ_{lat} became smaller

with increasing temperature down to as low as $0.94 \pm 0.60 \text{ WK}^{-1}\text{m}^{-1}$ at 1073 K, but it was not linearly proportional to T^{-1} . Hence, while the phonon-phonon Umklapp scattering dominates, there are also contributions from other scattering factors. The κ_{lat} values also decreased as the amount of the Ti-substitution increased, reaching the lowest value of $1.57 \pm 0.25 \text{ WK}^{-1}\text{m}^{-1}$ ($x = 0.2$) at 373 K and $0.45 \pm 0.22 \text{ WK}^{-1}\text{m}^{-1}$ ($x = 0.15$) at 1073 K. This is the lowest κ_{lat} value ever reported for all the Magnéli WO_{3-x} phases, even lower than that of the famous crystallographic shear $\text{W}_{20}\text{O}_{58}$ [174]. It is possible that the wide, empty pseudo-hexagonal tunnels running through the $\text{W}_{18}\text{O}_{49}$ structure along the b axis act as natural scattering centers for phonons without affecting charge transportation, resulting in the low $\kappa_{\text{lat}} < 1 \text{ Wm}^{-1}\text{K}^{-1}$. In addition, the co-existence of smaller grains and larger grains in doped sample contribute to lower the κ_{lat} via grain boundary scattering effect. Moreover, as κ_{lat} of sample $x = 0.25$ is larger than those of other samples across all temperature range, confirming the importance of the intrinsic properties of $\text{W}_{18}\text{O}_{49}$ phase. Initially, the uncertainty of κ_{lat} of $\text{W}_{18}\text{O}_{49}$ -based material is as large as the value κ_{lat} itself making the figure unreliable as reported by Kaiser., *et al* 2017 for $\text{WO}_{2.72}$ material [175], due to the limitation of deducing method and the contribution of large uncertainty from the calculation of κ_{el} . Nevertheless, significantly lower σ value in sample $x = 0.15$ and $x = 0.2$ lead to the notable reduction in the standard deviation of both κ_{el} and κ_{lat} , indicating more reliable nature of κ_{lat} value and the real properties of the $\text{W}_{18}\text{O}_{49}$ phase.

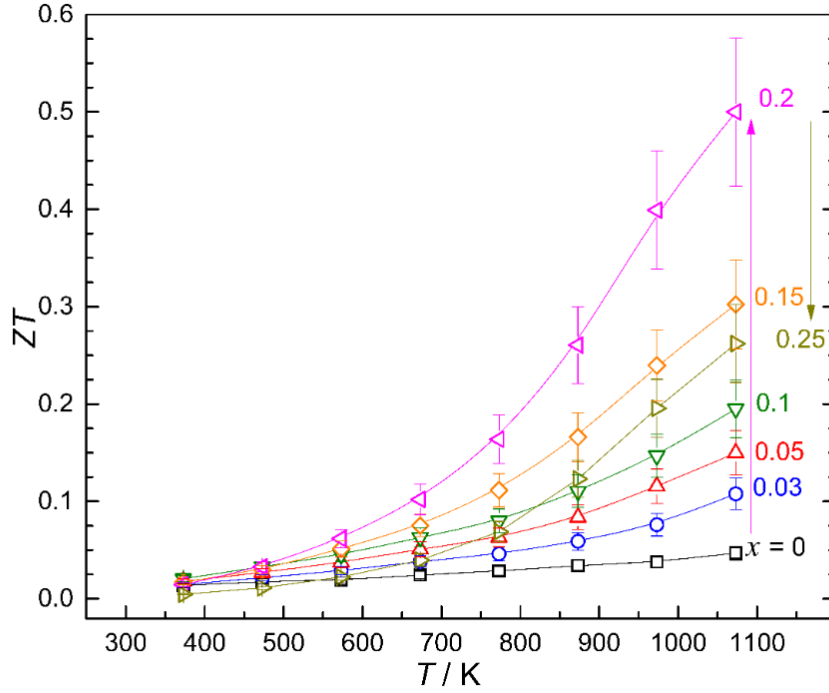


Figure 4.9. Temperature dependence of dimensionless figure of merit ZT for $(W_{1-x}Ti_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.25$)

The dimensionless figure of merit $ZT = S^2\sigma T(\kappa_{el} + \kappa_{lat})^{-1}$ of $(W_{1-x}Ti_x)_{18}O_{49}$ ($0 \leq x \leq 0.25$) was calculated and shown in Figure 4.9. The uncertainty was derived from those of $S^2\sigma$ and κ_{tot} . The highest acquired $ZT = 0.5 \pm 0.08$ at 1073 K for $x = 2$ sample, and for sample without secondary phase $ZT = 0.20 \pm 0.03$ at 1073 K ($x = 0.1$). The thermoelectric enhancement by carrier tuning of this work is limit by the solubility level of Ti, hence the resulting ZT is only mediocre. Assuming that a high enough σ and carrier concentration reduction level without affecting the electronic band structure, it is possible to predict theoretically the thermoelectric performance by using the simple model for non-degenerate n-type semiconductors with broad conduction band and negligible hole conduction as follows [176,177]:

$$S = -\frac{k}{e} \left[\eta - \left(r + \frac{5}{2} \right) \right] \quad (1)$$

$$\sigma = ne\mu \quad (2)$$

$$n = N_v \exp(\eta) \quad (3)$$

where η is the reduced Fermi energy, N_v is the effective density of state, k is the Boltzmann constant, r is a constant scattering parameter, e is the electrical charge of electron, and n is the electron concentration. If the carrier mobility, the density of states, and the conduction mechanism are unchanged regardless of the carrier concentration, the relationship between S and σ can be expressed as $S = -(k/e) \ln \sigma + A$, with A as a constant. It is thereby possible to assume that S is linearly proportional to $\ln \sigma$, and the Jonker-type linear approximation of S and $\ln \sigma$ was plotted in Figure 4.10 (a) for $(W_{1-x}Ti_x)_{18}O_{49}$ sample without secondary phase ($x = 0, 0.03, 0.05, 0.1$). The experimental value of S and σ fitted well with the linear approximation, which ratify the prediction. Consequently, the $S^2\sigma$ values were calculated with respect to the linear dependence of S and $\ln \sigma$ and plotted in Figure 4.10 (b). In addition, the respecting plotted S , σ , $S^2\sigma$ values of sample $x = 0.15, 0.2$ were in close agreement with the prediction. The appearance of secondary phase might have detrimental effect on the Seebeck coefficient of the sample $x = 0.15, 0.2$, leading to the failing out from the prediction relation between S and σ . The predicted maximum $S^2\sigma$ of $0.9 \text{ mWK}^{-2}\text{m}^{-1}$ was obtained at $|S| = 127.63 \text{ } \mu\text{V K}^{-1}$ and $\sigma = 551.92 \text{ Scm}^{-1}$. This $S^2\sigma$ value is almost comparable for the state-of-the-art value of $Zn_{1-x}Al_xO$ by Ohtaki, *et al.* [18] The ZT values were also calculated based on the predicted $S^2\sigma$ and the κ_{el} values calculated as a function of σ where the L value was calculated according to the equation $L = 1.5 + \exp(-|S|/116) [10^{-8} \text{ W } \Omega \text{ K}^{-2}]$, with the κ_{lat} as a constant value of $0.5 \text{ WK}^{-2}\text{m}^{-1}$ taken from the sample with $x = 0.1$. As plotted in Figure 4.10 (c), the highest predicted ZT at 1073 K was 0.96 at $|S| = 192.90 \text{ } \mu\text{V K}^{-1}$ and $\sigma = 198.46 \text{ Scm}^{-1}$. The actual ZT values of sample $x = 0.15, 0.25$ were very close to the prediction. Accordingly, this prediction presents the possibility of enhancing $W_{18}O_{49}$ material thermoelectric performance by carrier concentration

tuning to achieve practical ZT at 1073 K, should a more suitable dopant found, or there is a method to raise Ti solubility limit.

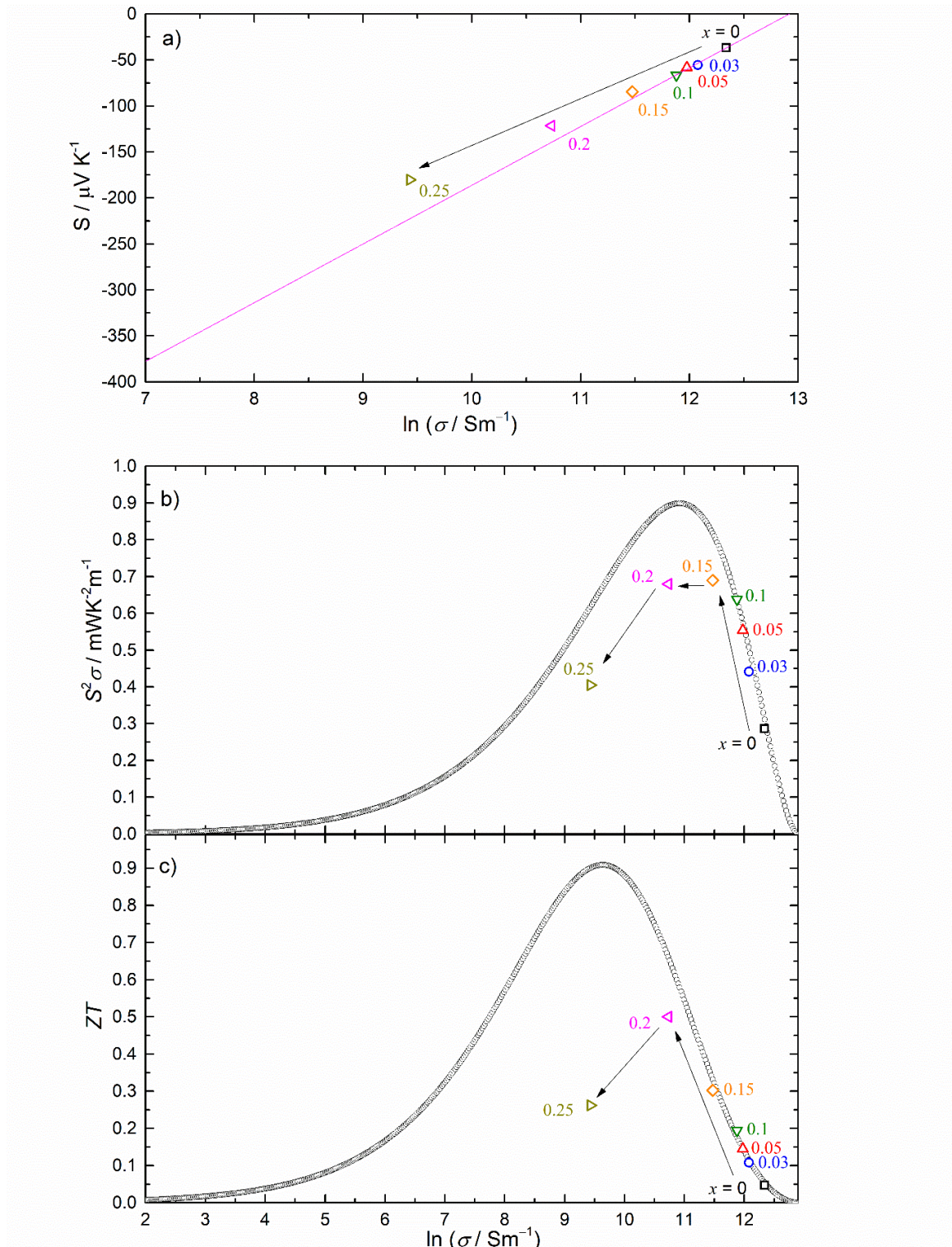


Figure 4.10. (a) Jonker-type linear analysis of the Seebeck coefficient, S , and logarithmic electrical conductivity, $\ln\sigma$, for $(W_{1-x}Ti_x)_{18}O_{49}$ ($x \geq 0$) at 1073 K. The predicted data (magenta solid line) was used to calculate (b) $S^2\sigma$ and (c) ZT . Here, the value of lattice thermal conductivity was assumed to be $0.5 \text{ WK}^{-1}\text{m}^{-1}$.

4.4. Conclusions.

In conclusion, we studied the crystal structure and high-temperature thermoelectric properties of the Magnéli phase of $(W_{1-x}Ti_x)_{18}O_{49}$ ($0 \leq x \leq 0.25$). The undoped sample expressed metallic behavior with large σ and relatively small $|S|$. The Ti-substitution significantly reduced σ , improved $|S|$, eventually improved $S^2\sigma$. Highest $ZT = 0.5 \pm 0.08$ at 1073 K was acquired for $x = 2$ sample, and for sample without secondary phase $ZT = 0.20 \pm 0.03$ at 1073 K ($x = 0.1$). Since the material has higher than 1073 K operation temperature, the ZT values can be expected to be larger at higher temperature. Most of the contribution to κ_{tot} came from κ_{el} , and κ_{lat} was found to be remarkably low as $0.45 \pm 0.22 \text{ WK}^{-1}\text{m}^{-1}$ at 1073 K, which could be intrinsically originated from the void tunnels in the crystal structure. The solubility limit for Ti dopant falls between $x = 0.1$ and $x = 0.15$, which limit the degree performance enhancement by carrier tuning via Ti-doping. The Jonker prediction promise the $W_{18}O_{49}$ -based material better thermoelectric performance with the ZT value as high as 0.9 should there be more suitable dopant or a method to boost Ti solubility limit.

**Chapter 5. Preliminary results on the studies of high
temperature thermoelectric properties of $(W_{1-x}M_x)_{18}O_{49}$ – (M =
Nb, V, Ta)**

5.1. Experimental details

Samples of $(W_{1-x}M_x)_{18}O_{49}$ ($x = 0, 0.05, 0.1, 0.15$), with M being Ta, Nb, V, were synthesized by direct reaction of single metal oxides as starting materials. WO_3 (Kishida Chemical, 99.9%), WO_2 (Wako, 99.9%), and TiO_2 rutile form (Kanto Chemical, 99.9%), were weighed according to the target elemental compositions including oxygen, and mixed by ball milling at 300 rpm for 1 h. The mixtures were then molded into pellets by applying a uniaxial pressure of 100 MPa, sealed in evacuated quartz ampules, and heated to 1073 K taking a period of 8 h, maintained at this temperature for 24 h, cooled to room temperature taking 8 h. After the first heating cycle, the pellets were thoroughly ground, pelletized at 100 MPa and annealed again for an additional 24 h at 1073 K to improve the homogeneity. Subsequently, the pellets were reground and loaded into graphite dies with an inner diameter of 10 mm. The dies were placed in the spark plasma sintering furnace (SPS) PLASMAN CPS-I-03121 (S. S. Alloy). For the SPS treatment, the furnace chamber was evacuated to the pressure of ≤ 10 Pa, and the sample was heated up to 1423 K at a heating rate of 100 K min^{-1} under uniaxial pressure of 50 MPa, maintained for 15 min and the pressure was released, and cooling rate was controlled at 20 K min^{-1} to room temperature. The pellet was detached from the graphite die, the lining carbon paper was peeled off, and the surface of the pellet was polished with SiC abrasive papers to remove all possible carbon contamination. All the samples showed the relative density of approximately 100% of the theoretical density of $W_{18}O_{49}$ ($d_{th} \approx 7.21 \text{ g cm}^{-3}$).

Powder X-ray diffraction (PXRD) data were collected using a Rigaku MiniFlex 600 diffractometer with $Cu \text{ K}\alpha$ radiation within the range of $5^\circ \leq 2\theta \leq 90^\circ$, $\Delta 2\theta = 0.01^\circ$. Surface morphologies and elemental compositions of the sample were studied on a JEOL JCM-6000Plus NeoScope scanning electron microscope (SEM) equipped with energy-dispersive

spectroscopy (EDS). The electrical conductivity σ and Seebeck coefficient S were measured under Ar atmosphere simultaneously by dc four-probe method and temperature differential method, respectively, on an Ozawa Science RZ2001i. The reproducibility of the σ and the S measurements was confirmed by well overlapped results on heating and cooling paths in the range of 300 – 1073K. The thermal diffusivity α and specific heat C_p at 300 – 1073 K were measured simultaneously on Kyoto electronics LFA-502 by laser-flash method under vacuum. The absolute values of C_p were obtained from a comparative method using a molybdenum. The total thermal conductivity was calculated using the relation $\kappa_{\text{tot}} = \alpha C_p d_s$, where d_s is the sample density.

For microstructure observation, all samples (of size approximate 0.25 cm² and thickness from 2 – 3mm) were polished by abrasive SiC papers with grit size gradually increasing from 320 to 2000. Then the samples were polished by 3 μm diamond suspension to achieve finer condition and remove any damage from the previous polishing steps. The samples were then sonicated in acetone and deionized water for 15 mins each to discard any diamond and contamination residue. After the polishing process, the samples underwent thermal etching process, for grain boundary revealing, in Ar atmosphere at 1000°C within 1 hour with heating and cooling rate of 100°C/h.

5.2. Results and discussion

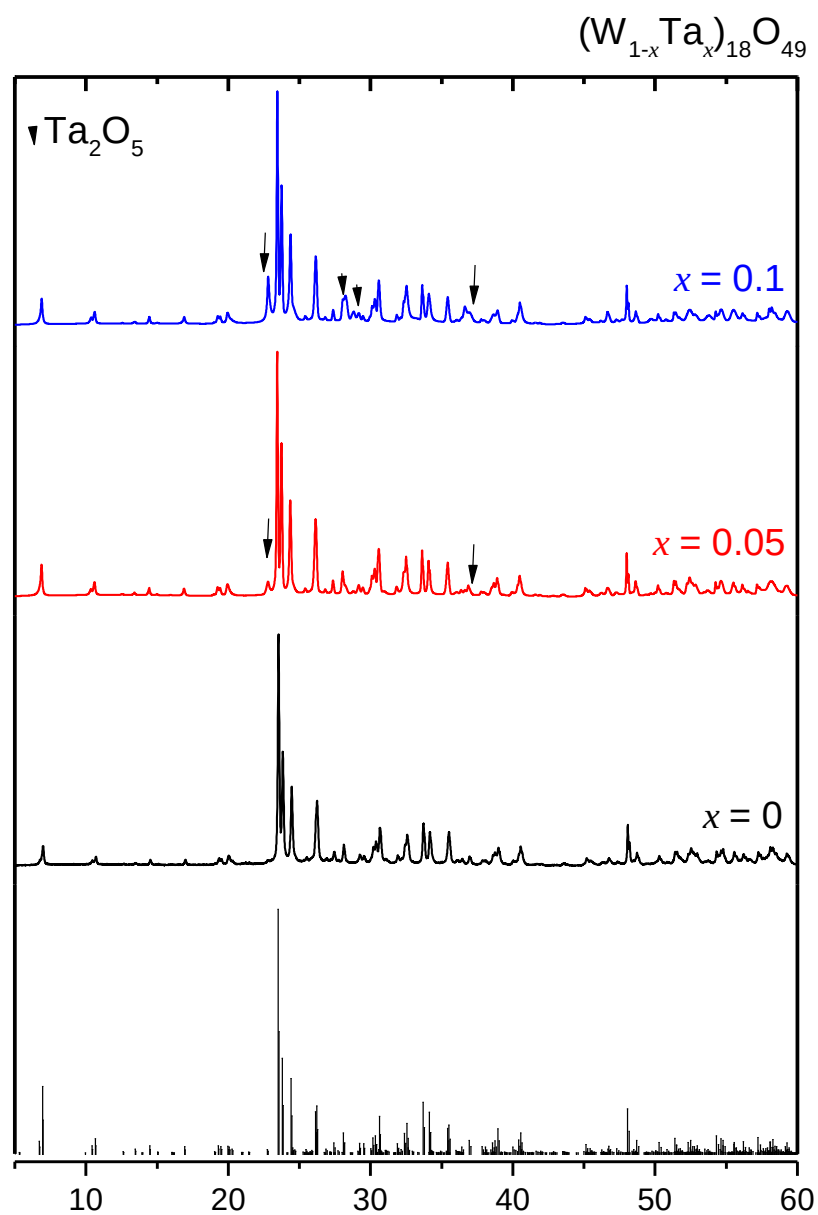


Figure 5.1 Powder XRD patterns for sintered $(W_{1-x}Ta_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.15$)

Table 5.1. The lattice parameters of the $W_{18}O_{49}$ phase for $(W_{1-x}Ta_x)_{18}O_{49}$ samples

$(W_{1-x}Ta_x)_{18}O_{49}$	a (ang.)	b (ang.)	c (ang.)
0	18.031	3.782	14.331

0.05	18.3161	3.7824	14.0290
0.1	18.3123	3.7825	14.0249
0.15	18.3133	3.7824	14.0260

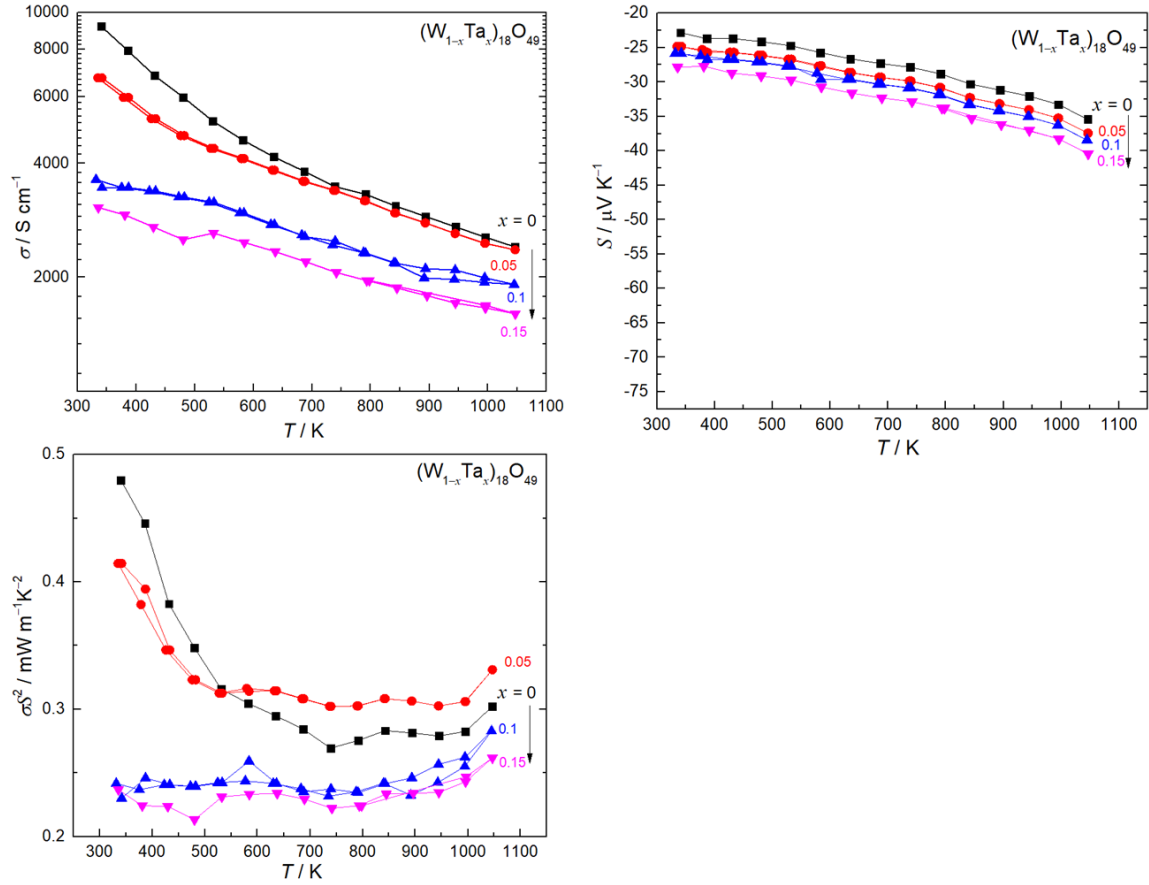


Figure 5.2. Temperature dependence of the electrical conductivity σ , the Seebeck coefficient S , the power factor $S^2\sigma$ of $(W_{1-x}Ta_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.15$).

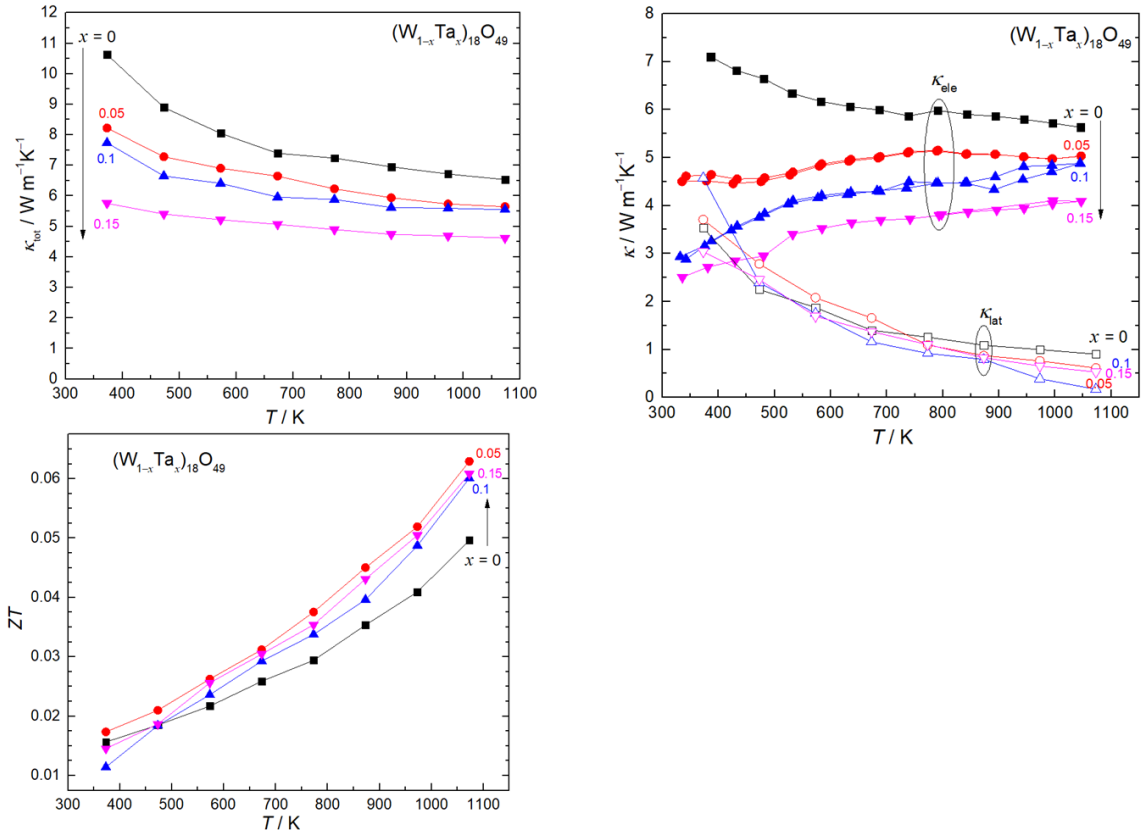


Figure 5.3. Temperature dependence of the total thermal conductivity κ_{tot} , the electronic component of thermal conductivity κ_{el} , the lattice component of thermal conductivity κ_{lat} , and the ZT value for $(\text{W}_{1-x}\text{Ta}_x)_{18}\text{O}_{49}$ samples ($0 \leq x \leq 0.25$).

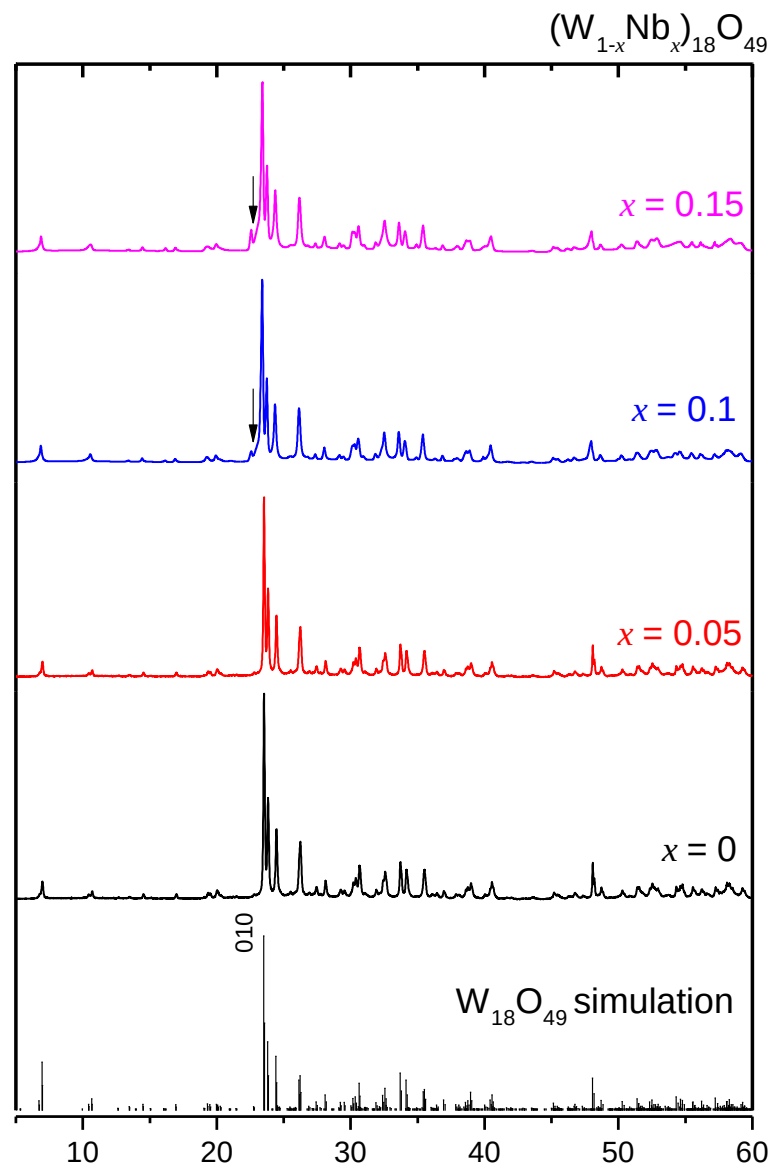


Figure 5.4. Powder XRD patterns for sintered $(W_{1-x}Nb_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.15$)

Table 5.2. The lattice parameters of the $W_{18}O_{49}$ phase for $(W_{1-x}Nb_x)_{18}O_{49}$ samples.

$(W_{1-x}Nb_x)_{18}O_{49}$	a (ang.)	b (ang.)	c (ang.)
0	18.031	3.782	14.331
0.05	18.3209	3.7901	14.0321

0.1	18.3028	3.7903	14.0165
0.15	18.3112	3.7912	14.0242

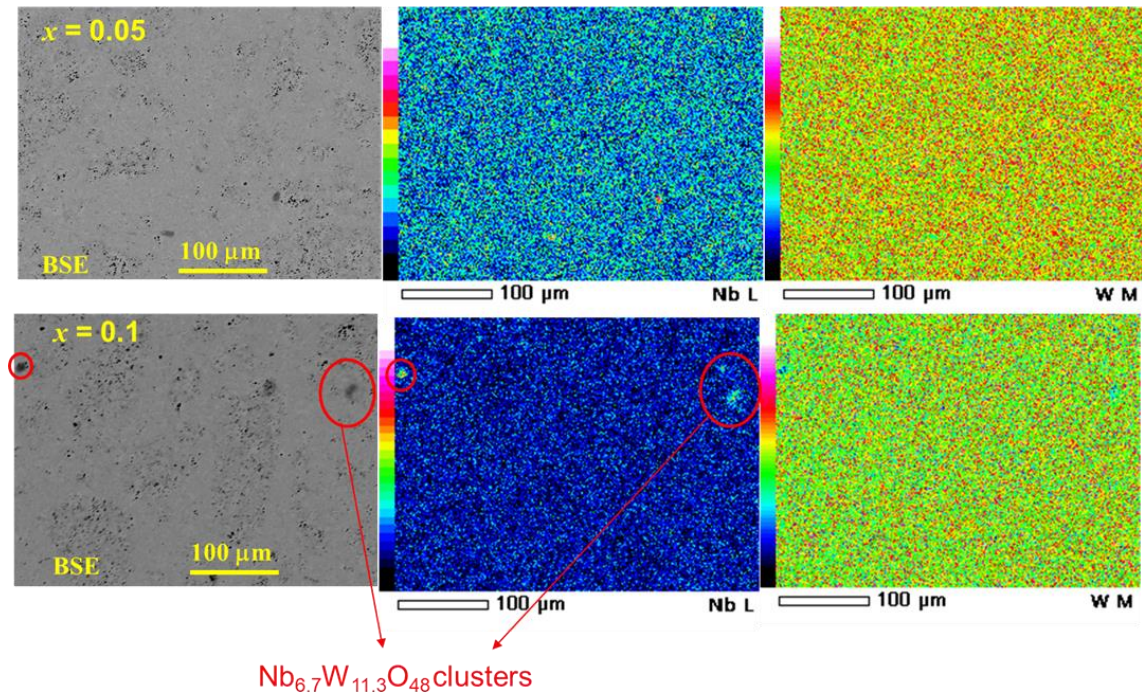


Figure 5.5. BSE and EDS mapping results of $(W_{1-x}Nb_x)_{18}O_{49}$.

Table 5.3. Chemical compositions of $(W_{1-x}Nb_x)_{18}O_{49}$ ($0 \leq x \leq 0.1$). The chemical compositions were calculated by assuming the sum of W and Ti being 18, and O being 49. The standard deviation of the composition is given in the parentheses.

$(W_{1-x}Nb_x)_{18}O_{49}$	Nb	W	O
0.05	0.9(6)	16.6(7)	47.9 (7)
0.1	1.9(8)	15.7(6)	48.1(7)

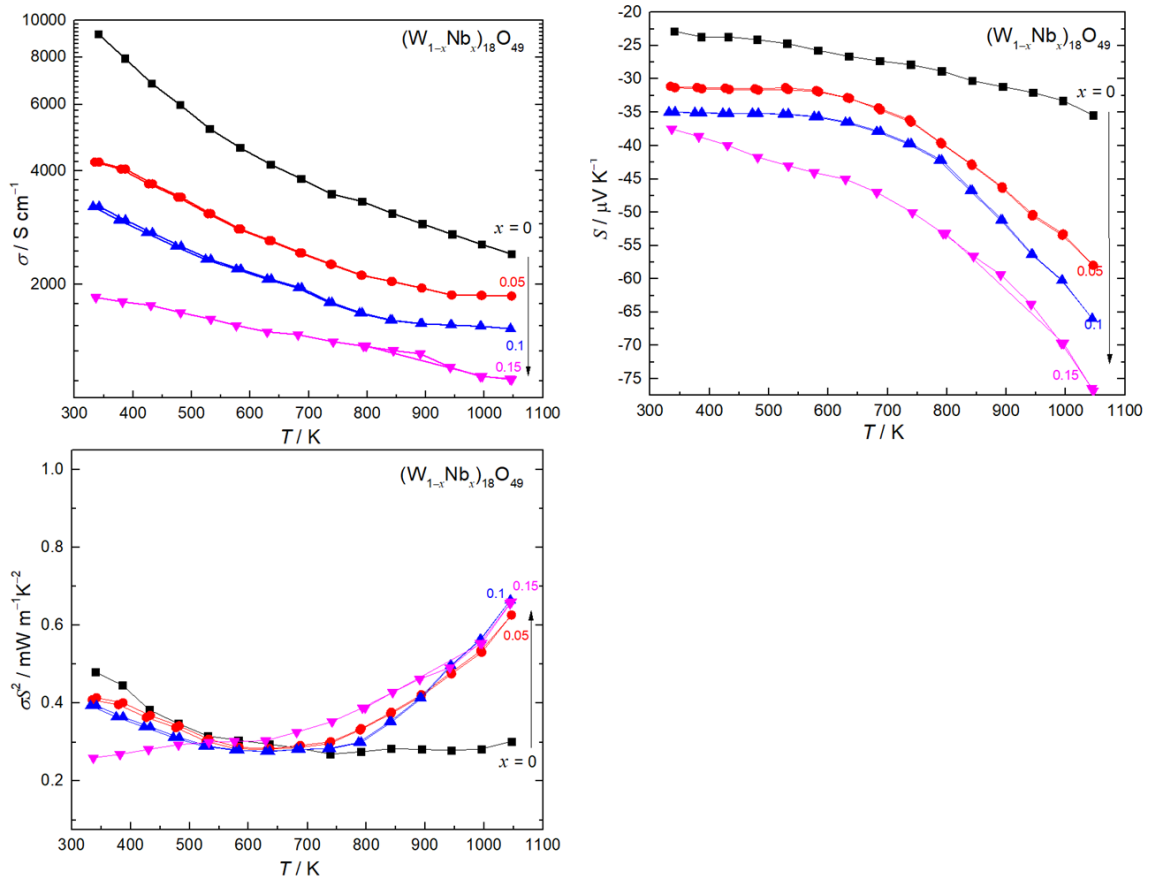


Figure 5.6. Temperature dependence of the electrical conductivity σ , the Seebeck coefficient S , the power factor $S^2\sigma$ of $(W_{1-x}Nb_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.15$).

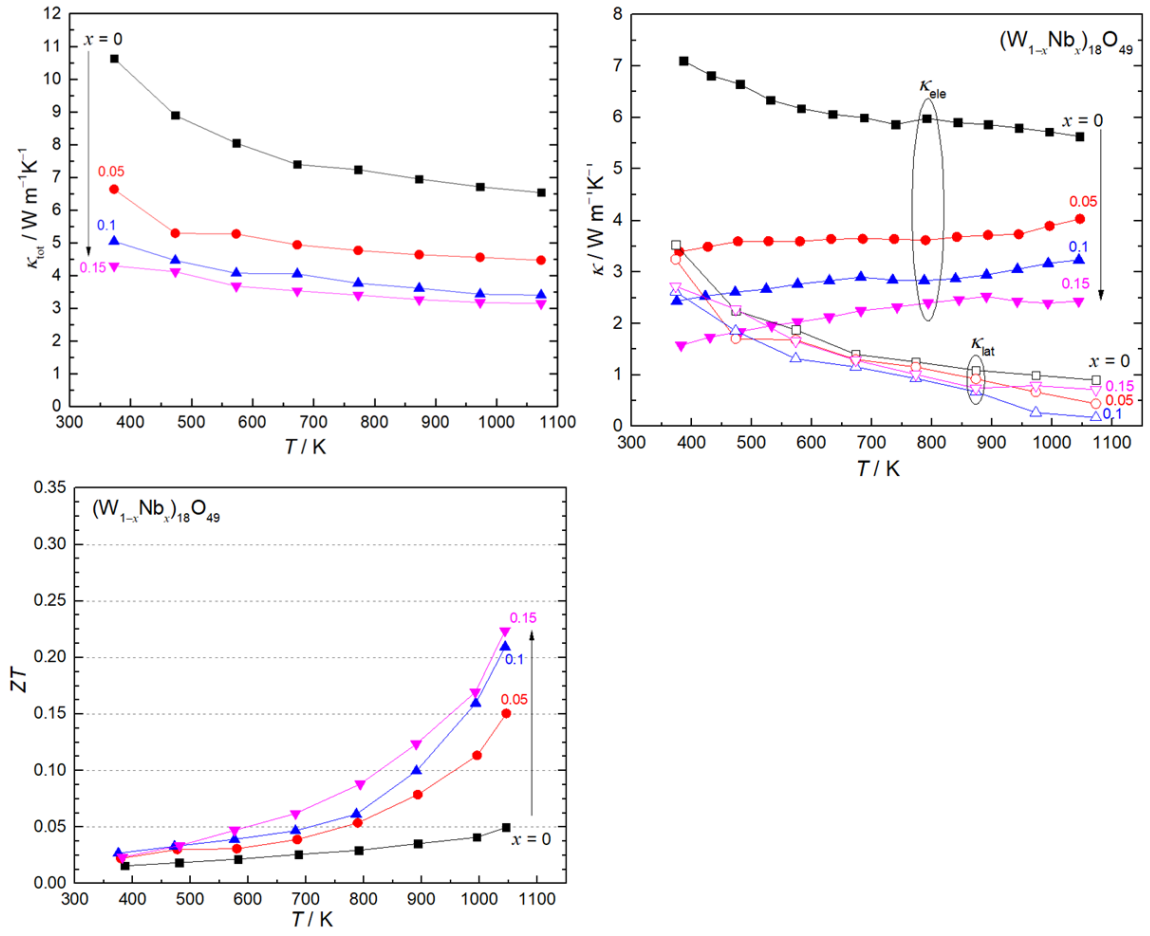


Figure 5.7. Temperature dependence of the total thermal conductivity κ_{tot} , the electronic component of thermal conductivity κ_{el} , the lattice component of thermal conductivity κ_{lat} , and the ZT value for $(\text{W}_{1-x}\text{Nb}_x)_{18}\text{O}_{49}$ samples ($0 \leq x \leq 0.5$)

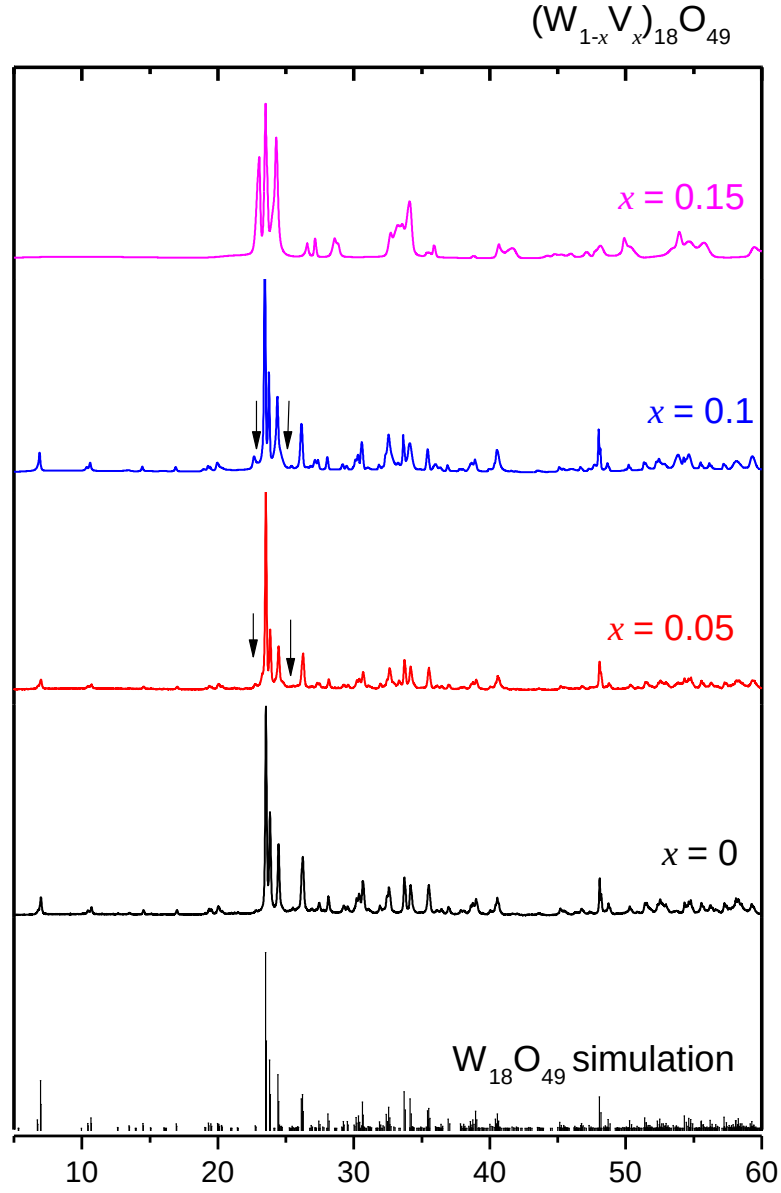


Figure 5.8. Powder XRD patterns for sintered $(W_{1-x}V_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.15$)

Table 5.4. The lattice parameters of the $W_{18}O_{49}$ phase for $(W_{1-x}V_x)_{18}O_{49}$ samples

$(W_{1-x}V_x)_{18}O_{49}$	a (ang.)	b (ang.)	c (ang.)
0	18.031	3.7825	14.3312
0.05	18.310	3.7823	14.0213

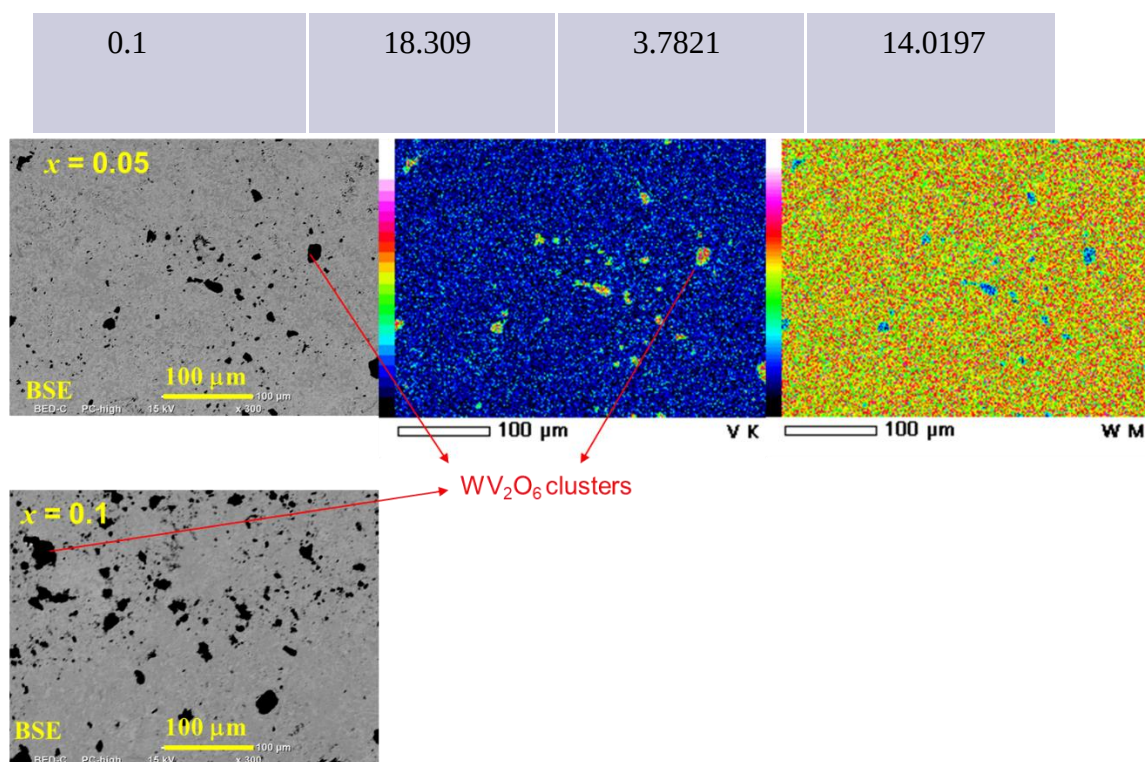


Figure 5.9. BSE and EDS mapping results of $(W_{1-x}V_x)_{18}O_{49}$

Table 5.5. Chemical compositions of the clusters in the sample $(W_{1-x}V_x)_{18}O_{49}$ ($x = 0.05$).

	Atm %
V	12.18 (4)
W	23.8 (6)
O	64.02 (6)

Table 5.6. Chemical compositions of main phase in the sample $(W_{1-x}V_x)_{18}O_{49}$ ($x = 0.05$)

	Atm %

V	0.5 (1)
W	28.3 (7)
O	70.6 (12)

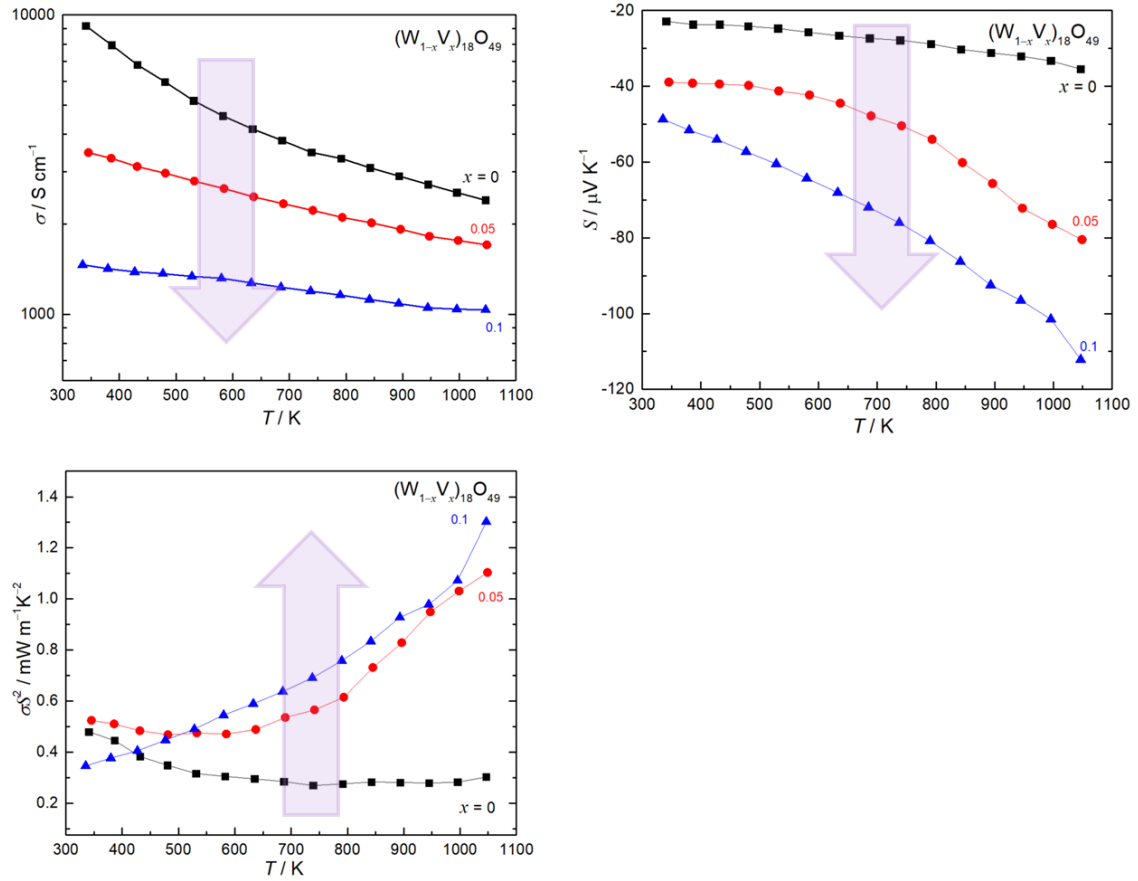


Figure 5.10. Temperature dependence of the electrical conductivity σ , the Seebeck coefficient S , the power factor $S^2\sigma$ of $(W_{1-x}V_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.1$).

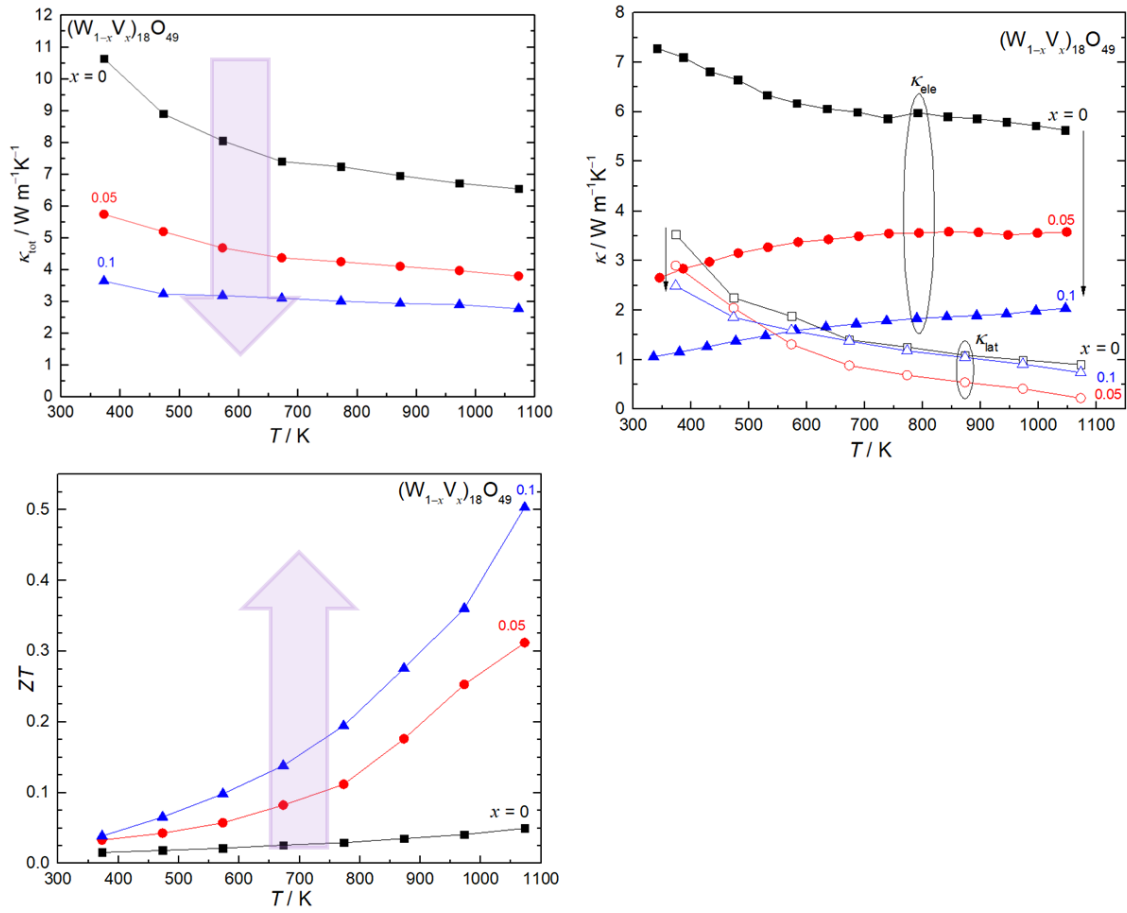


Figure 5.11. Temperature dependence of the total thermal conductivity κ_{tot} , the electronic component of thermal conductivity κ_{el} , the lattice component of thermal conductivity κ_{lat} , and the ZT value for $(W_{1-x}V_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.1$)

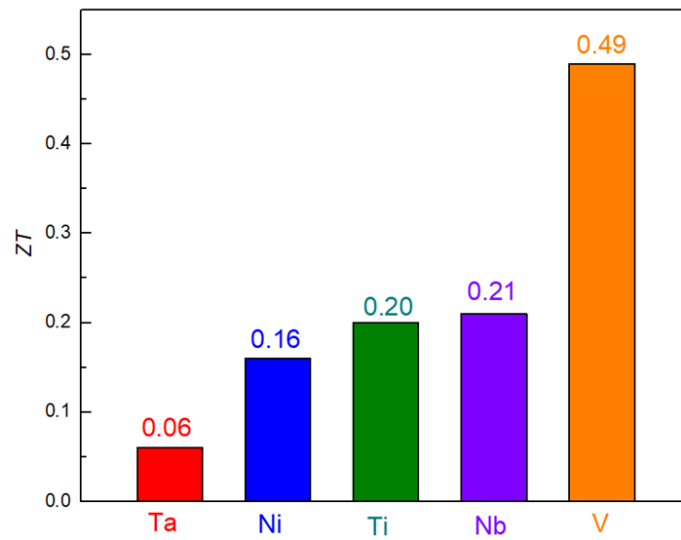


Figure 5.12. Maximum ZT value at 1073K for comparison of thermoelectric performance of $W_{18}O_{49}$ – based materials with different dopants at 10 atomic percentage.

All Ta doped sample's patterns show secondary phase of Ta_2O_5 . Suspect that doping was unsuccessful. Ta_2O_5 and $W_{18}O_{49}$ phases are completely separated. There is no secondary phase observed in the XRD pattern of $(W_{1-x}Nb_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.15$), indicating the possibility of successful doping. Sign of WV_2O_6 was observed in all $(W_{1-x}V_x)_{18}O_{49}$ samples ($0 \leq x \leq 0.1$). With sample with V content $x = 0.15$, totally different pattern was observed, corresponding to the failure in the synthesis of target materials. Lattice parameters of all sample main $W_{18}O_{49}$ phase rarely changed, since the $W_{18}O_{49}$ is large with low packing density, allows possibility for substitutions. EDS and BES analysis confirmed the separation of Ta_2O_5 and $W_{18}O_{49}$ in Ta doped samples. In Nb doped samples, Nb elements were uniformly distributed across observed surface, with consistent chemical composition analysis, confirmed success doping effect. In the other hand, EDS and BSE analysis in V doped sample show clusters of WV_2O_6 phase, confirmed the finding from XRD results. It is suspect that the Vanadium oxide reacted with Tungsten oxide, and the favored products was WV_2O_6 phase, not the thermal diffusion effect.

For all doped sample, σ was decreased due to either substitution effects or the presents of alien grains and secondary phase structures. $|S|$ were increase for Nb and V doped samples, especially in V doped samples. Ta doped samples yield disappointed result due to the doping effects did not happen, and the presence of Ta_2O_5 clusters is detrimental to both σ and S properties. Thermal conductivity was reduced due to the reduction of σ , equivalent to the lower carrier concentration and smaller κ_{ele} . The lattice component of thermal conductivity in all samples was also slightly reduced, due to enhanced scattering effects from defects and secondary grains structures. The ZT value was improved for Nb and V doped samples,

remarkably in V doped samples for its high Power factor. However, more studies are needed to interpret the meaning of large $|S|$ in this materials.

5.3. Conclusion

More works on the micro-structure of V doped and Nb doped $W_{18}O_{49}$ are required to understand the effect on TE properties. Carrier concentration measurement is needed to confirm the tuning effect. Ta doping is completely unsuccessful. V doped samples show significantly higher Seebeck coefficient in compared with Ti doped and Nb doped samples at the same atomic percentage, which is interesting, and needed more investigation.

Chapter 6. Conclusions and Developments

6.1. Synthesis and doping routes for Tungsten suboxide with adaptive structures.

Even though the tungsten oxides phases WO_x with ($2 \leq x \leq 3$) can be mathematically classified as a series of crystallographic structures, the synthesis of the single phase is still challenging due to the tendency of thermodynamic transformation to a more stable phase, and the influence of the oxygen partial pressure. Moreover, the CS phase $W_{20}O_{58}$ also has the tendency of breaking down into the mixture of $W_{18}O_{49} + WO_3$. Nevertheless, the PC phase $W_{18}O_{49}$ is stable and suitable for doping using diffusion mechanism with dopants.

Manipulating the electrical properties of tungsten suboxides by varying the ratio of O and W was not successful because the samples could not be isolated as a single-phase material. Ni doping to lower the electrical conductivity and enhance thermoelectric performance was unsuccessful because of the more thermodynamically stable $NiWO_4$ phase. Ta and Ti have proven to be good dopant candidate for improving the thermoelectric performance of the $W_{18}O_{49}$ -base materials.

6.2. Direct synthesis by SPS and the anisotropic thermoelectric properties of $W_{18}O_{49}$.

Apart from synthesis by solid-state reaction in vacuum, $W_{18}O_{49}$ materials could be synthesized directly by reactive SPS method where the reaction and formation of the phase took place in less than 15 minutes. As the result, the process significantly improved the synthesis efficiency of polycrystalline $W_{18}O_{49}$ monolithic ceramic.

In addition, anisotropic thermoelectric properties of $W_{18}O_{49}$ could be partially influenced by the increment of applied pressure during the SPS. The ordered orientation of crystallite

under high pressure offers an intrinsically low thermal conductivity materials, despite its metallic nature. Theoretically, anisotropy could even be significantly strengthened by applying even higher uniaxial pressure, thus, ZT was enhanced by employing this technique to 0.08 at 1073 K under sintered pressure of 50 MPa in comparison with the ZT of 0.06 of the less oriented samples due to the much lower thermal conductivity. This finding could open pathway for a new type of very anisotropic or layer by layer thermoelectric materials. Hypothetically, since the material could be synthesized as nano rod and nano tube formed, the prospect of using very anisotropic starting materials to enhance the anisotropy or layer by layer materials is possible. Moreover, the high electrical properties and low intrinsic lattice thermal conductivity could promise good thermoelectric materials synthesized via quantum confinement process.

6.3. Low thermal conductivity with enhance Seebeck coefficient, power factor and ZT value in $(W_{1-x}Ti_x)_{18}O_{49}$ material.

Samples of $(W_{1-x}Ti_x)_{18}O_{49}$ ($x = 0, 0.03, 0.05, 0.1$) were synthesized by direct solid state reaction of single metal oxides (WO_3 , WO_2 , and TiO_2 rutile form) in vacuum followed by densification via spark plasma sintering method. The PXRD patterns of all samples match the $W_{18}O_{49}$ simulation structure without any observable Ti-based phase or secondary phase. The lattice parameters of Ti-substituted samples are within 0.1% difference from those of the pure sample. The backscattered electron images showed no sign of secondary phase, and the EDS elemental mapping showed random distributions of Ti and W without any segregation, suggesting a good homogeneity of the elemental compositions of the samples.

The samples expressed metallic behavior with large σ and relatively small $|S|$. The Ti-substitution significantly reduced σ , improved $|S|$, and enhanced $S^2\sigma$. However, the high κ values limited the highest acquired ZT as 0.2 at 1073 K. Most of the contribution to κ came from κ_{el} , and κ_{lat} was found to be remarkably low as $0.49 \text{ Wm}^{-1}\text{K}^{-1}$ at 1073 K, which could be

originated from the void tunnels in the crystal structure. Switching the electrically conductive behavior of $(W_{1-x}Ti_x)_{18}O_{49}$ material with small thermal conductivity and significantly improved ZT

The added amount of TiO_2 in the precursor was pushed over the solubility limit in $W_{18}O_{49}$. The samples were no longer monophasic with the appearance of secondary $W_{20}O_{58}$ phase. However, the coexistence of the two phases was stable due to the compatibility of the two structures, indicating a composite-material possibility. The thermal conductivity was significantly reduced and ZT value was boosted to 0.5 at 1073 K for sample $x = 0.2$.

In addition, the switching of electrically conductive behavior was also observed for sample $x = 0.2$ where it is no longer metallic. As the contribution of electronic thermal conductivity was no longer dominant, the intrinsic low lattice thermal conductivity of $W_{18}O_{49}$ was confirmed and is superior to the crystallographic shear structure $W_{20}O_{58}$ at high temperature regime. The lattice thermal conductivity is as low as 0.5 W/mK at 1073 K is remarkable, which assumingly originated from the tunnel structures $W_{18}O_{49}$ phase. The switching behavior also confirmed the prediction by Migas et al [120] about the ability to manipulate carrier concentration in $W_{18}O_{49}$ material.

Furthermore, WO_2 has been shown to be critical to facilitate the forming of the suboxide tungsten phase, where the sample $x = 0.28$, without WO_2 as the starting materials, did not show reactions between WO_3 and TiO_2 powders. The sample $x = 0.25$ with high concentration of $W_{20}O_{58}$ phase showed very inferior properties both in electrical conductivity and thermal conductivity in comparison to samples with completely dominate $W_{18}O_{49}$ phase, indicating $W_{18}O_{49}$ as a more promising candidate for thermoelectric applications.

6.4. Outlook for further development and future work

The $W_{18}O_{49}$ based materials exhibited remarkably low lattice thermal conductivity with very high electrical conductivity in comparing to other n-type oxide materials. The drawback is the small Seebeck coefficient which eventually lead to the highest achievable ZT of 0.5 at 1073 K. As the basic requirement for real thermoelectric application is ZT higher than 1, the $W_{18}O_{49}$ based materials needs significant improvements in order to be practical. Since the intrinsic lattice thermal conductivity is the advantage of this materials, works to enhance Seebeck coefficient are critical.

Furthermore, Seebeck coefficient could be substantially increased via quantum confinement technique. In addition, enhanced anisotropic properties and the layer by layer material synthesis have not been elucidated, and could be highly promising.

Moreover, the promising results of $W_{18}O_{49}$ -based materials have revealed possibilities for oxide with adaptive structures. Many other oxide systems also possess adaptive structure such as the Tungsten Bronze system that has yet been explored for thermoelectric application. With the depleting situation of fossil fuels and the increasing of waste heat, the quests for a practically industrial thermoelectric materials have never been so urgent. The never-ending exploration for a new, better and more advanced material is always the top priority.

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List of publications.

Peer-reviewed papers:

- [1] N.Q.M. Tran, M. Ohtaki, K. Suekuni, High temperature thermoelectric performance of $(W_{1-x}Ti_x)_{18}O_{49}$, Journal of European Ceramic Society, (accepted 12, 2021)
- [2] N.Q.M. Tran, M. Ohtaki, K. Suekuni, Rapid Synthesis of $W_{18}O_{49}$ via Reactive Spark Plasma Sintering with Controlled Anisotropic Thermoelectric Properties, Evergreen, 02 (2021) 344-350.
- [3] D. Van Hoang, A.T. Thanh Pham, H.K. Thi Ta, T.H. Nguyen, N.K. Pham, L.T. Hoa, V.C. Tran, O. Michitaka, Q.M. Nhat Tran, J.-H. Park, J.-K. Lee, S.-D. Park, T.-S. Ju, H. Park, S. Park, T.B. Phan, J. Alloys Compd. 844 (2020) 156119.
- [4] D.L. Bui, H.T. Le, H.K. Nguyen, K. Suekuni, K. Hashikuni, N.Q.M. Tran, K. Wojciech, M. Ohtaki, Thermoelectric Quaternary Sulfide $Cu_{2+x}Zn_{1-x}SnS_4$ ($x = 0-0.3$): Effects of Cu Substitution for Zn, Materials Science & Engineering B, 272 (2021) 115353.

Conference presentations

- [1] N.Q.M. Tran, M. Ohtaki, K. Suekuni, Selective synthesis of $WO_{2.72}$ penta-columnar phase and its reduced lattice thermal conductivity at high temperature.
Part of: Proceedings of the 38th International Conference on Thermoelectrics and The 4th Asian Conference on Thermoelectrics, 2019.
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(Poster)
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