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<https://doi.org/10.5109/7157998>

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出版情報 : Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 9, pp.334-342, 2023-10-19. 九州大学大学院総合理工学府

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## Exploring the Magnéli Phase of Transition Metal Oxides: A Promising Frontier for Thermoelectric Advancements

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**Abstract:** Thermoelectric materials convert heat energy into electrical energy. They have the potential to be used in a variety of applications, including power generation, waste heat recovery, and temperature control. Several transition metal suboxides, also known as Magnéli phases, are a promising class of thermoelectric materials because of their high electrical conductivity, low thermal conductivity, and chemical stability. In this review article, we discuss the Magnéli phase of five different transition metal suboxides: titanium suboxide ( $TiO_x$ ), tungsten suboxide ( $WO_x$ ), molybdenum suboxide ( $MoO_x$ ), vanadium suboxide ( $VO_x$ ), and niobium suboxide ( $NbO_x$ ). We focus on their crystal structure, electrical and thermal properties, and potential applications as thermoelectric materials. We conclude that the Magnéli phases have the potential to be high-performance thermoelectric materials. However, further research is needed to optimize their properties and develop new synthesis methods.

**Keywords:** thermoelectric, Magnéli phase, transition metal suboxides

### 1. Introduction:

Renewable energy resources and energy-efficient technologies are important for the future energy revolution. Thermoelectric technology allows for direct conversion of heat energy into electrical energy. The thermoelectric effect is used in thermoelectric modules, which are assembled into thermoelectric generators. Although thermoelectric generators have proven to be reliable in the past, affordable and non-toxic materials are required to expand their role in the future [1]. In 1821, the Seebeck effect was discovered, which creates an electromotive force in a circuit when there is a temperature difference at the joint of two metals. The generated current and electromotive force are related to this phenomenon. The voltage difference ( $\Delta V$ ) increases with the temperature difference ( $\Delta T$ ) between metal joints. The Seebeck coefficient is a property-based constant that varies among materials, with metals having a low coefficient of about several  $\mu V/K$  and semiconductors having a high coefficient of about 200  $\mu V/K$  [2].

The Seebeck coefficient ( $\alpha$ ) is defined as

$$\alpha = \frac{\Delta V}{\Delta T} \quad (1)$$

where  $\Delta V$  represents voltage difference in volts, while  $\Delta T$  represents temperature difference in Kelvin. The performance of a material is described by the dimensionless quantity called the figure of merit ( $ZT$ ), which reflects the requirements for a good thermoelectric material. The challenge in thermoelectric research since the late 50s has been to increase  $ZT$  of materials which

includes both electrical and thermal properties, as shown in equation (2).

$$zT = \frac{\alpha^2 \sigma}{k} T \quad (2)$$

A perfect thermoelectric material has glass-like thermal conductivity and crystal-like electronic transport capabilities, satisfying the idea of a "phonon-glass electron-crystal" described by Slack [3].

Another property is called thermal conductivity ( $k$ ) which is caused by lattice vibrations (phonons) and heat-carrying charge carriers. It can be described as

$$k = k_{lat} + k_{el} \quad (3)$$

which  $k_{lat}$  is the lattice thermal conductivity and  $k_{el}$  is the electronic thermal conductivity.

The  $k_{el}$  can be calculated with the Wiedemann-Franz law stating that the ratio of the electronic part of thermal conductivity ( $k_{el}$ ) to electrical conductivity ( $\sigma$ ) in a metal is proportional to temperature ( $T$ ) [4].

$$k_{el} = L\sigma T \quad (4)$$

Theoretically, the proportionality constant  $L$ , known as the Lorenz number, is equal to

$$L = \frac{k}{\sigma T} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} \text{ V}^2 \text{K}^{-2} \quad (5)$$

where  $k_B$  is Boltzmann's constant, and  $e$  is the elementary charge. The Wiedemann-Franz law shows that the ratio of thermal conductivity to electrical conductivity,  $\kappa/\sigma$ , is constant for different metals under the same temperature [5].

Thermoelectric oxides are gaining attention for their stability, cost-effectiveness, and eco-friendliness. They offer the potential for high-temperature applications and can convert thermal gradients into electricity [6]. Layered cobaltite like  $\text{Na}_x\text{CoO}_2$  and  $\text{Ca}_3\text{Co}_4\text{O}_9$  [7] as well as other families of thermoelectric oxides including zinc oxide (ZnO), perovskites, and tungsten bronze structured oxides are showing high-temperature stability. ZnO has the highest n-type ZT values and sodium cobaltite has the highest p-type ZT values among all oxide candidates [8]. Other oxide materials like  $\alpha$  and  $\gamma\text{Al}_2\text{O}_3$  doped sintered ZnO and sintered  $\text{CuAlO}_2$  also have high thermoelectric properties [9, 10]. Although oxide materials have lower thermoelectric properties compared to compounds containing elements like tellurium and antimony, they are suitable for high-temperature applications because of their superior stability in oxidizing environments [10].

Among metal oxides, Magnéli phase oxides, including titanium and tungsten, have the potential for thermoelectric use because of their low thermal conductivities and metallic-like electrical conductivities [11]. Arne Magnéli is a pioneer in researching transition metal sub-oxides and shear plane dislocations. His research led to the discovery of conductive Titanates and perovskites. He studied Tungsten, Molybdenum and Titanium sub-oxides and found dislocation planes in their crystalline structure, which accounted for their electrical conductivity and lubricious properties. This mechanism is also observed in graphite and graphene. Magnéli phases have semi-metallic characteristics and similar electrical properties to carbon. Because of the demand for inert conductive materials, there is significant research being done on Magnéli materials [12]. Magnéli et al. investigated transition metal oxides using XRD. They found comparable compositions expressed by  $\text{Ti}_n\text{O}_{2n-1}$  ( $n=2, 3, \dots$  etc.) and expected that they may be formed from the rutile structure. They proposed the crystallographic shear structure principle, which involves dividing the main structure into blocks parallel to a shear plane (Fig. 1a), translating the blocks relatively by shear vector (Fig. 1b), and removing overlapping parts as shown in (Fig. 1c) [13-15].

The partial reduction of certain transition metal oxides leads to crystallographic shear planes with altered metal linkage and retained octahedral coordination. Shear planes are observed in oxides based on  $\text{ReO}_3$  and rutile structures with changes in corner/edge sharing to edge/face sharing. The structural changes in rutile with increasing oxygen deficiency reveal regular arrays of shear planes forming "shear compounds". Shear planes are present even with low oxygen deficiencies [16]. In this review article, an elaborate and comprehensive discussion will be presented on the Magnéli phase of five different transition metal suboxides,  $\text{TiO}_x$ ,  $\text{WO}_x$ ,  $\text{MoO}_x$ ,  $\text{VO}_x$ , and  $\text{NbO}_x$  with a

special focus on their potential application as thermoelectric materials.

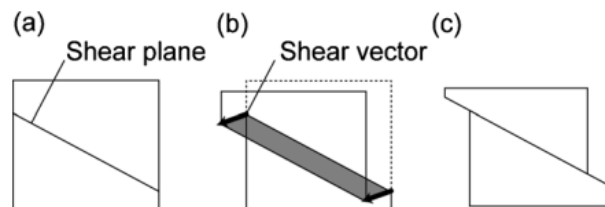


Fig. 1: schematic diagram of crystallographic shear operation. Reprinted from [13], with the permission of AIP Publishing.

## 2. Titanium suboxides Magnéli phases

Magnéli phases for  $\text{TiO}_x$  are a class of sub-stoichiometric titanium oxides with a chemical formula of  $\text{Ti}_n\text{O}_{2n-1}$ , where  $n$  varies from 3 to 9 (and more typically between 4 and 6) [17, 18]. Despite all three forms of Titanium oxides (rutile, anatase, and brookite) being composed of  $\text{TiO}_6$  octahedron basic units, their frameworks differ, resulting in distinct properties for each crystal [19]. Arne Magnéli first investigated the Magnéli phase of  $\text{TiO}_x$  in the 1950s, after developing a phase diagram of a Ti-O system [20]. The Magnéli phase is formed by the crystalline lattice of rutile  $\text{TiO}_2$ , in which a lack of oxygen results in delocalized electrons in the d band [21]. The recent focus on these materials is a result of their exceptional electrical conductivity, chemical stability, and remarkable ability to resist corrosion [21].  $\text{TiO}_x$  shows a triclinic crystal structure and is considered to be a mixed-valence compounds due to the presence of both  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$  ions in their compositions [21]. Also,  $\text{TiO}_x$  exhibits a remarkable level of conductivity, particularly for values of  $n$  equal to 3, 4, and 5, after which there is a decline in conductivity for larger  $n$  values [18].

Magnéli phases are difficult to obtain in a pure form due to their similar lattice parameters [12]. The Magnéli phase crystal lattice can be understood by comparing it with the crystal lattice of  $\text{TiO}_2$ . The formation of  $\text{TiO}_2$  phases is explained by changes in the octahedral packing of  $\text{TiO}_2$  due to the removal of O atoms. Oxygen defects distort  $[\text{TiO}_6]$  octahedral structure, leading to Magnéli phase formation with increasing defect concentration. Magnéli-phase crystal structure has  $\text{TiO}_2$  octahedra blocks with an oxygen deficiency for each  $n^{\text{th}}$  layer, resulting in shear planes in the structure where the 2D chains become face-sharing. This reduces the symmetry of the crystal system from tetragonal to triclinic as the unit cell size increases [22, 23]. The crystal structures of  $\text{TiO}_x$  including  $\text{Ti}_3\text{O}_5$  [24, 25],  $\text{Ti}_4\text{O}_7$  [26, 27],  $\text{Ti}_5\text{O}_9$  [28, 29],  $\text{Ti}_6\text{O}_{11}$  [28, 30, 31],  $\text{Ti}_7\text{O}_{13}$ ,  $\text{Ti}_8\text{O}_{15}$ , and  $\text{Ti}_9\text{O}_{17}$  [28, 30] are shown in Fig. 2.

$\gamma\text{-Ti}_3\text{O}_5$  displays metallic behavior, whereas  $\delta\text{-Ti}_3\text{O}_5$  exhibits semiconducting properties. The transition

between the two phases is induced by a Mott-Hubbard metal-insulator transition, and the alteration in electrical conductivity is due to a disconnection in the conducting pathways within the crystal [24]. Both  $\text{Ti}_4\text{O}_7$  and  $\text{Ti}_5\text{O}_9$  are oxides with mixed valence states.  $\text{Ti}_4\text{O}_7$  has equal numbers of  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$  positions, while  $\text{Ti}_5\text{O}_9$  has a 3:2 ratio of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  positions. These oxides have structures similar to rutile and contain rutile-like blocks that are infinite in x and y dimensions [32].

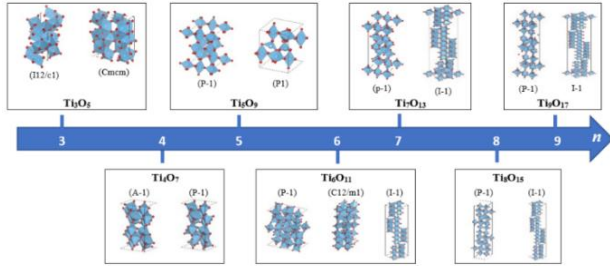


Fig. 2: Crystal structure of Titanium suboxides.

Harada et al. [13] synthesized and examined the thermoelectric properties of  $\text{Ti}_n\text{O}_{2n-1}$  which was synthesized by solid-state reaction followed by hot pressing in a carbon die. All sub-stoichiometric specimens are Magnéli phases, with regularly introduced crystallographic shear planes. Electrical conduction is  $n$ -type, with higher carrier concentration and lower electrical resistivity and Seebeck coefficient for greater oxygen deficiency. Lattice thermal conductivity decreases with oxygen deficiency, which indicates that crystallographic shear planes scatter phonons but not carriers. The hot-pressed  $\text{TiO}_{1.90}$  had the highest thermoelectric ZT of 0.13 at 773 K [13]. Temperature dependence of electrical conductivity, Seebeck coefficient and ZT of some  $\text{TiO}_x$  ( $x=1.95, 1.9, 1.85$ , and  $1.8$ ) were shown in Fig. 3. In addition, H. Lee et al. [33] deposited  $\text{TiO}_x$  with sub-stoichiometric composition via the atmospheric plasma spray method, using varying  $\text{H}_2$  gas ratios in the torch hardware. Oxygen deficiencies increase electrical conductivity but decrease Seebeck coefficient. The material has reduced thermal conductivity due to the presence of pores and interfaces.  $\text{TiO}_{1.93}$  material had a ZT value of 0.132 at 750 K. L. Hao et al. [34] used Spark plasma sintering (SPS) followed by carbon reduction to create Magnéli phase  $\text{Ti}_n\text{O}_{2n-1}$  composites. the value  $n$  depending on the reduction temperature and holding time. With increasing holding time, the amount of  $\text{TiO}$  increased while the amount of  $\text{Ti}_3\text{O}_5$  decreased.  $\text{Ti}_9\text{O}_{17}$  and  $\text{Ti}_8\text{O}_{15}$  were formed at 10 h holding time, and  $\text{Ti}_3\text{O}_5$  phase was also formed at 15 and 20 h holding time. Compared to rutile  $\text{TiO}_2$  prepared by SPS, the thermoelectric properties were considerably enhanced, including electrical conductivity, thermal conductivity, Seebeck coefficient, power factor (PF), and ZT value. At 20 hours of holding time, the samples achieved a maximum PF of

$6.5 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$  at 973 K and a maximum ZT value of 0.1 at 873 K [34]. Another Magnéli phase of  $\text{Ti}_5\text{O}_9$  ceramics were made by hot press solid-state reaction between anatase  $\text{TiO}_2$  nanopowder and Ti powder at 950 °C and 40 MPa. A small polaron hopping mechanism causes electrical conductivity to change with temperature. Vibrational entropy during polaron hopping is negligible, and data can be explained with a modified Heikes–Chaikin–Beni formula. ZT value was 0.3 at 1076 K [35].

Yuan, Z., et al. [19] synthesized Reduced  $\text{Ti}_{1-x}\text{Nb}_x\text{O}_{2-\delta}$  ceramics using a solid-state process, followed by 10 hour annealing in a reducing  $\text{H}_2$  environment at 1573 K. They showed that the resistivities decreased with temperature and showed semiconductor behavior, while increasing Nb doping levels increased resistivities for fixed temperatures. Seebeck coefficients were negative, indicating electron carriers, and increased gradually with higher Nb doping levels. Small polaron conduction was observed in electrical transport, however, thermal conductivities increased with temperature, with lattice thermal conductivity being the predominant contributor. At 380 K, the Nb doping level with  $x = 0.20$  produced the greatest ZT value of 0.016, about 2.9 times greater than the undoped  $\text{TiO}_2$  sample. Similarly,  $\text{Ti}_{1-x}\text{Nb}_x\text{O}_{2-\delta}$  was synthesized using a standard solid-state reaction approach, but it was then annealed for 10 hours at 1473 K in a reducing environment of 90% Ar-10%  $\text{H}_2$ . At 380 K, the greatest ZT value of 0.023 was found for  $x=0.01$ , which is 2.6 times more than the undoped  $\text{TiO}_2$  sample [36]. D. Zhou et al. [37] used a high-pressure and high-temperature (HPHT) approach to incorporate Ta into  $\text{TiO}_2$ . Ta reduced  $\text{TiO}_2$  to Magnéli phase  $\text{TiO}_x$  (mostly  $\text{Ti}_8\text{O}_{15}$ ) and produced sub-micron  $\text{Ta}_2\text{O}_5$ . The addition of Ta inhibited grain growth. The sample's hardness and conductivity increased while the Seebeck coefficient, lattice thermal conductivity, and total thermal conductivity decreased. This synergistic optimization was achieved with increased Ta addition. At 973 K, the maximum ZT value of the composite ceramic was 0.176. Moreover, They added Nb to  $\text{TiO}_2$  using HPHT. The optimal Nb concentration was found to be  $x=0.23$ . The composite ceramics consisted of  $\text{TiO}_2$ ,  $\text{Ti}_4\text{O}_7$ ,  $\text{NbO}_2$ , and  $\text{NbO}$ , with a unique nanometer pore structure appearing on the grain of the sample. The thermoelectric properties of the samples were influenced by  $\text{NbO}$ , with a significant increase in thermal conductivity and 'metallic conductive behavior at high concentrations. Repeated high-temperature testing reduced the  $\text{NbO}$  phase, leading to a composite  $\text{NbO}_2$  and  $\text{Ti}_4\text{O}_7$  phase with improved ZT value and reduced thermal conductivity. The maximum ZT value obtained was 0.313 at 973 K after repeated high-temperature tests [38]. M. Mikami et al. [39] investigated the thermoelectric characteristics of  $\text{TiO}_2$  with oxygen defects as well as the  $\text{Ti}_n(\text{O}, \text{N})_{2n-1}$  Magnéli phase. The mixing ratio of  $\text{TiO}_2$  and



TiN can be changed to adjust oxygen deficiency and the n index of the Magnéli phase. Oxygen shortage promotes electron doping, which dramatically lowers. Seebeck coefficient decreases with electron doping, yet the PF value increases at high temperatures due to the absolute value of Seebeck coefficient and the temperature increase.

The nanometer-order periodic planar defect structure of the Magnéli phase can aid phonon scattering and lowering. The  $\text{Ti}_7\text{O}_{13}$  Magnéli phase sample had an estimated ZT value of 0.4 at 1150 K.

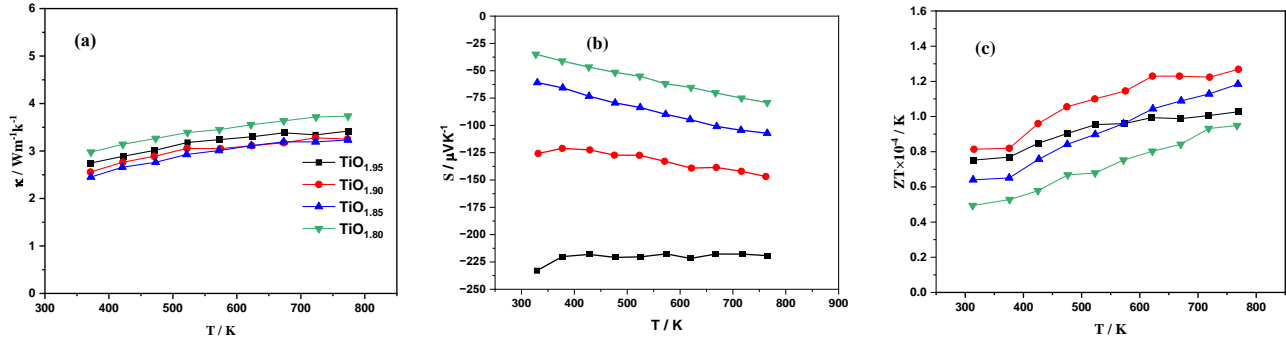


Fig. 3: Temperature dependence of (a) electrical conductivity (b) Seebeck coefficient (c) ZT of  $\text{TiO}_x$ . Reprinted from [13], with the permission of AIP Publishing.

### 3. Tungsten suboxides Magnéli phases

There are several sub-stoichiometric structures of  $\text{WO}_x$ , ( $2 < x < 3$ ) and the crystal structures of Magnéli phases are monoclinic for  $\text{W}_{18}\text{O}_{49}$ ,  $\text{W}_{20}\text{O}_{58}$ ,  $\text{W}_{17}\text{O}_{47}$ , and  $\text{W}_{25}\text{O}_{73}$ , orthorhombic for  $\text{W}_{32}\text{O}_{84}$  and  $\text{W}_3\text{O}_8$ , and tetragonal for  $\text{W}_5\text{O}_{14}$  [40] as shown in Fig. 4. An intriguing method involves using crystallographic shear (CS) to decrease lattice thermal conductivity  $k_{lat}$  by boosting phonon scattering. CS plane structures emerge when a transition metal is partially reduced, and oxygen layers are removed from the structure. In the tungsten-oxygen system, insulating  $\text{ReO}_3$ -type  $\text{WO}_3$ , semiconducting phase  $\text{W}_{20}\text{O}_{58}$  with CS planes, metallic phase  $\text{W}_{18}\text{O}_{49}$  with pentagonal columns (PC), and metallic rutile-type  $\text{WO}_2$  are seen with varying coupling of the  $[\text{WO}_6]$  octahedral [41].

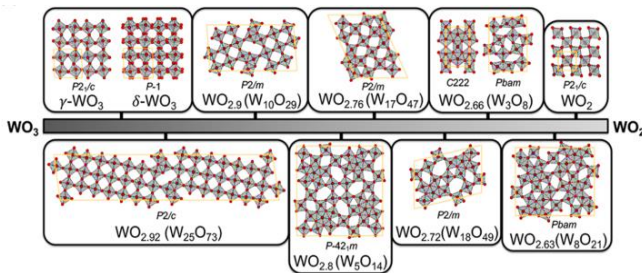
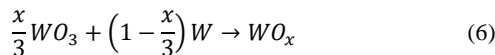


Fig. 4: Crystal structures of tungsten oxides. Reprinted (adapted) with permission from [42]. Copyright 2023 American Chemical Society.

Kaiser et al. [41] investigates the solid-state reaction of tungsten oxides with tungsten in the composition range of  $\text{WO}_x$  ( $2.50 \leq x \leq 3$ ) during spark plasma sintering (SPS).



They revealed the formation of a new phase " $\text{WO}_{2.82}$ " between  $2.72 \leq x \leq 2.90$ , which might have the composition  $\text{W}_{12}\text{O}_{34}$ . The thermoelectric properties of the materials are

continuously tunable with the oxygen-to-tungsten ratio. The lattice thermal conductivity is significantly reduced until 700 K for the sample with the composition  $x = 2.84$ , which contains the phases  $\text{W}_{18}\text{O}_{49}$  and " $\text{WO}_{2.82}$ ". the introduction of multiple phases is a way for reducing the thermal conductivity due to increased phonon scattering at the phase interfaces. For high-temperature applications, CS planes might be fewer phonon scattering centers. ZT of  $\text{WO}_x$  were shown in Fig. 5a.

Tran et al. [43] synthesized Single phase  $\text{W}_{18}\text{O}_{49}$  directly from  $\text{WO}_3$  and  $\text{WO}_2$  via reactive SPS, which is faster than conventional methods. The reaction between  $\text{WO}_3$  and  $\text{WO}_2$  is more suitable than  $\text{WO}_3$  and metal W powder because of similarities in the coordination environment. Anisotropic thermoelectric properties and the effect of applied pressure (perpendicular or parallel) were observed in the synthesized samples, resulting in low thermal conductivity. ZT was increased to 0.08 at 1073 K for the sample sintered under 50 MPa pressure as shown in Fig. 5b. So,  $\text{W}_{18}\text{O}_{49}$  shows metallic behavior and promises to be a cost-effective n-type thermoelectric material. They also investigated the high-temperature thermoelectric characteristics of  $(\text{W}_{1-x}\text{Ti}_x)_{18}\text{O}_{49}$  [44]. The undoped  $\text{W}_{18}\text{O}_{49}$  sample exhibited metallic behavior with high electrical conductivity and a low Seebeck coefficient. Ti substitution at the W site decreased carrier concentration while increasing Seebeck coefficient and thus PF at high temperatures up to  $x = 0.2$ . The top ZT value was 0.50 at 1073 K for  $x = 2$ , while the lowest ZT value was 0.20 at 1073 K ( $x = 0.1$ ). Ti dopant has a solubility limit between  $x=0.1$  and  $x=0.15$ , limiting performance increase via carrier concentration tweaking for the inherently overdoped  $\text{W}_{18}\text{O}_{49}$ -based oxide. In addition, Kieslich et al. used SPS to synthesize  $\text{W}_{1-x}\text{Ta}_x\text{O}_{2.90}$ . The reduction in thermal conductivity of Ta-containing samples was achieved by adding  $\text{Ta}_2\text{O}_5$  to the  $\text{WO}_3/\text{W}$  reaction mixture. The addition

resulted in a 30% decrease in thermal conductivity over the measured temperature range. This was due to phonon scattering by shear planes and micron-sized inclusions. The electronic properties were not affected by the substitution, which ultimately led to an enhancement in thermoelectric performance and a relatively high ZT value of 0.15 at 1100 K for n-type metal oxides [45].

#### 4. Molybdenum suboxides Magnéli phases

Like  $\text{WO}_x$ , there are several sub-stoichiometric structures of  $\text{MoO}_x$ , ( $2 < x < 3$ ) as shown in Fig. 6.  $\text{Mo}_9\text{O}_{26}$  and  $\text{Mo}_8\text{O}_{23}$  [46] have edge-sharing  $[\text{MoO}_6]$  octahedrons, while  $\text{Mo}_5\text{O}_{14}$  [47] and  $\text{Mo}_{17}\text{O}_{47}$  [48] have pentagonal  $\text{MoO}_7$  bipyramids with edge-shared  $\text{MoO}_6$  octahedrons.  $\text{Mo}_4\text{O}_{11}$  has a unique structural motif of corner-sharing  $\text{MoO}_6$  octahedrons and  $\text{MoO}_4$  tetrahedrons and it demonstrated exceptional efficacy as a composite electrocatalyst for the methanol oxidation reaction (MOR) [49].

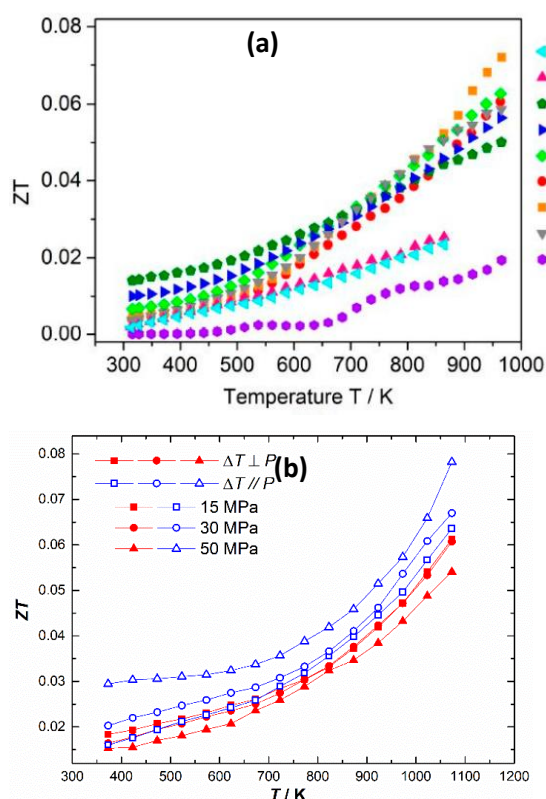


Fig. 5: Temperature dependence of ZT (a) WO<sub>x</sub> samples (2.80 ≤ x ≤ 2.98) [41] (b) P // and ⊥ directions for W<sub>18</sub>O<sub>49</sub> [43]

The stoichiometric phases of molybdenum oxide have different crystal structures, with  $\alpha$ - $\text{MoO}_3$  having a van der Waals layered orthorhombic structure and  $\beta$ - $\text{MoO}_3$  having a monoclinic structure [42, 50]. The Magnéli phase  $\text{Mo}_8\text{O}_{23}$ , on the other hand, displays a superlattice modulation that is likely caused by a concerted pairwise rotation of  $[\text{MoO}_6]$  octahedra in the perovskite  $\text{Mo}_4\text{O}_{15}$  layers [3]. Conversely,  $\text{Mo}_4\text{O}_{11}$

exhibits a resistivity abnormality that is attributed to a charge density wave associated with partial nesting of Fermi surfaces. These investigations exemplify the diverse properties and behaviors of Molybdenum Magnéli phases.

Khailla et al. [51] measured the electrical conductivity and Seebeck coefficient of  $\text{MoO}_3$ ,  $\text{MoO}_2$ ,  $\text{Mo}_4\text{O}_{11}$ ,  $\text{Mo}_8\text{O}_{23}$ ,  $\text{Mo}_9\text{O}_{26}$ ,  $\text{Mo}_{13}\text{O}_{38}$ , and  $\text{Mo}_{17}\text{O}_{47}$  up to 300 °C. It has been observed that the conductivity value increases at room temperature when there is deviation from stoichiometry. So,  $\text{MoO}_3$  and its suboxides display semiconductor behavior. At low temperatures,  $\text{MoO}_2$  exhibits a semimetal-like character of  $10^{-2} \Omega^{-1}\text{cm}^{-1}$  instead of a semiconductor. The thermoelectric power shows that oxides are n-type semiconductors up to 300°C. Kaiser et al. [52] prepared  $\text{Mo}_x$  ( $2 \leq x < 3$ ) from  $\alpha\text{-MoO}_3$  and Mo powder via SPS. The synthesis of  $\text{Mo}_{18}\text{O}_{52}$ ,  $\text{Mo}_{17}\text{O}_{47}$ , and  $\gamma\text{-Mo}_4\text{O}_{11}$ , despite their narrow composition ranges, resulted in single-phase products. Among these products,  $\text{Mo}_{17}\text{O}_{47}$  exhibited the highest PF. On the other hand,  $\text{Mo}_{18}\text{O}_{52}$  proved to be an intrinsic narrow-gap semiconductor with extremely low thermal conductivity across the entire temperature range. It also displayed a high p-type Seebeck coefficient at room temperature and a p–n transition at 440 K. In contrast,  $\text{MoO}_2$ ,  $\gamma\text{-Mo}_4\text{O}_{11}$ , and  $\text{Mo}_{17}\text{O}_{47}$  demonstrated poor metallic conductivity. Additionally, a new reversible transition was discovered at 450 K through specific heat measurements in  $\gamma\text{-Mo}_4\text{O}_{11}$ .

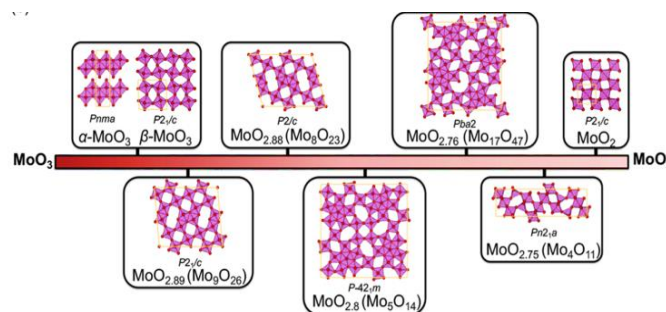


Fig. 6: Crystal structure of molybdenum oxides and molybdenum suboxides. Reprinted (adapted) with permission from [42]. Copyright 2023 American Chemical Society.

## 5. Vanadium suboxides Magnéli phases

In the crust of the Earth, vanadium ranks sixth among transition metals and is the 20<sup>th</sup> most common element. Some literature suggests it's the fourth most abundant after iron, titanium, and manganese [53]. The mixed-valence vanadium oxides can be categorized into two series: Magnéli and Wadsley.  $V_3O_7$  and  $V_6O_{13}$  in the Wadsley series undergo a phase transition at 5.2 K and 155 K, respectively [53-55]. In the Magnéli series, all except  $V_7O_{13}$  (metallic) exhibit a transition from paramagnetic to antiferromagnetic and have an antiferromagnetic ground state at low temperatures. These include  $V_3O_5$ ,  $V_4O_7$ ,  $V_5O_9$ ,  $V_6O_{11}$ ,  $V_7O_{13}$ ,  $V_8O_{15}$ , and  $V_9O_{17}$  with varying phase transition temperatures [56].

The Magnéli series of compounds based on vanadium is a group of highly versatile substances that possess substoichiometric oxygen composition and have a formulation of  $V_nO_{2n-1}$  ( $3 \leq n \leq 9$ ). The structure may be traced back to rutile and corundum, where crystallographic shear (CS) planes form as a result of the structural combination of edge-sharing octahedral chains in the rutile structure and face-sharing octahedral links in the corundum structure. These CS planes are characteristic features in early transition metal oxides with low oxygen content, resulting in metal reduction and a rise in charge carrier concentration. The presence of CS planes restricts the mean free path of phonons and reduces thermal conductivity as they interrupt the periodic structure. Moving from  $V_2O_3$  to  $VO_2$ , the extremities of the V-O phase diagram of the  $V_nO_{2n-1}$  Magnéli series exhibit a reduction in the d-band occupation across the series, thereby altering the electronic properties that can give rise to insulating ( $V_3O_5$ ), metallic ( $V_7O_{13}$ ), or semiconducting ( $V_6O_{11}$ ,  $V_8O_{15}$ ,  $V_9O_{17}$ ) behavior at room temperature [57, 58].

Nagasawa et al. [59] discussed the electrical and thermoelectric characteristics of  $V_nO_{2n-1}$  ( $n=3, 4, 5, 6, 7$ , and 8). The behavior of these compounds at different temperatures is investigated. Notably,  $V_3O_5$  displays semiconductor properties, with its electrical conductivity varying based on temperature, and its anisotropic nature is minimal.  $V_4O_7$  exhibits a transition from metal to semiconductor behavior around 244 K, accompanied by changes in activation energy. Similarly,  $V_5O_9$  and  $V_6O_{11}$  undergo metal-semiconductor transitions with varying activation energies and thermoelectric properties.  $V_7O_{15}$  maintains metallic conductivity, while  $V_8O_{15}$  showcases a metal-semiconductor transition near 70 K. These transitions correlate with magnetic changes in the compounds and potentially indicate first-order transitions. Overall, the study sheds light on the intricate interplay of electronic and magnetic properties in these vanadium oxide compounds. M. Joos et al [57] synthesized  $V_6O_{11}$  via SPS and determined the phase purity of 96.64 wt%. The SPS-treated  $V_6O_{11}$  material exhibits a maximum PF of  $(4.9 \pm 0.8) \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-2}$  and a thermal conductivity  $\kappa$  of  $(2.72 \pm 0.06) \text{ Wm}^{-1}\text{K}^{-1}$  at a temperature of 600 K.

## 6. Niobium suboxides Magnéli phases

Niobium suboxides are a class of compounds where the ratio of niobium to oxygen is greater than 2.5 such as  $Nb_{25}O_{62}$ ,  $Nb_{47}O_{116}$ ,  $Nb_{22}O_{54}$ , and  $Nb_{12}O_{29}$  as shown in Fig. 8. They are part of a family of compounds known as crystallographic shear phases of niobium oxide, which have received attention for their unusual electronic and magnetic properties, as well as their performance as intercalation electrode materials for lithium-ion batteries [60]. These compounds feature blocks of niobium-oxygen octahedra as structural units, and this block structure leads to a coexistence of flat and dispersive energy bands, corresponding to localized and delocalized electronic

states. Electrons localize in orbitals spanning multiple niobium sites in the plane of the blocks [60].

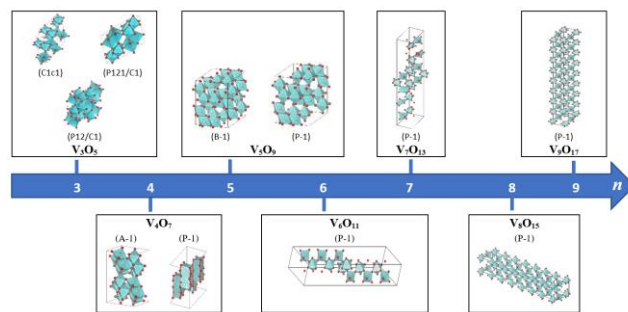


Fig. 7: Crystal structure of Vanadium suboxides

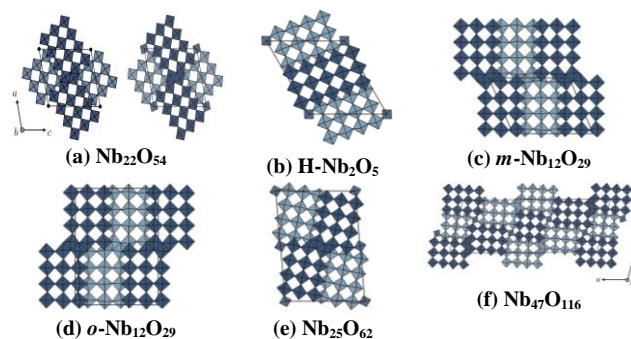


Fig. 8: a) Idealized (left) and locally distorted (right) crystal structure of  $Nb_{22}O_{54}$ . Crystal structures of b)  $H-Nb_{25}O_{62}$ , c) monoclinic  $Nb_{12}O_{29}$ , d) orthorhombic  $Nb_{12}O_{29}$ , e)  $Nb_{25}O_{62}$ , and f)  $Nb_{47}O_{116}$ . Reprinted figure with permission from [60]. <https://doi.org/10.1103/PhysRevB.99.075151>. Copyright 2023 by the American Physical Society.

Researchers have discovered that achieving such low lattice conductivities in defective oxides can be approached by utilizing crystallographic shear defects and complex block structures. This approach can tune the thermal conductivity in oxides with phonon scattering lengths at the 0.5-5 nanometer length scale, resulting in ZT values as high as 0.21 when measured at 1000K. At 1050K, the thermoelectric figure of merit for the material can be greater than 0.15, and the Seebeck coefficient can be more negative than  $-80 \mu\text{V/K}$ . Over a temperature range of 450 to 1050K, the lattice thermal conductivity can be less than  $3 \text{ Wm}^{-1}\text{K}^{-1}$ , and the electrical conductivity can be greater than  $20000 \text{ S/m}$  [61]. Besides the stoichiometric phases  $Nb_2O_5$  and  $NbO_2$ , there are many  $Nb_2O_{5-x}$  phases [61]. Thermoelectric measurements of  $NbO_x$  were shown in Fig. 9. A homologous sequence of structurally similar niobium oxide phases with the general formula  $Nb_{3n+1}O_{8n-2}$ ,  $n=5, 6, 7, 8$  (e.g.,  $Nb_{16}O_{38}$ ,  $Nb_{19}O_{46}$ ,  $Nb_{22}O_{54}$ ,  $Nb_{25}O_{62}$ ) can summarize these. In addition, other oxides with the formulas  $Nb_{12}O_{29}$  ( $12Nb_2O_5-2O$ ) and  $Nb_{94}O_{232}$  ( $47Nb_2O_5-3O$ ) can form [61].



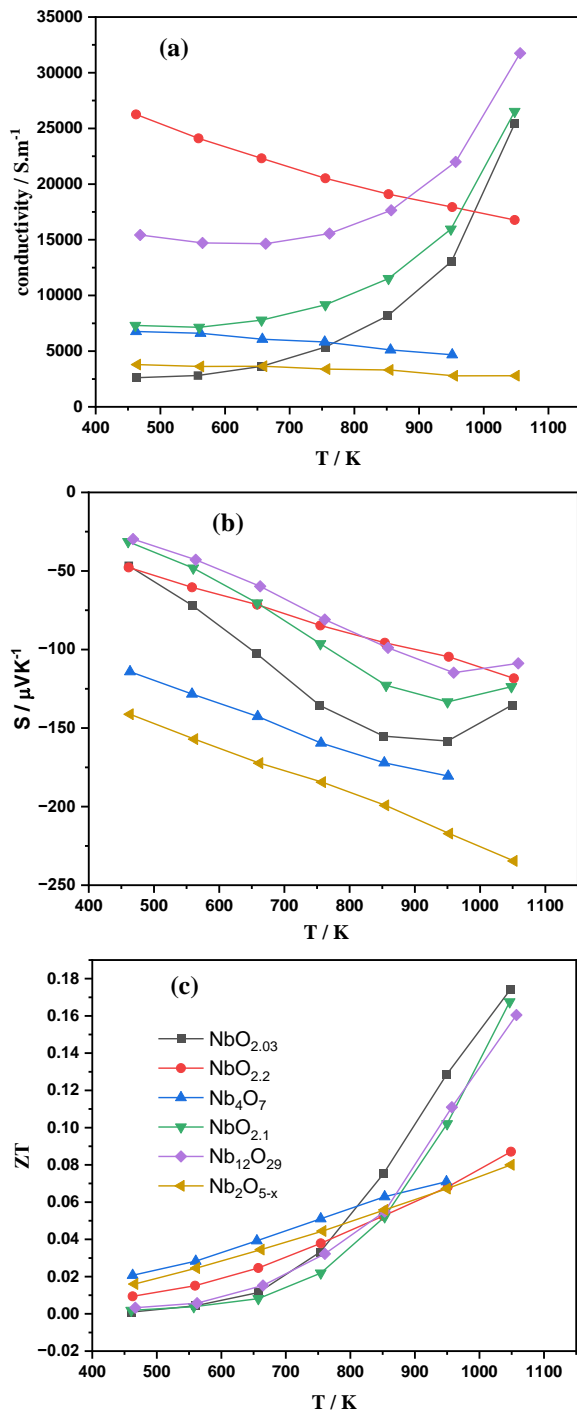


Fig. 9: Temperature dependence (a) electrical conductivity (b) Seebeck coefficient (c) ZT of NbO<sub>x</sub> [61].

## 7. Challenges and Future Developments

Magnéli phases have shown promise as thermoelectric materials, but they also come with limitations and challenges. One challenge is the difficulty in obtaining monophasic materials, as seen with titanium sub-oxides of the Magnéli phase [62]. Also, Most Magnéli series phases, however, are unstable at high temperatures and are oxidized or reduced to nearby metal oxides such as V<sub>n</sub>O<sub>2n-1</sub> phases, eventually

providing the compositional end phases VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub> [57]. Synthetic and processing challenges, especially for metastable and nanostructured materials, hinder the advancement of Magnéli phases [57]. Another limitation is the relatively low thermoelectric performance of n-type oxides compared to p-type oxides [63]. However, recent developments have shown that Magnéli oxides can achieve relatively low thermal conductivities and metallic-like electrical conductivities, making them promising n-type thermoelectric [12]. The enhancement of conversion efficiency in thermoelectric materials is challenging, but multiphase thermoelectric materials, including Magnéli phases, provide new approaches to enhance the electronic transport properties [11]. Overall, while Magnéli phases have potential, further research is needed to overcome the challenges and improve their thermoelectric performance.

## 8. Conclusion:

Magnéli phases are a promising class of thermoelectric materials with a wide range of potential applications. Their high electrical conductivity and low thermal conductivity make them attractive for a variety of high-temperature applications. Magnéli phases of transition metal oxides like TiO<sub>x</sub>, WO<sub>x</sub>, MoO<sub>x</sub>, VO<sub>x</sub>, and NbO<sub>x</sub> with discussion of their potential application as thermoelectric materials.

However, there are still some challenges that need to be addressed before the Magnéli phases can be fully commercialized. These challenges include optimizing their thermoelectric properties and developing new synthesis methods. Despite these challenges, we believe that Magnéli phases have the potential to revolutionize the field of thermoelectrics. With further research and development, they could become the leading choice for thermoelectric applications in the future.

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