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Short Review

Magnéli oxides as promising *n*-type thermoelectrics

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Abstract: The discovery of a large thermopower in cobalt oxides in 1997 lead to a surge of interest in oxides for thermoelectric application. Whereas conversion efficiencies of *p*-type oxides can compete with non-oxide materials, *n*-type oxides show significantly lower thermoelectric performances. In this context so-called Magnéli oxides have recently gained attention as promising *n*-type thermoelectrics. A combination of crystallographic shear and intrinsic disorder lead to relatively low thermal conductivities and metallic-like electrical conductivities in Magnéli oxides. Current peak-zT values of 0.3 around 1100 K for titanium and tungsten Magnéli oxides are encouraging for future research. Here, we put Magnéli oxides into context of *n*-type oxide thermoelectrics and give a perspective where future research can bring us.

1. Introduction

In the complex energy landscape of the future the materials choice in application oriented technologies is of particular importance and the materials must fulfill today's sustainability criteria such as high abundance, low toxicity and long-term stability. Oxide based materials usually fulfill all criteria and consequently they attracted a lot of interest in context of thermoelectric research [1,2,3]. In addition, oxides take advantage of low-cost and scalable preparation techniques such as consolidation and simultaneous preparation using spark plasma sintering [4,5]. On the other hand, the primarily ionic metal-oxygen bond lead to unfavorable intrinsic properties of oxides that makes an optimization of their thermoelectric properties particularly challenging. Therefore it is not surprising that current state of the art materials are non-oxide materials, for example lead and bismuth tellurides [6], silicides [7], and Zintl compounds [8]. However, the discovery of a large thermopower in cobalt oxides more than 15 years ago [9] has triggered a surge of interest, and today a few oxide materials are known that exhibit fascinating thermoelectric properties.

In general, in thermoelectrics the ultimate goal is the maximization of the thermoelectric figure of merit $zT = (\alpha^2\sigma/\kappa)\cdot T$ with α being the thermopower, σ the electrical conductivity, κ the thermal conductivity and T the absolute temperature. The interrelation of the different parameters makes an optimization for all kind of materials difficult, however, today different approaches are known to decouple material properties for example, the introduction of crystalline interfaces on different length scales which (i) decrease the thermal conductivity due to grain boundary scattering and further (ii) introduce electron filtering mechanisms [10,11].

Among the many available oxide materials, layered *p*-type conductors exhibit the best thermoelectric performances with *zT* values of 1.4 at 1000 K ($Bi_{1-x}Ba_xCuSeO$) and 1.2 at 873 K ($Ca_3Co_4O_9$) [3,12]. Their good performances originate from high carrier mobilities within the layers and relatively low thermal conductivities. Nowadays, there is a gap in the thermoelectric performance between *n*-type and *p*-type materials, the latter showing superior properties that must be closed for wide commercialization of oxide-based thermogenerators. Current state of the art *n*-type oxide materials, which have been studied intensively during the past decade, include co-doped zinc oxides, indium tin oxides and strontium titanates. Although thermoelectric performances of *n*-type materials were steadily enhanced, today, only a few reports exist with *zT* values of 0.6 ($Zn_{0.96}Al_{0.02}Ga_{0.02}O$ at 1273 K) and 0.45 ($In_{1.8}Ge_{0.2}O_3$ at 1273 K) [13,14].

2. Crystallographic shear in Magnéli oxides

The reduction of transition metal oxides such as TiO_2, V_2O_5, MoO_3 and WO_3, either with the corresponding metal or by hydrogen gas, leads to the introduction of crystallographic shear (CS) planes as structure motif, see Figure 1a [18]. Within the crystal structure the coordination of the metal cation remains basically unchanged and the anion coordination number is increased to accommodate the reduced metal to oxygen ratio. In case of a ReO_3-like parent structure, for example MO_3 (M = Mo^{6+}, W^{6+}), the reorganization leads to the introduction of planes where MO_6 octahedra are now edge-shared, so-called CS planes. In titanium oxides, which adopt the rutile-type as parent structure, face-sharing octahedra are introduced. Regarding the mechanism, the formation of CS planes starts with a perfect crystal and oxygen vacancies are introduced either by heating or chemical reduction. These vacancies emerge at the crystal surface and then diffuse to certain planes within the crystal where the energy of the vacant sites is minimized. In the last step, these vacancies are then eliminated by the introduction of corner/face sharing octahedra, the so-called crystallographic shear planes. A similar ordering mechanism of vacant sites is encountered in $Fe_{1-x}S$ and $Fe_{1-x}O$ compounds where the reduction of Coulomb interactions is the driving force [21]. Before A. Magnéli discovered the first homologous series of Ti_nO_{2n-1} and W_nO_{3n-2} in the 1950's [15,16] compounds such as $TiO_{1.90}$, $MoO_{2.75}$ and $WO_{2.90}$ were believed to be nonstoichiometric with a wide homogeneity range. Since then, electron imaging and diffraction techniques confirmed the proposed structural concept, and today many different homologous series including non-equilibrium structures have been discovered for many early transition metal oxides [17,18].

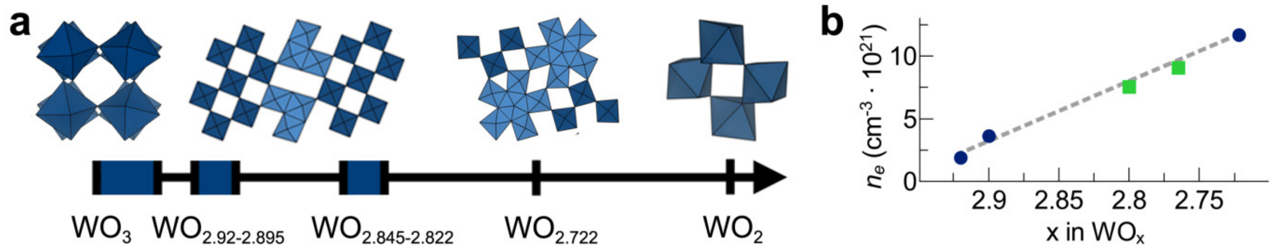

Figure 1. (a) Structure motifs in the quasi ternary system WO_3-WO_2 and (b) the corresponding carrier concentration (blue = experiment, green = theory; data adapted from Reference 18). Crystallographic shear planes lying on {102} planes and {103} planes are observed between 0.005 < x < 0.155. For larger values of x pentagonal columns are the dominating structure motif, as observed for $WO_{2.833}$ ($W_{24}O_{68}$) and $WO_{2.722}$ ($W_{18}O_{49}$) [19].

The introduction of CS planes is associated with a partial reduction of the metal centers. The electrons are available in *d* orbitals of the reduced metal centers and lead to *n*-type conduction. In order to understand the electronic structure in more detail, the nature of the partially filled *d* orbitals must be considered which crucially depends on the underlying crystal structure [22]. In general, with increasing reduction more charge carriers are introduced in the system as shown in Figure 1b for WO_3-WO_2 [19]. Therefore the carrier concentration, and in turn the electronic transport properties, can be altered by extent of reduction [23,24,25]. It is interesting to note that Magnéli oxides show a certain cycling stability of the physical properties as further oxygen loss is a known issue for most oxides at high temperatures. Detailed thermal stability studies on reactive sputtered tungsten oxide coatings reveal no phase transformations up to a temperature of 923 K [26]. However, at this stage of research it is crucial to focus at fundamental property-relationships rather than on device related issues.

3. Thermoelectric properties of Magnéli oxides

The thermoelectric properties of Magnéli oxides are strongly related to the CS plane density and accompanied charge carrier concentration. In 2010, Harada et al. investigated the high temperature thermoelectric properties of titanium oxides which belong to the homologues series Ti_nO_{2n-1} (n = 2, 3,...), and they explored the influence of CS planes on the thermal conductivities [28]. They concluded that CS planes in combination with their intrinsic disorder are effective scattering centers for phonons, which we demonstrated for tungsten Magnéli phases shortly after [25]. In general, bulk titanium and tungsten Magnéli oxides show thermal conductivities between 2 and 4 $Wm^{-1}K^{-1}$ over the whole temperature range. Structural engineering, for example the use of inclusions on different length scales or the preparation of bulk-nano composite materials, further decreased the thermal conductivity of Magnéli oxides to $\kappa \sim 2$ $Wm^{-1}K^{-1}$ [28,29,30]. Although the observed thermal conductivities are relatively low for oxide materials, oxyselenides show that there might be still room for improvements available ($Bi_{1-x}BaCuSeO$, $\kappa = 0.4$–0.8 $Wm^{-1}K^{-1}$) [30]. In particular, by applying a random-walk energy model [31] the amorphous (lower) limit of the thermal conductivity is calculated to ~ 1–1.5 $Wm^{-1}K^{-1}$ for Magnéli oxides which would further enhance thermoelectric performances.

Looking at the electronic transport properties, the conduction mechanism seems to vary with the extent of reduction. Whereas a clear metallic behavior was observed for highly reduced compounds such as polycrystalline $WO_{2.722}$ (ρ_{300K} ~ 0.1 mΩcm), polaron conduction with very low activation energies around 0.05 eV was found for less reduced compounds [24,32]. However, in a data-mining study, Gaultois et al. found a threshold electrical conductivity of approx. ρ < 10 mΩcm that all high-zT materials obey [33]. Such metallic materials are supposed to have low Seebeck coefficients, notwithstanding almost all high-performance thermoelectric materials violate this principle. For example, Na_xCoO_2 is metallic and the spin contribution to thermopower (or arguably, the unique band structure) lead to a unexpected high Seebeck coefficient (α_{300K} = 100 µV/K) and low electrical resistivity (ρ_{300K} = 0.2 mΩcm) [34]. Following the idea of spin contribution, the thermopower in polaron conductors is the available entropy (or energy) per carrier and indeed, the experimental results [35] for Magnéli oxides are in agreement with Heike's formula [36]. In general titanium oxides with thermopowers between 100–150 μVK^{-1} (Ti_nO_{2n-1}, n = 4, 5, 6, 8) show higher absolute Seebeck values than tungsten oxides 50–80 μVK^{-1} ($W_{20}O_{58}$) [27,28,35,38]. Note, that the properties strongly vary with the applied preparation technique due to the high intrinsic disorder and often mixtures of Magnéli oxides are characterized. This issue was earlier addressed by Tilley et al. who showed that in ampoule reactions the thermodynamic equilibrium state of Magnéli oxides is rarely achieved [20]. Present approaches, such as spark plasma sintering, lead to phase pure materials, however, diffraction domains are usually below 1 micron and show a high amount of structural disorder and strain [29]. Therefore, a detailed phase analysis with (synchrotron) PXRD techniques in combination with SEM and (HR) TEM investigations is essential. Today, the observed transport properties in Magnéli oxides result in peak-zT values of 0.3–0.4 at 1100 K for nitrogen doped titanium oxides and SPS-processed TiO_{2-x} nanoparticles [28,38]. An overview of current figure of merits in comparison with other *n*-type oxide materials is given in Figure 2.

So far, thermoelectric studies on Magnéli oxides rather have focused on structural engineering than on optimizing electronic transport properties. Consequently, bulk-nano Magnéli composite materials were identified to exhibit enhanced thermal transport properties due to interfacial phonon scattering. The natural next step towards improved thermoelectric performances is the optimization of electronic transport properties. Here, particularly interesting is the optimization of the charge carrier concentration towards an optimized power-factor. For tungsten Magnéli oxides, the optimal charge carrier concentration seems to be around 10^{20}–10^{21} $carrierscm^{-3}$ which corresponds to slightly oxidized $W_{20}O_{58}$. Since the thermoelectric figure is a combination of thermal and electronic transport properties, significant improvements are expected in upcoming years which are driven by improved electronic transport properties. In the high temperature regime (T > 1200 K), zT values of 0.6 seem to be easily accessible and in case powerful methodologies towards enhanced electronic properties will be discovered even larger values are expected which makes Magnéli oxides an interesting family for thermoelectrics.

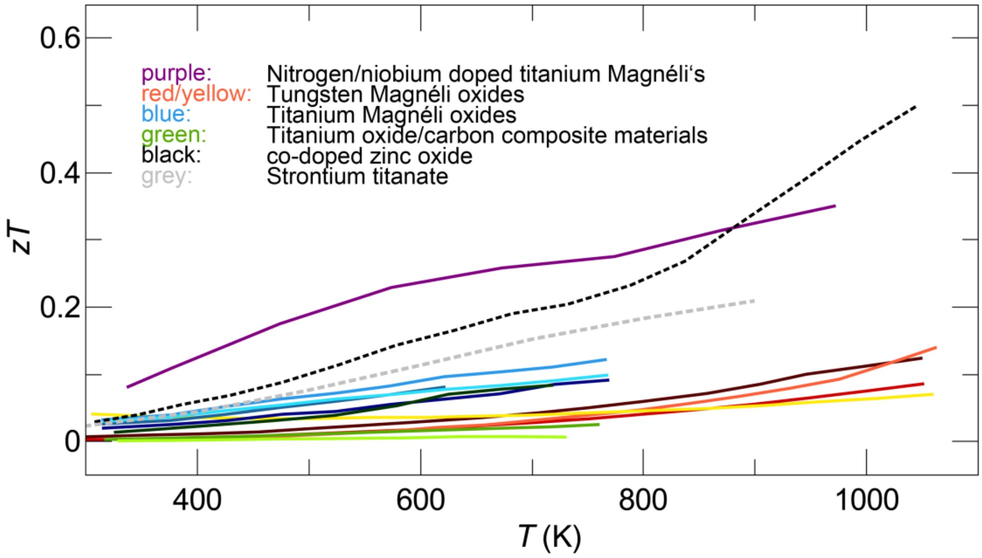

Figure 2. Overview of thermoelectric figures of merit of *n*-type Magnéli oxides in comparison with strontium titanate (containing yttrium stabilized zirconia nano-inclusions, YSZ) and co-doped zinc oxide. *zT* values were adapted from the literature, see references [4,14,25,27–29,35,37,38,40]. Note, zinc oxides have been investigated for a long time as *n*-type thermoelectric oxides but only a few reports exist that report *zT* values larger than 0.4.

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