Near-Broken-Gap Alignment between FeWO₄ and Fe₂WO₆ for Ohmic Direct p–n Junction Thermoelectrics

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ABSTRACT: We report a near-broken-gap alignment between p-type FeWO₄ and n-type Fe₂WO₆, a model pair for the realization of Ohmic direct junction thermoelectrics. Both undoped materials have a large Seebeck coefficient and high electrical conductivity at elevated temperatures, due to inherent electronic defects. A band-alignment diagram is proposed based on X-ray photoelectron and ultraviolet–visible light reflectance spectroscopy. Experimentally acquired nonrectifying I–V characteristics and the constructed band-alignment diagram support the proposed formation of a near-broken-gap junction. We have additionally performed computational modeling based on density functional theory (DFT) on bulk models of the individual compounds to rationalize the experimental band-alignment diagram and to provide deeper insight into the relevant band characteristics. The DFT calculations confirm an Fe-3d character of the involved band edges, which we suggest is a decisive feature for the unusual band overlap.

KEYWORDS: thermoelectric oxides, broken-gap junction, Ohmic contact, band alignment, p–n junction, computational first-principles modeling

INTRODUCTION

A known problem of state-of-the-art thermoelectric generators (TEGs) is their low thermal stability and poor environmental friendliness, as they are built up from low melting point intermetallic alloys, containing toxic and scarce elements such as Pb, Te, and Bi. The use of oxide thermoelectrics (TEs) promises increased temperature stability, better environmental compatibility, and lower costs through the use of more abundant elements and is hence likely to expand the field of application of TEs. TEGs, however, are not only limited by the TE material properties but also limited by the electric and thermal contacts between the materials and the metal interconnects, which pose additional challenges. It is essential to establish good nonrectifying (“Ohmic”) contacts between the TE material and the metal interconnect, while avoiding interdiffusion, melting, and oxidation of the contact materials. This often makes it unavoidable to use expensive noble metal interconnects. At the same time, it must be ensured that the thermal expansion coefficients of the individual components such as TE materials, interconnect, solder, and diffusion barrier do not differ too much from one another in order to avoid failure of the module during thermal cycling.

Many of these issues could be tackled by the approach of Shin et al. through the use of oxide TEs with a direct p–n junction, hereby omitting the metal interconnects at the hot side. However, p–n junctions are usually not Ohmic but exhibit rectifying behavior, which represent large parasitic resistances in the device. A solution to the rectifying behavior is a broken-gap junction couple, well-known in the field of photovoltaics. A broken-gap junction forms a charge accumulation region instead of a charge depletion zone, which leads to fully Ohmic characteristics.

In this work, we study the p–n junction of the TE couple p-type FeWO₄ and n-type Fe₂WO₆. The two phases show no reactivity toward each other and can be regarded as coexistent. We combine experimental studies with ab initio calculations on the individual materials to establish a model for the band alignment between the two materials. Our findings support a near-broken-gap junction alignment, with a nonrectifying junction behavior. The implementation of broken-gap junctions in direct junction TEGs could give them a significant advantage over their diode-like alternatives without the need of high-temperature thermionic emission.

EXPERIMENTAL SECTION

Fe₂WO₆ was synthesized by the standard solid-state reaction route. The starting materials Fe₂O₃ (STREM chemicals 99.8%) and WO₃ (Sigma-Aldrich 99.9%) were mixed stoichiometrically, thoroughly ground in an agate mortar, and pressed into 10 mm pellets with a cylindrical die. The pellets were reacted at 950 °C for 16 h in a covered alumina crucible. The pellets were reground and the procedure was repeated three times.
pressed together by springload to ensure good electrical contact. A resistive heater on one side of the sample allowed us to measure in-plane Seebeck and conductivity under identical conditions. The background was calibrated to the reference spectrum of a BaSO4 reference sample.

The Seebeck coefficient of Fe3WO4 (□) and FeWO4 (■) as a function of inverse temperature.

Figure 1. (a) Conductivity and (b) Seebeck coefficient of Fe3WO4 (□) and FeWO4 (■) as a function of inverse temperature.

RESULTS AND DISCUSSION

FeWO4. The electric conductivity of FeWO4 follows a thermally activated trend, with a smooth transition at about 500 °C, as seen in Figure 1a. The p-type conductivity is maintained over the entire temperature range, which is evident from the positive Seebeck coefficient plotted in Figure 1b. The p-type charge carriers have been described as small polaron holes, localized on Fe sites, representing oxidized Fe3+ species. The Seebeck coefficient below 500 °C is nearly constant (see Figure 1b). In the Hubbard model for correlated systems, this indicates a region of constant charge carrier concentration,
which can be attributed either to a specific doping level or to a frozen-in defect concentration. Activation energies are obtained from a ln(σT) versus 1/T plot, as these materials conduct in a polaron hopping manner with a diffusion-like mechanism. The conductivity activation energy of 0.18(2) eV in the constant charge carrier region is thus equal to the polaron mobility migration barrier. The experimental value of 0.18(2) eV is close to the theoretically predicted minimum migration barrier of 0.14 eV.\(^{30}\) Above 500 °C, a decrease in the Seebeck coefficient can be identified, which indicates an increase in the charge carrier concentration. The conductivity activation energy now reflects both concentration (formation) and mobility (migration) of the charge carriers. Assuming that the mobility migration barrier of 0.18(2) eV remains unchanged, the total conductivity activation energy of 0.52(3) eV results in a charge carrier formation energy of 0.34 eV, which is again close to the theoretically predicted formation energy of 0.48 eV.\(^{30}\) As this energy is too small to be half the band gap and to reflect intrinsic ionization, it may rather be attributed to a charge carrier formation reaction in the form of oxygen interstitials or cation vacancies. This would result in a standard enthalpy of the formation of the point defect and two hole charge carriers of 0.34 eV \(\times 3 \approx 1\) eV, which is a typical value for the formation of oxygen excess or cation deficiency defects from \(\text{O}_2(g)\). According to DFT calculations, Fe vacancies are the most stable intrinsic defects,\(^{30}\) and if formed alone (without simultaneous formation of \(W\) vacancies), they must be accompanied by exsolution of an iron-rich phase, such as a binary iron oxide. The leveling out below 500 °C in both conductivity and Seebeck coefficient—as indicated above—is accordingly interpreted as a region of the frozen-in defect formation reaction or an overtaking of a slight nonstoichiometry in the cation ratio inherent to the synthesis.

Band gap measurements for \(\text{FeWO}_4\) are quite consistently around 2 eV in the literature,\(^{26,30,31}\) and supported by our DFT calculations, which will be discussed in a later section. Optical reflectance measurements, analyzed in a Kubelka–Munk plot, revealed a major indirect absorption edge at 1.48(2) eV, which is too low to be in the region of the band gap (shown in the Supporting Information Figure S11). DFT calculations suggest major parallels in the density of states (DOS) near the band gap between \(\text{FeWO}_4\) and \(\text{FeO}_2\);\(^{32}\) we thus compare the two briefly in the following. Balberg et al. reported an absorption feature at \(\approx 1.3\) eV\(^{33}\) assigned to the \(5\text{T}_{2g} \rightarrow \text{E}_g\) transition,\(^{34}\) which effectively “blackens-out” higher absorption edges. Although they could observe the hint of an absorption edge at 2 eV, representing the band gap, this was not possible for \(\text{FeWO}_4\). For the construction of the band-line diagram (see below), we assume a band gap of 2.00 eV for \(\text{FeWO}_4\).

\(\text{Fe}_2\text{WO}_6\). Likewise, thermally activated conductivity is observable in an Arrhenius plot for \(\text{Fe}_2\text{WO}_6\) with two straight lines and a transition at 650 °C. The negative Seebeck coefficient indicates n-type conductivity over the accessible temperature range. A decrease in the absolute Seebeck coefficient coincides with the transition in the Arrhenius plot at 650 °C. The conductivity is of small polaron hopping nature with electrons localized on Fe sites, representing reduced Fe\(^{2+}\) states.\(^{35}\) In an earlier publication, we have investigated the electrical transport and oxygen nonstoichiometry of \(\text{Fe}_2\text{WO}_6\) in detail, based on a defect chemical description.\(^{36}\)

Band gap estimates for \(\text{Fe}_2\text{WO}_6\) are not straightforward and several energies have been reported in the literature. Optically measured band gaps are often reported to be of 1.5–1.7 eV,\(^{37}\) which is close to, but smaller than the absorption edge visible for our sample in the Kubelka–Munk-plot occurring at 1.84(2) eV (see Supporting Information Figure S11). A band gap smaller than 1.66 eV would indicate a degenerate semiconductor with the Fermi level in the valence band (as this corresponds to the valence band off-set (VBO) determined for our sample by XPS), contradicting the nondegenerate semiconductor properties from conductivity measurements. Our DFT calculations (see Figure 6) predict a band gap of 2.3 eV, which is much larger than the experimentally obtained values. However, it should be noted that the calculations do not include any defects or mixed valence states in the structure, and it is possible that the presence of oxygen vacancies and reduced iron species lowers the band gap significantly. We take the band gap estimate of 1.84 eV as a realistic assumption for the construction of the band diagram. As indicated above, the two tungstates show related yet opposite characteristics. The charge-carrying species of one of the tungstates represents the matrix component of second tungstates, and vice versa—specifically: In the divalent iron matrix of \(\text{FeWO}_4\), \(\text{Fe}^{3+}\) represents an electron hole, whereas in \(\text{Fe}_2\text{WO}_6\) the opposite situation is given, with \(\text{Fe}^{3+}\) representing an extra electron in the trivalent iron, the host structure. \(\text{FeWO}_4\) and \(\text{Fe}_2\text{WO}_6\) are the only ternary compounds in the phase diagram of the \(\text{Fe–W–O}\) system and have been shown to coexist as separate phases.\(^{38–40}\) The lattice constants of \(\text{FeWO}_4\) and \(\text{Fe}_2\text{WO}_6\) prior and after being in contact with each other at high temperatures for an extended period of time did not change significantly and there is no indication for the formation of other phases. For comparison, in the solid solutions of \(\text{Fe}_{1−x}\text{Mn}_x\text{WO}_4\), the a-axis lattice parameter shows a high sensitivity on the Mn content, varying by more than 0.1 Å.\(^{41}\) We therefore expect \(\text{FeWO}_4\) and \(\text{Fe}_2\text{WO}_6\) to be separated by a large miscibility gap in a quasi-binary-phase diagram.

**Electronic Junction between \(\text{FeWO}_4\) and \(\text{Fe}_2\text{WO}_6\).** The \(I–V\) characteristics of the \(p–n\) junction are shown in Figure 2a.

\[\begin{align*}
\text{Figure 2.} & \quad \text{(a) Logarithmic } I–V \text{ characteristics of the } p–n \text{ junction of } \text{Fe}_2\text{WO}_6 \text{ and } \text{FeWO}_4 \text{ from room temperature to } 900 \degree C. \quad \text{(b) Junction } ASR \text{ as a function of temperature.}
\end{align*}\]
attribute this to the collective resistances of setup wiring and current collectors, which cannot be fully eliminated in the two-electrode three-wire measurements. The individual material resistances are by 1 order of magnitude lower compared to the measured total junction resistance, indicating that the majority of voltage drops across the junction and not in the individual materials.

The Ohmic behavior of the p−n junction points toward the band alignment of a broken-gap junction. A broken-gap junction forms between materials with a large difference in electron affinities, where the respective band gaps do not overlap.

Bringing such two materials into contact results in a flow of electrons from the p-type to the n-type, as the Fermi level of the p-type lies above the Fermi level of the n-type.

This leads to a charge accumulation region at the junction in contrast to a charge depletion zone in classic staggered junctions.

With the Fermi level aligned in equilibrium, charge transfer takes place directly between the p-type valence band and the n-type conduction band. A schematic illustration of the broken band junction is shown in Figure 3.

X-ray Photoelectron Spectroscopy. To confirm the validity of this type of band alignment, X-ray photoelectron spectroscopy (XPS) measurements were carried out. XPS provides insight on the Fermi level position via the work function (Φ) with respect to the vacuum level, and VBO with respect to the Fermi level, and allows calculation of the electron affinity (χ). From the primary electron onset, the VBO with respect to the Fermi level can be obtained, whereas the secondary electron cutoff gives the work function (Φ), which is the position of the Fermi energy with respect to the vacuum level. Intensity onsets can, in most cases, be extracted from linear fits intersects, between the baseline and leading edge of the onset slope.

Following this practice, VBOs with respect to the Fermi energy were determined to be 1.66 eV and 0.17 eV for Fe2WO6 and FeWO4, respectively (see Figure 4b,d). The primary electron onset for FeWO4 shows a peculiar double onset, shifted by 1.2 eV to which we will return in a later section. Secondary electron cutoff for Fe2WO6 produced a work function of 4.51 eV. The cutoff for FeWO4, however, is not accessible by this method as the onset is smeared out, which is likely to stem from tail states, surface space charge, or surface roughness. An exclusion principle based on the confidence interval of the baseline was used to determine the real onset in FeWO4 (described in the Supporting Information). Applying this method resulted in a work function of 4.32 eV for FeWO4.

Nonrectifying, low contact resistance is also typical for tunnel junctions at low biases.10 These tunnel junctions however usually depend highly on the applied bias and show a characteristic breakdown region of negative differential resistance in forward bias, due to a bias-driven misalignment between the n-type conduction band and p-type valence band, when crossing a critical transition point. At further increased forward bias, beyond the negative resistance region, the tunnel junctions behave like typical rectifying p−n junctions with exponential current increase. For the iron tungstate junction, the tunneling junction explanation can be ruled out, due to the absence of a breakdown region and of an exponential growth region.

Below temperatures of 500 °C, the junction shows an activation energy of 0.42(2) eV in an Arrhenius plot. The activation energy has to be attributed to the potential barrier arising from the charge accumulation layer forming at the junction.

Figure 3. Schematic illustration of a broken-gap junction in (a) reverse bias, (b) equilibrium, and (c) forward bias.

Figure 4. X-ray photoemission spectral narrow scans of selected regions. The narrow scans (a,c) depict the secondary electron cutoff, representing the work function of Fe2WO6 and FeWO4. Narrow scans (b,d) show primary electron onset narrow scans, representing VBOs with respect to the Fermi energy of Fe2WO6 and FeWO4.
produces the same work function as the linear extrapolation method.

**Junction Band Alignment.** From work function ($\Phi$), VBO, and band gap ($E_g$), a simple band-alignment diagram can be constructed and the electron affinity ($\chi$) can be calculated. Electron affinities $\chi_n = 2.49$ eV and $\chi_p = 4.33$ eV were calculated for FeWO$_4$ and Fe$_2$WO$_6$, respectively, from the relation

$$\chi = \Phi + E_{\text{VBO}} - E_s$$

The schematic energy band diagram is shown in Figure 5. The vacuum level is taken as the reference point. The Fermi level of the p-type FeWO$_4$ lies 0.19 eV higher in energy than $E_f$ for the n-type Fe$_2$WO$_6$, fulfilling the condition $\Phi_p < \Phi_n$ for nonrectifying p–n junctions. It becomes clear that the alignment is not a fully broken one but rather a near-broken-gap junction, as the CBM of Fe$_2$WO$_6$ still lies 0.16 eV above the VBM of FeWO$_4$. Near-broken-gap junctions, however, can still exhibit the Ohmic behavior of full-broken-gap junctions, assuming band tails to enable the crossing between the conduction and valence band. We thus suggest a band bending, as described in Figure 3b, where the n-type conduction band bends downward and the p-type valence band bends upward, forming an s-shape-like alignment.

**DFT Calculations.** The DOS obtained from *ab initio* density functional calculations are shown in Figure 6 and provide additional insight into the dominant character of the crucial bands involved. Hybrid functional HSE potentials are capable of providing an accurate description of complex structures. We present results from HSE03 calculations, which shows better correspondence to experiments than HSE06. The DOS is spin-averaged for clarity and limited to the section that is relevant for the band gaps. A more detailed spin-resolved DOS plot in an extended range is available in the Supporting Information in Figure S13. The calculations assume perfect crystallinity at 0 K without the presence of defects, mixed valencies, or surface effects. Thus, no interband gap states occur and the Fermi level is put to the valence band edge at zero energy. In Figure 6, the DOS plot of Fe$_2$WO$_6$ is shifted downward to represent the band alignment and the dashed line indicates the common Fermi level, as proposed by our XPS results.

![Figure 5. Schematic illustration of the band alignment between FeWO$_4$ and Fe$_2$WO$_6$ before equilibrium. The alignment resembles a near-broken-gap junction, with the Fermi level of FeWO$_4$ lying higher than that of Fe$_2$WO$_6$, thus resulting in a charge accumulation region at equilibrium in contrast to a charge depletion zone in staggered junctions.](image)

![Figure 6. DFT (HSE03)-calculated projected densities of states for (a) FeWO$_4$ and (b) Fe$_2$WO$_6$. The energy scales are shifted by the difference in their work functions to indicate the junction alignment as proposed above. The contributions are averaged over spin for clarity. The common Fermi level is indicated by a dotted line and the gray overlays display band gaps.](image)

Our DFT calculations predict a band gap of 2.00 eV for FeWO$_4$ in good accordance with previously reported DOS of FeWO$_4$ using a hybrid functional. The main band gap is followed by a second band gap of 1.1 eV, between the localized Fe-3d state and lower-lying filled O-2p bands. This second band gap is indeed observable in Figure 4d, as a second onset shifted by 1.2 eV in the XPS primary electron onset. GGA+U calculations are not able to reproduce the isolated Fe-3d band above the O-2p valence bands. It should be emphasized that the VBM of FeWO$_4$ is a cationic state, in contrast to an anionic state that is usually the case for binary/ternary semiconductors (e.g., from the common anion rule).

The calculations predict a band gap of 2.3 eV for Fe$_2$WO$_6$, which is experimentally estimated at 1.84 eV. Intraband gap states from oxygen vacancies and reduced Fe species are not considered in the calculations and would expectedly reduce the calculated band gap. The VBM of Fe$_2$WO$_6$ is mainly composed of O-2p, and the CBM is dominated by Fe-3d bands. Since the VBM of FeWO$_4$ and the CBM of Fe$_2$WO$_6$ are both of the Fe-3d character, the band alignment, as proposed above, conclusively takes place between bands of the same character. To date, the band alignment between semiconducting transition-metal oxides in heterojunctions is not well-investigated. We would like to emphasize that several other transition-metal oxides, containing, for example, Co or Mn, show cationic states at the VBM. It remains open whether the presence of a low-lying cation band is generally beneficial for the formation of Ohmic p–n junctions and can be exploited. Mentionable here is the p–n junction between Ca$_3$Co$_4$O$_9$ and CaMnO$_4$ reported by Kanas et al., showing nonrectifying behavior. The p-type Ca$_3$Co$_4$O$_9$ does indeed show a cationic Co-3d band at the valence edge. We can compare this to the well-investigated heterojunction of n-ZnO and p-NiO, where both VBMs are dominated by O-2p bands. Sultan et al. undertook a study on band alignment and $I$–$V$ characteristics of ZnO/NiO heterojunctions, showing a staggered band alignment and rectifying behavior with a “turn-on” voltage of 0.9 V. Based on band gap values for ZnO (3.28 eV) and NiO (3.45 eV), they show a staggered band alignment with $\Delta_{\text{CB}} = 2.82$ eV and $\Delta_{\text{VB}} = 2.65$ eV offsets for conduction and valence bands, respectively. This leaves a band discontinuity $\Delta_{\text{VB}} - \Delta_{\text{CB}}$ of merely 0.63 eV between ZnO conduction and NiO valence band edge.
Despite the small band discontinuity that junction exhibits rectifying behavior. For comparison, the FeWO$_4$/Fe$_2$WO$_6$ heterojunction in thermal equilibrium results in a band discontinuity of CB$_{FeWO_4} - $ VB$_{FeWO_6} = 0.35$ eV.

**CONCLUSIONS**

We have investigated FeWO$_4$ and Fe$_2$WO$_6$ as a model p–n couple for high-temperature direct junction TEs. In contact, these materials stay p-type/n-type, show no reactivity toward broken-gap junctions in transition-metal oxide p–n junction TEs. They circumvent the rectifying diode behavior of classic staggered-gap junctions and their large parasitic resistance.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c19341.

X-ray powder diffraction patterns, lattice parameters, and crystal structures of FeWO$_4$ and Fe$_2$WO$_6$: XPS survey-scan spectra of FeWO$_4$ and Fe$_2$WO$_6$: XPS secondary electron cutoff narrow scan of FeWO$_4$ for determination of the onset and work function; Kubelka–Munk plots for FeWO$_4$, and Fe$_2$WO$_6$: I–V measurements in an extended temperature and bias range; and spin-resolved projected DOS (HSE03) for FeWO$_4$ and Fe$_2$WO$_6$ (PDF)

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Notes

The authors declare no competing financial interest.

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