Single-step preparation and consolidation of reduced early-transition-metal oxide/metal n-type thermoelectric composites

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Reduced early transition metal oxides/metal composites have been identified here as interesting thermoelectric materials. Numerous compositions in the Nb-rich portion of the WO3–Nb2O5 system have been studied, in composite formulations with elemental W. Spark plasma sintering (SPS) has been employed to achieve rapid preparation and consolidation of composite materials containing W metal precipitates with characteristic length scales that range from under 20 nm to a few microns, that exhibit thermal conductivities that are constant from 300 K to 1000 K, approximately 2.5 W m−1 K−1. Thermoelectric properties of these n-type materials were measured, and the highest-performing compositions were found to reach figure of merit zT values close to 0.1 at 950 K. The measurements point to higher zT values at yet-higher temperatures.

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FIG. 1. WO$_3$–Nb$_2$O$_5$ phases tend to form complex tetragonal tungsten bronze structures, which feature 3-dimensional slabs of corner-sharing NbO$_6$ octahedra connected by WO$_4$ tetrahedra. W$_3$Nb$_{14}$O$_{44}$ is one such example of many possible homologues; the size of the slabs can be changed with W/Nb composition. The high polyhedral connectivity is important for good electrical transport, while the intrinsic structural defects (such as the crystallographic shear planes and W/Nb site substitution) are important for low thermal transport.

I. INTRODUCTION

The promise of solid-state energy conversion and the recovery of energy from waste heat in devices that have no moving parts has led to vigorous research on thermoelectric materials. However, widespread deployment of thermoelectric modules has been limited by some combination of low efficiency, low crustal abundance of the key elements in routinely-studied thermoelectrics, and poor thermal stability of materials. Oxide materials potentially help address some of these issues, but few high-performance $n$-type materials have been discovered. The performance of thermoelectric materials is usually measured by the figure of merit $zT$ given by $zT = (S^2T)/(\rho\kappa)$; a function of the electrical resistivity $\rho$, the Seebeck coefficient $S$, and the thermal conductivity $\kappa$ of the material at temperature $T$. A recent data mining study carried out by some of us,$^1$ had pointed out that empirically, high performing thermoelectric materials operating at (typically) 1000 K have Seebeck coefficients in the range of 200 $\mu$V K$^{-1}$ to 300 $\mu$V K$^{-1}$, and electrical resistivities close to $1 \times 10^{-3}$ $\Omega$ cm. In many oxide materials, attaining high Seebeck coefficients is frequently not as challenging as achieving these relatively metallic resistivity values.$^2$ In addition, small-unit-cell oxides such as spinels, perovskites, and rutiles, are usually highly connected, and therefore have relatively high lattice thermal conductivities, which is undesirable. In this study, early transition-metal oxides with relatively large unit cells, prepared as composites with metals, have been rationally selected as potentially being able to overcome the pitfalls of high resistivity coupled with low thermal conductivity that many bulk oxides display.

The WO$_3$–Nb$_2$O$_5$ phases selected for study here tend to form complex tetragonal tungsten bronze structures, which feature 3-dimensional slabs of corner-sharing NbO$_6$ octahedra connected by WO$_4$ tetrahedra.$^3$ Nb$_2$O$_5$ has many polymorphs, but the dominant
room-temperature phase is a layered structure with distorted and irregular Nb polyhedra. This poor structural connectivity is not ideal for electrical transport and electronic doping. However, WO$_3$–Nb$_2$O$_5$ phases can be doped to have low electrical resistivity, in part because of the highly connected 3D structures that derive from the perovskite aristotype. Highly connected structures also tend to have high thermal conductivity, but this is mitigated in the tungsten bronze structure-types because of the complex, large-unit cell structures. In the study here, which W/Nb substitution, oxygen deficiency, and crystallographic shear (Figure 1) also potentially decrease thermal conductivity. Indeed, Winter and Clarke have shown the thermal conductivity of stoichiometric $d^0$ analogues to the materials studied here to be about 2 W m$^{-1}$ K$^{-1}$ from 300 K to 1300 K.

In this contribution, the thermoelectric properties of composite samples from the Nb-rich portion of the WO$_3$–Nb$_2$O$_5$ system are reported. The samples were prepared in single step of short duration that combined preparation from starting materials (elemental metals and oxides) with consolidation. The technique employed for the one-step preparation and consolidation was spark-plasma sintering or SPS, perhaps more accurately referred to as current-assisted pressure-activated densification. This is a rapid preparatory route to react materials, with typical reaction taking minutes, instead of hours or days, and yielding dense, consolidated solids that can be directly employed for physical property measurements. The preparation of phase-pure single-cation WO$_3$–$\delta$ and multi-cation Cr$_2$WO$_6$ have been previously demonstrated using SPS, proving that ion mobility is sufficient to allow diffusion and phase equilibrium in WO$_3$ systems at these reaction temperatures and time-scales. Conventional solid-state preparation of the materials W–Nb–O oxide materials studied here requires extended heat treatments at high temperatures (e.g., 1350°C in sealed platinum crucibles). In addition to being time-consuming, extended heat treatments at high temperatures also result in difficulties with stoichiometry control, because of volatilization of precursor oxides; a problem often encountered in the preparation of oxides of W. Furthermore, the final product of conventional preparation is usually powder that must be consolidated and densified before physical property measurements can be performed. In this work, SPS was used to prepare dense pellets of (W$_{1.083}$O$_3$)$_x$(Nb$_{2.1}$O$_5$)$_{1-x}$ from a mixture of binary oxides and metal powders in less than 30 min per sample.
FIG. 2. A typical SPS densification profile during sample processing. SPS was used to prepare dense pellets of \((W_{1.083}O_{3.0})_x(Nb_{2.1}O_5)_{1-x}\) composites from a mixture of binary oxides and metal powders in under 30 min. 80 MPa of uniaxial pressure was applied and the sample was heated rapidly from 673 K to 1473 K at 170 K/min, annealed for 6 min at 1473 K, then rapidly cooled at 180 K/min. The temperature profile below 673 K was estimated, as the pyrometer is unreliable below 673 K.

FIG. 3. SPS was used to prepare 14 samples that were subsequently characterized to elucidate the evolution of thermoelectric properties with composition in the \((W_{1.083}O_{3.0})_x(Nb_{2.1}O_5)_{1-x}\) phase system. After measurement of room temperature electrical properties, smaller subsets of samples were investigated more thoroughly.

II. METHODS

Fourteen compositions were chosen based on reported stable phases,\(^{10}\) even though the crystal structure was not known in all cases. Stoichiometric \(WO_3\), \(Nb_2O_5\), or \((WO_3)_x(Nb_2O_5)_{1-x}\) (\(d^0\) oxides) are electrical insulators, so the materials were doped with 0.5 electrons per metal cation by adding corresponding amounts of elemental metal to the initial mixture. Tungsten was treated as a \(d^6\) donor, so 1/12 molar equivalents of W were added for every equivalent of \(WO_3\)—1/10 equivalents of Nb, treated as \(d^5\), were added for each \(Nb_2O_5\). The final compositions of \((W_{1.083}O_{3.0})_x(Nb_{2.1}O_5)_{1-x}\) are consistent with the W/Nb ratio determined after preparation, by elemental analysis using energy-dispersive X-ray spectroscopy (EDX).

Polycrystalline samples were made by simultaneous reaction and consolidation of binary oxide and elemental powders (\(WO_3\), 99.9%, Sigma-Aldrich; \(Nb_2O_5\), 99.99%, Sigma-Aldrich, W, 99.99%, Sigma-Aldrich; Nb, 99.8%, Sigma Aldrich) using spark plasma sintering on an instrument from FCT Systeme GmbH, Germany. In a chamber base pressure of 10 torr of argon, 80 MPa uniaxial pressure was applied using a 9 mm inner-diameter graphite die (EDM-4, POCO graphite). The sample was then heated rapidly to 1473 K at 150 K/min, annealed for 6 min at 1473 K, then rapidly cooled at 180 K/min (Figure 2). X-ray diffraction (XRD) of the resulting dense pellets was performed using a laboratory instrument (Philips X’Pert diffractometer, Cu K\(\alpha\) radiation). After initial room-temperature
electrical transport measurements, a subset of these samples was subjected to more rigorous study (Figure 3).

High-resolution synchrotron XRD data on finely-ground powder was acquired at 295 K at beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory, using an average wavelength of \( \sim 0.4137 \text{Å} \) with a diffractometer that has been described in detail by Wang et al.\(^{11}\) The precise wavelength was determined using a mixture of Si (SRM 640c) and Al\(_2\)O\(_3\) (SRM 676) NIST standards run in a separate measurement. Samples were contained in 0.8 mm diameter Kapton capillaries and the packing density was low enough that absorption was not noticeable. Rietveld refinement was performed using the TOPAS 5 Academic program suite.\(^{12}\) Instrument profile parameters were determined using Si (SRM 640c) and LaB\(_6\) (SRM 660b) NIST lineshape standards, run in separate measurements.

Scanning electron microscopy (SEM) was performed on an FEI XL30 microscope using a backscatter electron (BSE) detector; EDX data were collected with an EDAX Si-drift detector. Typical accelerating voltages were 15 keV or 20 keV. To prepare samples for SEM, pellets were mounted in epoxy and polished with successively finer abrasives; the final polishing step was performed with 0.25 \( \mu\text{m} \) colloidal diamond suspension on MicroCloth. A thin layer of Pd–Au, 2 nm to 5 nm, was sputtered on the surface to alleviate charging during imaging. The brightness and contrast of the micrographs presented have not been post-processed in any way. Particle size analysis was performed using ImageJ\(^{13}\) on 2500× magnification micrographs, areas of approximately 33 \( \mu\text{m} \times 33 \mu\text{m} \), to visualize the smallest features, some of which remain sub-pixel diameter even at this magnification. A minimum size cutoff threshold of 0.05 \( \mu\text{m}^2 \) was used to minimize false positives.

The high-temperature (950 K max) electrical resistivity and Seebeck coefficient were measured with an ULVAC Technologies ZEM-3. Samples had approximate dimensions of 9 mm × 3 mm × 3 mm. Measurements were performed in a helium under-pressure, and data was collected through three heating and cooling cycles to ensure sample stability and reproducibility. No changes in electrical properties were observed between cycles, and analysis of the lab XRD patterns from materials after measurements showed no changes in structure nor new phases. Additionally, comparing BSE micrographs collected before and after electrical property measurements revealed no change in microstructure.

The thermal conductivity, \( \kappa \), was calculated from the density \( \rho \), thermal diffusivity \( \alpha \),
FIG. 4. Synchrotron XRD was performed on a subset of 8 samples in the $\text{W}_{1.083}\text{O}_3x(\text{Nb}_{2.1}\text{O}_5)_{1-x}$ series. Although specific W–Nb–O phases could not be determined due to the insensitivity of XRD to the many of the possible superstructures in these materials, the presence of BCC W in most samples is evident. The intensity of reflections from W metal increases with increasing $x$ from $x = 0.02$ to $x = 0.13$.

FIG. 5. X-ray diffractogram and two-phase Pawley refinement of $(\text{W}_{1.083}\text{O}_3)_{0.02}(\text{Nb}_{2.1}\text{O}_5)_{0.98}$, modeled using $\text{WNb}_{12}\text{O}_{33}$ and W. Reflections from elemental W are well described, but reflections from the primary phase are poorly fit at low $Q$ when using reported W–Nb–O crystal structures as starting models.

and heat capacity $C_p$, using the relation $\kappa = \rho \alpha C_p$. The densities of consolidated samples were measured using helium pycnometry (MicroMeritics AccuPyc 1340 Pycnometer). To reduce the large systematic errors often introduced by measuring the heat capacity, the temperature-dependent heat capacity was estimated using the empirical Neumann-Kopp rule based on the chemical composition and literature values for the heat capacity of $\text{WO}_3$ and $\text{Nb}_2\text{O}_5$, as outlined by Leitner et al. The estimated error for the heat capacity introduced by this method was $< 3\%$ at 300 K, and $< 5\%$ at 1000 K. The thermal diffusivity ($\alpha$) was measured using a Netzsch LFA 457 laser flash system. The samples for the thermal diffusivity measurements were machined to be coplanar with a thickness of between 1 mm and 2 mm and a diameter of 8 mm. The samples were then spray coated with colloidal graphite on both sides to ensure maximum optical absorption and emissivity. Thermal diffusivity was measured in an argon gas atmosphere from 308 K to 1050 K at intervals of 50 K. A final measurement at 308 K was taken after cooling to ensure reproducibility of the measurements and to ensure the coatings remained intact. The thermal diffusivity values were determined using the model of Clark and Taylor, which corrects for radiative losses.

III. RESULTS AND DISCUSSION

Powder XRD reveals the presence of elemental, body-centered cubic (BCC) W in many samples, in addition to peaks characteristic of W–Nb–O phases (Figure 4). A sample re-
FIG. 6. Backscatter electron micrographs (W<sub>1.083</sub>O<sub>3</sub>)<sub>x</sub>(Nb<sub>2.1</sub>O<sub>5</sub>)<sub>1−x</sub> (<em>x</em> = 0.02, 0.13, 0.31) at 200× and 2500× magnification reveal small W metal precipitates (white) homogeneously distributed throughout samples with low W content (<em>x</em> ≤ 0.13). The smallest inclusions are sub-pixel diameter (<20 nm), whereas the larger inclusions are a few microns in length, covering a wide range of relevant length scales to interact with phonons. The average size and number of precipitates increases with <em>x</em> in this regime. This microstructure is stable after repeated thermal cycling up to 950 K, the highest temperatures measured. At high W content (<em>x</em> ≥ 0.31), the microstructure is poorly controlled, and there are larger domains of multiple minor phases, tens of microns in width).

Refinement is shown in Figure 5, using monoclinic WNb<sub>12</sub>O<sub>33</sub> (space group <em>C</em>2, with refined parameters very near those reported by Roth <em>et al.</em>9) and BCC W for the model. The fit is able to account for the elemental W but is unable to describe the primary phase reflections, particularly at low <em>Q</em>. The exact W–Nb–O phases were not able to be determined using powder XRD, as their crystal structures have large unit cells with many atomic positions, and structural similarity leads to many coexisting phases that complicate analysis. Furthermore, the XRD patterns of the many phases can only be distinguished by weak superstructure peaks at very low angles (<em>Q</em> < 1.5 Å<sup>−1</sup>) created by O ordering, which contributes only weakly to the total X-ray scattering compared to the more electron-rich W and Nb atoms in the materials.

SEM was performed to investigate the microstructure of the samples, and to reveal the disposition of the multiple phases in each sample. There were no noticeable differences between cross-sections taken from the top or sides of the pellets, suggesting the microstructures are uniform. As opposed to previous studies where single-phase W-containing oxides were prepared by SPS in a single step,<sup>7,8</sup> we observe multiple phases in this W–Nb–O system. BSE micrographs combined with EDX reveal the presence of W-rich inclusions with a wide range of length scales (Figure 6). Owing to the small precipitate size and large interaction volume of EDX, approximately 1 µm in diameter, EDX is unable to unambiguously determine the precise atomic composition, though it is likely these precipitates are W metal and give rise to the W metal reflections observed by XRD. The smallest inclusions are <20 nm, whereas the larger inclusions are approximately 500 nm along their narrow
FIG. 7. The average size of W metal precipitates measured in BSE micrographs and the area fraction of precipitates increases smoothly with W content when $x \leq 0.13$ in $(W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}$. To minimize false detection events, only precipitates larger than $0.05 \mu m^2$ (effective diameter of 250 nm) were used for this analysis.

axis and up to $2 \mu m$ long. The dimensions of these precipitates are ideal for scattering phonons with a broad wavelength distribution and lead to low thermal conductivity at low temperature, as shown later.

At low W content ($x \leq 0.13$), W metal secondary phase inclusions are homogeneously distributed and quite small, with median sizes of a few hundred nanometers, suggesting possible solubility at high temperature and phase segregation due to precipitation upon rapid cooling (180 K/min) after the SPS hold at 1473 K. The average size and area coverage of the precipitates increases in a controlled fashion with W content (Figure 7). This is consistent with the increasing intensity of reflections from W metal seen by XRD in this range. Although precipitates of sub-pixel diameter (<20 nm) can be seen in micrographs, only precipitates larger than $0.05 \mu m^2$ (effective diameter of 250 nm) were used for this analysis to minimize false detection events. The precipitate sizes appear to follow log-normal distributions, though meaningful fitting to extract statistical descriptors would require more statistics of particles with smaller sizes.

At high W content ($x \geq 0.31$), in contrast, the microstructure is less controlled, with multiple minor phases, existing as larger domains in excess of $10 \mu m$ in width. The presence of these minor phases not observed at lower W loadings suggests that these high-W compositions may sit in a three-phase field of the W–Nb–O ternary, while low-W compositions are two-phase. The W-rich inclusions transition from evenly dispersed sub-micron particles to unsystematic domains tens of microns in size. This is likely because the concentration and domain size of these inclusions increases with W content, up to some point at which they coalesce and segregate to minimize interfacial area, and therefore surface energy. This change in behavior may be related to the critical percolation threshold ($27\%$ site filling for a random close-packed three-dimensional lattice).\(^{18}\)
FIG. 8. \((W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}\) displays metallic electrical transport when \(x \leq 0.08\), and maximum electrical performance \((S^2/\rho)\) for thermoelectric considerations is seen at \(x = 0.08\). The electrical transport properties of the materials do not change after repeated thermal cycling up to the maximum temperatures measured, 950 K. One-step SPS prepared \(x = 0.02\) material (squares) has comparable properties to material of the same composition made using traditional solid-state methods (red line).

A. Thermoelectric properties

To determine the thermoelectric performance of the composites, electrical transport properties of \((W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}\) were measured up to 950 K (Figure 8). The thermoelectric performance is defined by the thermoelectric figure of merit, \(zT = S^2 \rho^{-1} \kappa^{-1} T\), which is a function of the material electrical resistivity \(\rho\), Seebeck coefficient \(S\), thermal conductivity \(\kappa\), and temperature \(T\). Through the compositional series, \(\rho\) increases with W content until \(x = 0.13\), after which it decreases continually, up to the highest W content measured. \(S\) changes predictably in opposition to the electrical resistivity with composition. The power factor, \(S^2 \rho^{-1}\), increases monotonically with temperature up to at least 950 K, the highest temperature measured. With regard to sample composition, the maximum power factor is obtained for samples with \(x = 0.08\).

Several samples were also made by conventional solid-state reaction of precursors in evacuated silica ampoules at 937 K for 48 hours,\(^\text{10}\) followed by densification using the same SPS processing. Samples made using this two-step process displayed similar X-ray diffraction patterns and high-temperature electrical transport properties (electrical resistivity and Seebeck coefficient) as analogous samples made using a one-step process.

Thermal conductivity was determined for a smaller subset of samples (Figure 9) to determine the influence of the microstructures observed in BSE micrographs (Figure 6). Densities used to calculate thermal conductivity were obtained through He pycnometry on consolidated pellets. Although the relative density (compared to the theoretical maximum single-crystal density) cannot be unambiguously known due to the presence of multiple phases and oxygen deficiency, the samples examined here are highly dense; scanning electron microscopy of polished cross-sections reveals no evidence of significant porosity, and comparison with known phases of similar composition shows the composites are of similar
FIG. 9. Very little W content, $x = 0.02$, is sufficient to decrease the thermal conductivity compared to Nb$_2$O$_5$, particularly at low temperatures where longer-wavelength phonons are the dominant carriers of heat. Despite the increase in electrical thermal conductivity, the total thermal conductivity $x = 0.02$ composites is reduced by 30% at 300 K compared to insulating Nb$_2$O$_5$. The thermal conductivity of these biphasic materials is largely invariant with temperature, likely because long-wavelength phonons at low temperatures are scattered by the W metal precipitates that span length scales of $< 20$ nm to a few microns. At high W content, the same reduction in thermal conductivity is not seen.

TABLE I. The densities of $(W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}$ composites measured by He pycnometry are compared with the single crystal densities of known crystal structures with similar composition. The densities of composites are consistently high due to the reduced nature of the composites.

| $x$ | nearest known crystal structure | $\rho_{\text{measured}}$ (g/cm$^3$) | $\rho_{\text{crystal}}$ (g/cm$^3$) | % density |
|-----|---------------------------------|----------------------------------|-------------------------------|----------|
| 0   | Nb$_2$O$_5$                      | 4.992(2)                         | 4.55                          | 110%     |
| 0.02| Nb$_2$O$_5$                      | 4.721(4)                         | 4.55                          | 104%     |
| 0.08| WNb$_{12}$O$_{33}$               | 4.928(2)                         | 4.76                          | 104%     |
| 0.13| W$_4$Nb$_{26}$O$_{77}$           | 5.114(2)                         | 4.93                          | 104%     |
| 0.53| W$_9$Nb$_8$O$_{47}$              | 6.360(2)                         | 5.93                          | 107%     |

density (Table I). The density of the composites is consistently higher by approximately 5%, owing to the reduced nature of the samples.

For $(W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}$ samples with low W content ($x \leq 0.13$), the thermal conductivity is approximately 2.5 W m$^{-1}$ K$^{-1}$, from 300 K to 1050 K (Figure 9). For comparison, the thermal conductivity of stoichiometric Nb$_2$O$_5$, prepared using the same SPS processing conditions, was measured as a reference. Although the thermal conductivity of Nb$_2$O$_5$ approaches the composites at high temperatures ($T > 1000$ K), it is clear the composites achieve a significantly lower thermal conductivity at room temperature, due to the scattering of long-wavelength phonons by the W-rich precipitates that span length scales from nanometers to microns. These low W-content composites have superior thermoelec-
FIG. 10. Physical property measurements reveal that the highest power factor and $zT$ achieved in these samples is for the $x = 0.08$ member, which achieves $zT = 0.1$ at 950 K, the highest temperature measured here. $\kappa zT$ is shown to provide a normalized $zT$ without consideration of thermal conductivity.

FIG. 11. W–Nb–O materials contextualized within the larger survey plot of current oxide thermoelectric materials reveals that W–Nb–O materials at 1000 K (X) are an exciting platform for potential $n$-type oxides. The $(W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}$ composites studied here have comparable performance to CaMnO$_3$ based materials, despite not having been optimized at this stage. The size of the circle is proportional to the material power factor. Dashed lines of constant power factor give bounds for reasonable thermoelectric performance, and this plot reveals the lack of high-performance $n$-type oxide materials. Data from.$^1$

tric performance in every regard compared to Nb$_2$O$_5$; Nb$_2$O$_5$ is too insulating to measure electrical resistivity, whereas $(W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}$ materials exhibit metallic electrical transport. Yet despite the much larger expected contribution from electrical carriers to thermal conductivity in these materials, their thermal conductivity is 30% less than that of insulating Nb$_2$O$_5$ at 300 K.

At high temperature in addition to the secondary phase inclusions, intrinsic defects in the crystal structure may also play a role (e.g., crystallographic shear planes, site defects from oxygen deficiency, and mass contrast from W/Nb site substitution), scattering short-wavelength phonons and reducing their ability to carry heat. Although the thermal conductivity of Nb$_2$O$_5$ approaches the composites at high temperatures ($T > 1000$ K), as it shares many of these intrinsic defects present in $(W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}$, the composites remain the materials with minimum thermal conductivity.

Taken together with electrical property measurements, thermal conductivity measurements reveal the largest $zT$ in this compositional series is achieved by the $x = 0.08$ member, where $zT = 0.1$ at 950 K, the highest temperature measured here (Figure 10).
IV. CONCLUSIONS

Early transition metal oxides were targeted using a datamining approach, and dense pellets of \( (W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x} \) composites were prepared by SPS, which led to simultaneous reaction and densification of \( WO_3, \) \( Nb_2O_5, \) \( W, \) and \( Nb \) powders in 6 min at 1473 K. The samples were doped to nominally have 0.5 electrons per metal cation. Backscattered electron micrographs revealed samples with low \( W \) content \( (x \leq 0.13) \) have \( W \) metal secondary phase inclusions with dimensions spanning from < 20 nm to \( \sim 2 \mu m. \) The average size and number of these precipitates in \( (W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x} \) composites increases controllably with \( W \) content up to at least \( x = 0.13, \) and the dimensions of these precipitates are ideal for scattering phonons with a broad wavelength distribution. Furthermore, these inclusions are stable even after repeated thermal cycling, as monitored by the electrical properties with cycling up to the highest temperatures measured, \( ie. \) 950 K. This leads to composite materials with reduced thermal conductivity across all temperatures investigated (300 K to 1050 K), even with \( W \) content as low as 0.3 mol% \( (x = 0.02 \) in \( (W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x}. \)

These \( (W_{1.083}O_3)_x(Nb_{2.1}O_5)_{1-x} \) composites are a promising platform for \( n \)-type oxide thermoelectric materials. Even without electronic optimization (\( e.g. \) doping studies), these composites are in the same performance class as \( CaMnO_3 \)-based materials, which have been heavily researched (Figure 11). Physical property measurements reveal that the highest power factor and \( zT \) achieved in these samples is for the \( x = 0.08 \) member, which achieves \( zT = 0.1 \) at 950 K. Although this is the highest temperature measured here, the materials are stable to higher temperatures, where the \( zT \) should be higher. Further studies should lead to improvement in electrical transport properties, and improved thermoelectric performance in this new class of \( n \)-type oxides that are stable at high temperature.

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