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Holistic quantum design of thermoelectric niobium oxynitride

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ABSTRACT

We have applied holistic quantum design to thermoelectric NbON (space group *Pm*-3*m*). Even though transport properties are central in designing efficient thermoelectrics, mechanical properties should also be considered to minimize their thermal fatigue during multiple heating/cooling cycles. Using density functional theory, elastic constants of NbON were predicted and validated by nanoindentation measurements on reactively sputtered thin films. Based on large bulk-to-shear modulus ratio and positive Cauchy pressure, ceramic NbON appears ductile. These unusual properties may be understood by analyzing the electronic structure. Nb–O bonding is of covalent–ionic nature with metallic contributions. Second neighbor O–N bonds exhibit covalent–ionic character. Upon shear loading, these O–N bonds break giving rise to easily shearable planes. Ductile NbON, together with large Seebeck coefficient and low thermal expansion, is promising for thermoelectric applications.

1. Introduction

In modern solid state physics and chemistry many advanced properties are considered, such as mechanical, magnetic, electrical, optical, and thermal, to name a few. Research fields are most commonly congregated around these properties, but often correlative approaches are lacking. For instance, studies of superconductors are governed by primary properties of these solids, namely electrical properties. However, superconductors can fail in applications due to their intrinsic brittleness, but mechanical properties aspects of superconductors are seldom considered [1,2]. Another example can be found in the field of hard and protective coatings. Mechanical properties are here central, but many other features could be detrimental in applications [3]. For example, thermal conductivity is relevant for redirecting heat from the tool surface, but this is rarely considered in design strategies [4]. Furthermore, in design of thermoelectrics, devices capable of converting heat directly into electricity without CO_2 emission, the Seebeck coefficient, electrical conductivity, and thermal conductivity are explored, where the former two are maximized and the latter one is minimized, to enhance their performance [5]. These properties are interconnected, which poses a great deal of challenge to understand the correlations and further commercialize these energy generation sources [5]. Commercial thermoelectrics, such as Bi_2Te_3 and SiGe, are brittle and of poor oxidation resistance [5]. Even though there are no movable mechanical parts in thermoelectric devices, poor mechanical performance under heating and cooling cycles often leads to failure. Their mechanical properties are hardly ever considered compared to their key transport properties [6–8].

In our previous work [9], we designed thermoelectric niobium oxynitride (NbON) derived from NbO (space group *Pm*-3*m*), which possesses the cubic symmetry with Nb and O atoms located at the Wyckoff 3c and 3d sites, respectively [10]. This oxide exhibits empty 1a and 1b Wyckoff sites and can be described within the NaCl structure (space group *Fm*-3*m*) with 25% ordered vacancies at metallic (4a) and nonmetallic (4b) sites. This simultaneous presence of ordered vacancies on both sublattices is peculiar. Using density functional theory [11], we explored the vacancy filling in NbO with Nb and N to design compounds with large Seebeck coefficients [9]. The most dominating effect was predicted for filling of 1b sites with N leading to a fivefold increased Seebeck coefficient, which was validated by measuring the Seebeck coefficient of NbON thin films [9]. At temperature of 800 °C the Seebeck coefficient of $-70\,\mu V\,K^{-1}$ was measured, which accounts for the largest absolute value ever reported for these compounds [9]. Clearly, these phases are interesting for thermoelectric applications. However, complementary investigations are necessary to assess their brittle/ductile mechanical behavior.

In this work, we apply holistic quantum design to NbON. This approach incorporates concerns about the mechanical properties of this thermoelectric phase. We calculate elastic properties using density functional theory [11] and then validate these by measuring the elastic (Young's) modulus of sputtered NbON. Based on the elastic response [12,13], we evaluate the brittle–ductile transition in NbON. Using density functional theory based molecular dynamics (MD), we obtain linear coefficient of thermal expansion for NbON. These properties are detrimental to minimize the thermal fatigue in these thermoelectrics [6].

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2. Theoretical methods

Elastic properties of NbON were calculated using density functional theory [11]. At 0 K, we applied the Vienna *ab initio* simulation package (VASP) with projector augmented wave potentials [14–16], parameterized within the generalized-gradient approximation by Perdew et al. [17]. The total energy in the VASP code was treated within the Blöchl approach [18] applying the converged Monkhorst–Pack [19] *k*-points meshes in the Brillouin zone. Full structural optimization was performed for NbON (50% filled 1b sites resulting in the nominal composition of $Nb_{0.46}O_{0.46}N_{0.08}$). The total energy convergence criterion in the VASP code was 0.01 meV within a 500 eV cut-off for the plane wave basis set. Strong correlations in NbON were treated within the Hubbard scheme [20] using our parameterization (effective Coulomb repulsion interaction parameter of -3.8 eV) [9]. The Coulomb repulsion was applied for correlated Nb 4d electrons, as discussed previously [9]. $Nb_{0.46}O_{0.46}N_{0.08}$ was described with 52 atoms and $6\times6\times6$ *k*-point grid. The bulk modulus (B) was obtained from the Birch–Murnagham equation of state [21] and all elastic constants were obtained by distorting the cubic NbON supercell and fitting with a second-order polynomial function [22]. Elastic modulus and Poisson's ratio were calculated from the elastic constants using the Hill approximation [23].

At finite temperatures, density functional theory based MD was applied to determine the linear coefficient of thermal expansion for $Nb_{0.46}O_{0.46}N_{0.08}$. For this purpose, the OpenMX code [24], based on the density functional theory [11] and basis functions in the form of linear combination of localized pseudoatomic orbitals [25] within the generalized gradient approximation introduced by Perdew et al. [17] was employed. The OpenMX code is computationally faster than the VASP code so it was used here for MD studies. The basis functions in the OpenMX code were generated within a confinement scheme [25,26] and specified as: Nb7.0-s2p1d1, O4.5-s2p1, and N4.5s2p1 (cutoff radius in Bohr radius units is associated with each chemical symbol and the last set of symbols defines primitive orbitals). These basis functions were critically evaluated elsewhere [27,28]. The energy cutoff (150 Ry) and the real space grid [29] of $63\times63\times63$ were adjusted to reach the accuracy of 10^{-6} Hartree/atom. The real space grid is the result of the applied energy cutoff, which is used in the calculation of matrix elements associated with Coulomb and exchange-correlation potentials as well as the solution of Poisson's equation. In these simulations, the MD time step was 1.0 fs. $Nb_{0.46}O_{0.46}N_{0.08}$ was run in the temperature range from 50 to 350 K within a velocity-scaled canonical ensemble for 2000 fs at each temperature. The MD runs were performed every 100 K and the velocity was scaled at every step (every 1.0 fs) within the canonical ensembles. In total 8000 MD steps were performed. The MD data were processed using the ASAP code [30] by evaluating the accumulated thermodynamic total energy averages for each MD run (see Fig. 1). The linear coefficient of thermal expansion (α) was estimated from the heat capacity (C_V) data at equilibrium volume (V) obtained using the total energy fluctuations within MD runs as follows:

$$\alpha=\frac{\gamma C_V}{3BV} \tag{1}$$

where γ is the Grüneisen parameter [31]. The Grüneisen parameter was calculated from the elastic constants [31,32]. At every temperature, different volumes were not probed. Instead, 0 K equilibrium volumes were used within every MD run and from the total energy fluctuations, as shown in Fig. 1, heat capacities were calculated with the ASAP code.

3. Experimental methods

NbON thin film samples were grown in a vacuum chamber with a base pressure of 5×10^{-5} Pa. Reactive pulsed DC magnetron sputtering technique with a power density of 7.6 W cm^{-2} and a frequency of 100 kHz was used for a Nb target (purity 99.95%), which was mounted on a magnetron. The substrate-to-source distance was 10 cm with the angle of 19° between the substrate and Nb source normal. One-side polished Si(1 0 0) single crystalline substrates were kept at the growth temperature of 500 °C. A sputtering gas mixture composed of Ar (99.9999%), O_2 (99.9995%), and N_2 (99.9995%) was employed with a total gas pressure of 0.9 Pa. The O_2 and N_2 partial pressures of 0.03 and 0.01 Pa, respectively, were applied for these reactive gases.

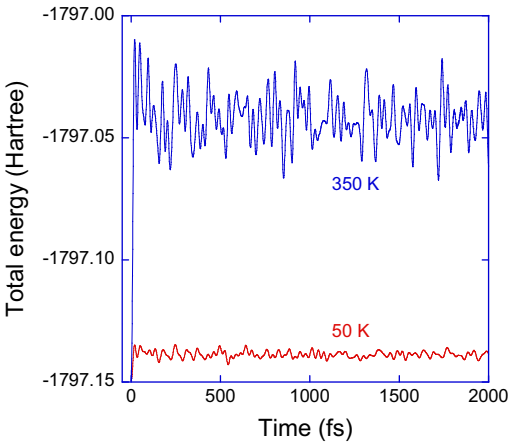

Fig. 1. (Color online) An example of density functional theory based MD oscillations at equilibrium volume of $Nb_{0.46}O_{0.46}N_{0.08}$ for two different temperatures.

The bonding and composition of NbON thin films were analyzed in a JEOL field-emission scanning electron microscope (JAMP-9500F) by X-ray photoelectron spectroscopy (XPS) with a K_α Al radiation (source energy 1486.6 eV) and a hemispherical electron energy analyzer (pass energy 20 eV). The energy calibration of the JAMP-9500F system was carried out with Au $4f_{7/5}$ (83.98 eV), Ag $3d_{5/2}$ (368.26 eV), and Cu $2p_{3/2}$ (932.67 eV) binding energies. Sputter cleaning of NbON thin films was carried out with 2000 eV Ar^+. The structural analysis of NbON samples was conducted by X-ray diffraction (XRD) in a Bruker AXS D8 discover general area detection diffraction system (GADDS) with Cu K_α radiation and the current and voltage setting of 40 mA and 40 kV, respectively. A pin-hole collimator with a diameter of 0.5 mm and an incidence angle of 18° were applied in the GADDS measurements. Nanoindentation experiments on these NbON thin films were carried out in a Hysitron TriboIndenter system. A Berkovich diamond tip, with the tip area function obtained on fused silica, was used for these measurements based on the Oliver and Pharr method [33]. The NbON samples were probed by 16 indents with the maximum penetration $<10\%$ of the film thickness (1.2 μm).

4. Results and discussion

The calculated elastic constants for $Nb_{0.46}O_{0.46}N_{0.08}$ are: $C_{11}=486$ GPa, $C_{12}=157$ GPa, and $C_{44}=74$ GPa. This accounts for the Poisson ratio and elastic modulus of 0.33 and 272 GPa, respectively. To test these quantum mechanical predictions obtained in this work, we synthesize NbON thin films and determine the elastic modulus using nanoindentation.

Based on the XPS analysis, 6 at% of N is incorporated in the NbON thin film grown here, which is consistent with the elastic recoil detection analysis data for a NbON film synthesized previously under identical growth conditions exhibiting 46 at% Nb, 46 at% O, and 8 at% N [9]. This difference may be due to surface sensitivity of XPS as well as surface contaminations [34,35]. To