Superior thermoelectric response in the 3R phases of hydrated Na$_x$RhO$_2$

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Density functional theory is used to investigate the thermoelectric properties of the 3R phases of Na$_x$RhO$_2$ for different Na vacancy configurations and concentrations. As compared to the analogous 2H phases, the modified stacking of the atomic layers in the 3R phases reduces the interlayer coupling. As a consequence, the 3R phases are found to be superior in the technologically relevant temperature range. The Rh $d_{x^2-y^2}$ orbitals still govern the valence band maxima and therefore determine the transport properties. A high figure of merit of 0.35 is achieved in hydrated Na$_{0.83}$RhO$_2$ at 580 K by water intercalation, which is 34% higher than in the non-hydrated phase.
the effects of hydration on the transport properties in the temperature range from 300 K to 800 K and demonstrate the great potential of the 3R-Na$_2$RhO$_2$ class of materials as thermoelectrics. The 3R phase turns out to be clearly superior to the 2H phase in the technologically relevant temperature range.

**Results**

We start from the experimental lattice parameters $a = 3.09$ Å and $c = 15.54$ Å of NaRhO$_2$ and construct a $2 \times 2 \times 1$ supercell. Afterwards we remove two Na atoms from different sites to obtain Na$_{0.83}$RhO$_2$. These configurations are named A1, A2, and A3. Similarly, we remove three Na atoms to obtain Na$_{0.75}$RhO$_2$ and name these configurations B1, B2, and B3. All the structures under investigation are shown in Fig. 1. The formation energy is calculated for each configuration by the relation

$$E_{\text{formation}} = E_{\text{Defect}} - E_{\text{Pristine}} + 12(1-x)E_{\text{Na}}.$$ 

Here $E_{\text{Pristine}}$ is the total energy of a supercell of pristine NaRhO$_2$. In addition, $E_{\text{Defect}}$ and $E_{\text{Na}}$ are the total energies of the defective supercell and of the isolated Na atom, respectively. The energy of an isolated atom is calculated by placing the atom in a cubic cell of 20 Å side length.

The formation energies of configurations A1, A2, and A3 amount to 7.83 eV, 6.73 eV, and 6.65 eV, respectively, and those of configurations B1, B2, and B3 to 11.54 eV, 10.34 eV, and 9.90 eV. These results show that for Na$_{0.75}$RhO$_2$ and Na$_{0.83}$RhO$_2$, respectively, the A3 and B3 configuration has the lowest energy. The latter structures are characterized by maximal distances between the defects, which indicates that Na vacancies do not cluster in Na$_{x}$RhO$_2$, at least not in the two systems under investigation. Moreover, a minimum energy of 6.65 eV is required for creating two Na vacancies in NaRhO$_2$ and an energy of 9.90 eV for creating three vacancies. In the following, we will discuss only the lowest energy structures A3 and B3 unless otherwise mentioned. In pristine NaRhO$_2$, the Rh–O bond length amounts to 2.07 Å and the thickness of the RhO$_6$ layer is 2.11 Å, which is larger than the thickness of the CoO$_6$ layer (1.82 Å) in NaCoO$_2$. Moreover, the bond angle $\angle$ Rh–O–Rh = 96.5° is smaller than the bond angle $\angle$ Co–O–Co = 98.35°. Next to vacancies the RhO$_6$ octahedra shrink slightly (the Rh–O bond lengths decrease by 0.02–0.05 Å), because the interlayer coupling through the Na atoms is reduced and the RhO$_6$ octahedra thus become a bit more compact, which also influences the electronic and thermoelectric properties of the material.

We determine the effects on the electronic band structure and corresponding density of states (DOS), for NaRhO$_2$, Na$_{0.83}$RhO$_2$, and Na$_{0.75}$RhO$_2$ in Fig. 2. NaRhO$_2$ has an indirect band gap of 1.33 eV along the $\Gamma$–M high symmetry direction. The valence band mainly is formed by the Rh 4$d_{xy}$ orbitals. The electronic band structures obtained for configurations A3 and B3 are similar to the pristine case, except for the introduction of holes with densities of 8.8 · 10$^{20}$ cm$^{-3}$ (A3) and 8.7 · 10$^{20}$ cm$^{-3}$ (B3). Besides the characteristic peak approximately 0.2 eV below the Fermi energy, the DOS of pristine NaRhO$_2$ shows $d_{xy}$ states down to $-0.75$ eV and between $-1$ eV and $-1.75$ eV, which is similar for Na$_{0.83}$RhO$_2$ and Na$_{0.75}$RhO$_2$ except for the states at the Fermi level, which have different effective masses and consequently result in different Seebeck coefficients.

The transport properties of hydrated and non-hydrated Na$_{0.83}$RhO$_2$ and Na$_{0.75}$RhO$_2$ are addressed in Fig. 3. We show the Seebeck coefficient and figure of merit for the temperature range from 300 K to 800 K. The Seebeck coefficient is positive in the whole range, indicating that the carriers are holes. We obtain room temperature values of $S = 63 \mu$VK$^{-1}$ and $S = 37 \mu$VK$^{-1}$ for non-hydrated Na$_{0.83}$RhO$_2$ and Na$_{0.75}$RhO$_2$, respectively. For hydrated...
and non-hydrated Na$_{0.83}$RhO$_2$ the Seebeck coefficient behaves rather similarly as a function of the temperature, except for the high temperature range where hydration reduces $S$. Moreover, according to Figs. 3(c) and 3(d), $zT$ at 300 K (room temperature) amounts to 0.16 and 0.06 in the two systems. The former value is twice that found for Na$_{0.85}$CoO$_2$ and Na$_{0.88}$CoO$_2$ in Ref. 5. Starting from almost the same value at 300 K, hydration enhances $zT$ over the whole temperature range, such that at 800 K a value of about 0.4 is reached. At 580 K a maximal increment of 34% due to hydration is achieved. For Na$_{0.75}$RhO$_2$ the Seebeck coefficient increases at 300 K from 37 $\mu$VK$^{-1}$ to 51 $\mu$VK$^{-1}$ under hydration, where this increment of about 30% remains essentially constant over the whole temperature range. A similar effect is also found for $zT$. At 800 K again a value of about 0.4 is reached.

The enhancement of $S$ under hydration results in higher $zT$ values. While the gross shape of the band structure changes little under hydration, see Fig. 4, the Rh 4$d$ bands become flatter in a narrow region around the Fermi level. This fact causes the effective masses and therefore the resistivity to increase and results in a higher Seebeck coefficient. Moreover, the long c-axis of the hydrated phase...
causes the Rh 4d states to shift down in energy towards the Fermi level, because the Rh–O overlap is reduced (increased bond length of 2.2 Å). In order to study possible disorder of the vacancies we have also calculated the Seebeck coefficient (not shown) of the higher energy configurations A1, A2, B1, and B2. For A2 and B2 the results are close to the values of the respective lowest energy configurations, because both have the vacancies in different RhO6 layers. In contrast, concentration of vacancies in the same RhO6 layer results in a significant reduction of S, which is, however, highly unlikely as certified by the previously listed formation energies.

Discussion
The NaRhO2 oxides are found to form a new class of materials with exciting thermoelectric features, even outperforming the 2H phases of the KxRhO2 system. In the latter the optimal thermoelectric performance is achieved at low temperature, whereas the modified stacking of the atomic layers in the novel 3R phases of NaRhO2 results in a dramatically enhanced thermoelectric response in the technologically relevant energy configurations A1, A2, B1, and B2. For A2 and B2 the results also calculated the Seebeck coefficient (not shown) of the higher level, because the Rh–O overlap is reduced (increased bond length of d = 2.2 Å). In order to study possible disorder of the vacancies we have considered 2x3x2 supercells, until the atomic forces reach values of less than 10 mRyd/Å. For the wave function expansion inside the atomic spheres a maximal angular momentum of lmax = 12 is employed and a plane-wave cutoff of Rcut = 7 with Gmax = 24 is used. Self-consistency is assumed when the total energy variation is less than 10−4 Ry. The transport behavior is investigated using BoltzTrap23, which employs a methodology that previously has demonstrated to yield quantitatively accurate values for the thermoelectric properties of metals and doped semiconductors24–26. It is based on semi-classical Boltzmann theory within the constant relaxation time approximation, i.e., the scattering rate is assumed to be independent of momentum and energy. This approximation allows the thermopower to be directly calculated from the band structure as a function of the carrier concentration and temperature26. We note that it has been demonstrated for layered oxides isostructural to the present compound that at elevated temperatures the lattice part of the thermal conductivity can be neglected as compared to the electronic part27. We use a k-mesh of 7 × 7 × 2 points for the band structure and density of states (DOS) and a dense k-mesh of 18 × 18 × 18 points for the thermoelectric calculations.

Methods
We study the effects of Na deficiency and hydration on the band structure of NaRhO2 using density functional theory as implemented in the Wien2k package28. The exchange-correlation potential is parametrized in the generalized gradient approximation29. We fully optimize the structure of Na2RhO2 for x = 1, 0.83, and 0.75, considering 2 × 2 × 1 supercells, until the atomic forces reach values of less than 10 mRyd/Å. For the wave function expansion inside the atomic spheres a maximal angular momentum of lmax = 12 is employed and a plane-wave cutoff of Rcut = 7 with Gmax = 24 is used. Self-consistency is assumed when the total energy variation is less than 10−4 Ry. The transport behavior is investigated using BoltzTrap23, which employs a methodology that previously has demonstrated to yield quantitatively accurate values for the thermoelectric properties of metals and doped semiconductors24–26. It is based on semi-classical Boltzmann theory within the constant relaxation time approximation, i.e., the scattering rate is assumed to be independent of momentum and energy. This approximation allows the thermopower to be directly calculated from the band structure as a function of the carrier concentration and temperature26. We note that it has been demonstrated for layered oxides isostructural to the present compound that at elevated temperatures the lattice part of the thermal conductivity can be neglected as compared to the electronic part27. We use a k-mesh of 7 × 7 × 2 points for the band structure and density of states (DOS) and a dense k-mesh of 18 × 18 × 18 points for the thermoelectric calculations.
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Author contributions
Y.S. performed the calculations. N.S. and U.S. wrote the manuscript.

Additional information
Competing financial interests: The authors declare no competing financial interests.

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