

High Thermopower with Metallic Conductivity in *p*-Type Li-Substituted PbPdO₂

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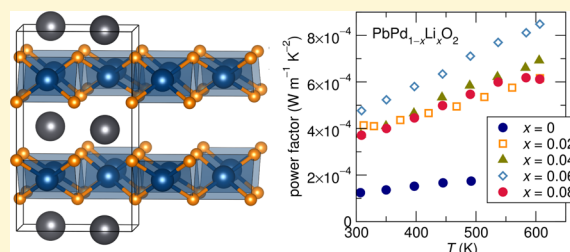
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ABSTRACT: PbPdO₂ is a band semiconductor with a band gap arising from the filled *d*⁸ nature of square-planar Pd²⁺. We establish that hole doping through Li substitution for Pd in PbPdO₂ results in a *p*-type metallic oxide with a positive temperature coefficient of resistance for substitution amounts as small as 2 mol % Li for Pd. Furthermore, PbPd_{1-x}Li_xO₂ demonstrates a high Seebeck coefficient and is therefore an oxide thermoelectric material with high thermopower despite the metallic conductivity. Up to 4 mol % Li is found to substitute for Pd as verified by Rietveld refinement of neutron diffraction data. At this maximal Li substitution, the resistivity is driven below the Mott metallic maximum to $3.5 \times 10^{-3} \Omega \text{ cm}$ with a Seebeck coefficient of 115 $\mu\text{V/K}$ at room temperature, which increases to 175 $\mu\text{V/K}$ at 600 K. These electrical properties are almost identical to those of the well-known *p*-type oxide thermoelectric Na_xCoO₂. Nonmagnetic Li-substituted PbPdO₂ does not possess a correlated, magnetic state with high-spin degeneracy as found in some complex cobalt oxides. This suggests that there are other avenues to achieving high Seebeck coefficients with metallic conductivities in oxide thermoelectrics. The electrical properties coupled with the moderately low lattice thermal conductivities allow for a *zT* of 0.12 at 600 K, the maximal temperature measured here. The trend suggests yet higher values at elevated temperatures. First-principles calculations of the electronic structure and electrical transport provide insight into the observed properties.



INTRODUCTION

Thermoelectric materials develop an electrical potential when subject to a temperature gradient because of the Seebeck effect and conversely develop a thermal gradient when subject to an electrical potential through the Peltier effect. Devices made from such thermoelectric materials are currently used for refrigeration and heating and are being widely explored for waste heat recovery.¹ To be effective, these materials must have low electrical resistivities to conduct the charge carriers with minimal loss, and a high Seebeck coefficient to produce sufficient voltages. Additionally, they should have minimal lattice thermal conductivity, because the thermal gradient must be maintained. These properties combine in a dimensionless thermoelectric figure of merit *zT* given by the formula $zT = S^2T/(\rho\kappa)$, where *S* is the Seebeck coefficient, ρ the electrical resistivity, and κ the total thermal conductivity, measured at temperature *T*. In addition to their utility, thermoelectric measurements provide deep insights into the electrical and thermal transport properties of materials, including insight into the underlying band structure.

Oxide materials possess many attractive qualities for waste heat recovery as they are generally lightweight materials with the potential for high-temperature air stability.^{2,3} However, oxide materials have not reached the level of performance of current state-of-the-art main group thermoelectrics. This is in part due to higher thermal conductivities compared to those of other material families but is additionally a result of low power factors (*S*²/ ρ). While many oxides possess favorable Seebeck coefficients, finding oxides with the necessary metallic conductivities while retaining these high Seebeck coefficients has proven to be difficult.⁴ Currently, the highest-performing oxide materials are *p*-type complex cobalt oxides that sprung from the discovery of high thermopower in metallic Na_xCoO₂.⁵ These compounds possess metallic resistivities yet retain high Seebeck coefficients. A key feature in all of the promising cobalt oxides are CoO₂ layers comprising mixed valent Co³⁺ and Co⁴⁺.

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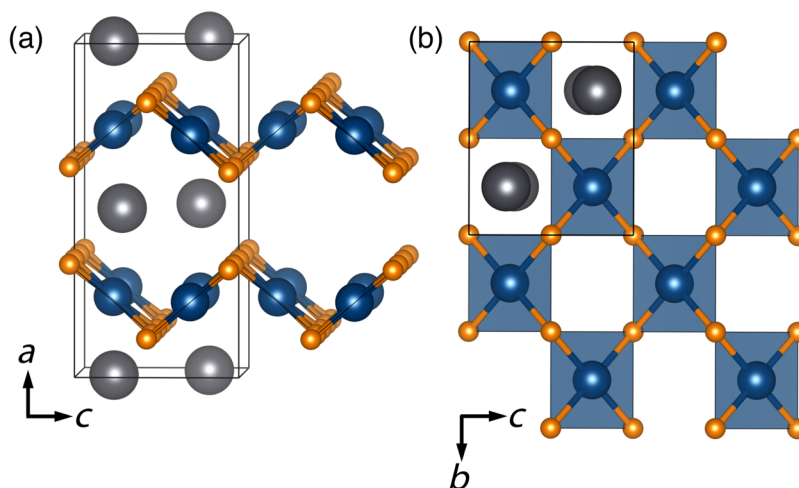


Figure 1. Depictions of the orthorhombic *Imma* (space group #74) crystal structures of PbPdO_2 . (a) Corrugated layers of corner-connected PdO_4 square planes, arranged in a checkerboard pattern as seen in the top view in panel b. Pb atoms (large spheres) are four-coordinate with O, capping PbO_4 square pyramids between the Pd–O layers.

The highly correlated, mixed valent cobalt ions provide the necessary electrical properties, and the layered structure results in a low thermal conductivity, giving rise to a modestly high thermoelectric performance.

With the promising performance of the complex cobalt oxides, research into the thermoelectric properties of other oxide materials has been of interest. Misfit rhodium oxides have been explored as the 4d analogues of the cobalt oxides and have shown comparable room-temperature Seebeck coefficients with metallic conductivities.^{6–8} However, the exploration of other 4d metal compounds has been relatively sparse.

Complex oxides of palladium are particularly interesting as many are known to undergo compositionally driven metal–insulator transitions with hole doping,^{9,10} and the transitional regime is often a fertile playground for thermoelectric research. PdO itself is driven metallic with as little as 1 mol % Li substitution.¹¹ *p*-Type oxide metals starting from nonmagnetic parent compounds are relatively uncommon, prompting the investigation of their thermoelectric properties. PbPdO_2 is an attractive material for thermoelectric investigation because of its layered nature of Pd square-planar units (suggesting potentially lower thermal conductivity) and the possibility for hole doping (suggesting control of electrical properties). PbPdO_2 , like many other complex palladium oxides, is a small band gap semiconductor. Below 100 K, the resistivity has been reported to display semiconducting behavior; i.e., it increases with decreasing temperature. Above 100 K, the material behaves like a metal with resistivity increasing with temperature.¹² The structure shown in Figure 1 consists of layers of Pb atoms, with the lone pairs pointing in the plane, alternating with layers of square-planar PdO_4 units. These PdO_4 square planes form a two-dimensional tilted checkerboard pattern.¹³ PbPdO_2 has attracted attention following suggestions from preliminary electronic structure calculations that it could behave potentially as a spin gapless semiconductor with appropriate substitution.^{14,15} More recent calculations using hybrid functionals have pointed to the existence of a small band gap.¹⁶ PbPdO_2 has been shown previously to incorporate Co^{17,18} and Cu¹⁹ onto the Pd site. The small band gap and potential to control electrical properties through aliovalent substitution, coupled with an interesting layered structure, make it attractive for exploring thermoelectric properties.

Here we report the thermoelectric performance of polycrystalline Li-substituted PbPdO_2 at elevated temperatures. Rietveld refinements of neutron diffraction patterns confirm the substitution of Li at the Pd site, with a solubility limit of approximately 4 mol % Li. With Li substitution, we observe a 10-fold decrease in the resistivity to below the Mott metallic limit without a precipitous drop in the Seebeck coefficient. Metallic conductivities with Seebeck coefficients nearing 200 $\mu\text{V/K}$ at 600 K are remarkable in a nonmagnetic oxide material and point to the need to explore other oxide systems for thermoelectric performance. The experimental results are backed up with density functional theory electronic structure calculations, including calculations of the Seebeck coefficient within Boltzmann transport theory, which suggest that the unusually high power factor is likely to have its origins in the unusual band structure, rather than being a result of spin or charge correlation.

METHODS

Polycrystalline samples of PbPdO_2 without and with Li substituting for Pd were prepared by heating stoichiometric amounts of PbCO_3 , PdO , and Li_2CO_3 powders. The precursors were finely ground using an agate mortar and pestle and pressed into pellets at 100 MPa. The pellets were placed on beds of powder of the same composition to prevent contamination from the alumina crucible. Reactions were conducted at 700 °C for 12 h. Samples were reground and reheated several times (typically three times) to ensure a complete reaction of the precursors.

Laboratory X-ray diffraction studies were conducted on samples mixed with a silicon standard on a Panalytical Empyrean diffractometer with $\text{Cu K}\alpha$ radiation. Neutron diffraction studies of samples loaded in vanadium cans at room temperature employed the constant $\lambda = 2.078$ Å wavelength from a Ge-(311) monochromator of the BT-1 neutron powder diffractometer at the National Institute for Standards and Technology (NIST).^a Neutron powder diffraction was conducted on the stoichiometric and the highest Li-substituted sample. Rietveld refinement was performed using the TOPAS academic software suite.²¹ Crystal structures were visualized using VESTA.²² Prior to the measurement of physical properties, the resulting powders were compacted into dense pellets using spark plasma sintering (SPS), following details described previously.²³ Densification was performed at 950 K, as measured by a pyrometer, for 15 min under vacuum, with residual Ar flow. Neutron diffraction measurements taken before and after the SPS treatment did not reveal any significant changes in the

structure or composition. Pycnometry measurements conducted on a Micromeritics AccuPyc 1340 Pycnometer confirm sample densities greater than 95% of the theoretical density for all samples. Elemental analysis was performed on the stoichiometric and most substituted samples by Galbraith Laboratories (Knoxville, TN). For the nominal composition PbPdO_2 , the analysis gave a Pb:Pd weight ratio of 60.9:28.0 (expected 59.9:30.8), and for the nominal 8 mol % Li-substituted sample, the analysis gave a Pb:Pd:Li ratio of 59.7:26.5:0.168 (expected 61.3:29.0:0.164). The Seebeck coefficient and electrical resistivity were measured in a He atmosphere under pressure using an ULVAC Technologies ZEM-3 instrument. Hall coefficients were measured at 11 K using a four-probe configuration on a Quantum Design Dynacool PPMS. Thermal diffusivity was measured using the laser flash technique between room temperature and 973 K under an air atmosphere on a Netzsch LFA 457 system. Pellets for the measurement, approximately 8 mm in diameter and 2 mm thick, were sprayed with a layer of carbon paint to minimize errors in the emissivity. The thermal conductivity was calculated using $\kappa = \alpha C_p \rho$, where α , C_p , and ρ are the thermal diffusivity, heat capacity, and density, respectively. The Cowan model²⁴ for determining diffusivity and the Dulong–Petit molar heat capacity ($C_p = 3R$) were employed.

The electronic structure of unsubstituted PbPdO_2 was calculated using density functional theory (DFT) as implemented in the Vienna *ab initio* Simulation Package Vasp^{25,26} with projector-augmented wave (PAW) pseudopotentials with scalar-relativistic corrections.^{27,28} A cutoff energy of 500 eV was employed, which is substantially above the requirements for the potentials and scalar-relativistic corrections. For structure optimization and band structure calculations, the Perdew–Burke–Ernzerhof exchange–correlation functional within the generalized gradient approximation (GGA–PBE) was employed.²⁹ The standard primitive unit cell of the conventional body-centered orthorhombic cell was obtained using Aflow.³⁰ A Γ -centered k -mesh of $8 \times 8 \times 8$ was used for structure optimization. The Brillouin zone paths for band structure calculations were adapted from ref 31. Additional calculations of the density of states (DOS) employed the HSE06 screened hybrid functional.³² Spin–orbit coupling (SOC) can be important for empty Pb^{2+} $6p$ states.³³ Calculations of the band structure with and without spin–orbit coupling verified that valence band states, which are the important consideration here, are not impacted by the exclusion of SOC. Transport properties were calculated at a constant carrier concentration using Boltzmann transport theory in the constant relaxation time approximation. We employed the BoltzTraP code³⁴ based on k -dependent eigenvalues obtained from DFT calculations performed with Vasp. Further details of how such calculations were performed are provided alongside the results of the calculations.

RESULTS AND DISCUSSION

Preparation and Characterization. Various amounts of Li were substituted into PbPdO_2 to study the change in electronic properties. Li^+ was expected to substitute for Pd^{2+} rather than Pb^{2+} because of their similar Shannon–Prewitt ionic radii: 0.590 Å for four-coordinate Li^+ , 0.64 Å for four-coordinate square-planar Pd^{2+} , and 0.98 Å for four-coordinate Pb^{2+} .³⁵ Rietveld refinement of neutron diffraction patterns was performed to confirm the location and amount of substitution of Li into the structure as Li poorly scatters X-rays. The samples studied here are post-SPS and represent the materials whose physical properties were measured. Figure 2 shows the Rietveld refinements of both (a) the stoichiometric PbPdO_2 and (b) the nominally substituted $\text{PbPd}_{0.92}\text{Li}_{0.08}\text{O}_2$, the results of which are summarized in Table 1. The Li occupancy on the Pd site for the nominally 8 mol %-substituted sample was determined to be 4.2(9)%. The Pd and Li occupancy was constrained to sum to 1. The excess Li is not observed in neutron diffraction, though elemental analysis matches the nominal Li content. The Li impurity phase is most likely too small to see in diffraction data.

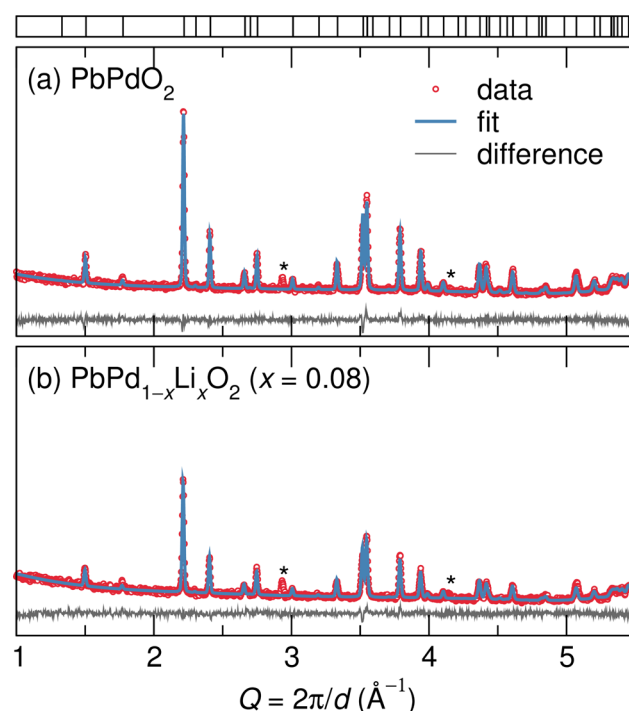


Figure 2. Rietveld refinements of neutron diffraction data of (a) pristine PbPdO_2 and (b) the nominally 8 mol %-substituted $\text{PbPd}_{0.92}\text{Li}_{0.08}\text{O}_2$, showing the quality of the fits. The top panel indicates the Bragg reflection marks for PbPdO_2 . Asterisks mark the positions of reflections from the vanadium sample can.

Table 1. Structural Parameters of PbPdO_2 at Room Temperature, As Determined by Rietveld Refinement of Neutron Diffraction Data^a

nominal composition	PbPdO_2	$\text{PbPd}_{0.92}\text{Li}_{0.08}\text{O}_2$
a (Å)	9.4394(4)	9.4358(6)
b (Å)	5.4508(2)	5.4487(3)
c (Å)	4.6514(2)	4.6470(3)
Pb occupancy	0.94(1)	0.927(9)
Li occupancy	—	0.042(9)
Pb z position	0.7751(6)	0.780(7)
O x position	0.3488(4)	0.3498(5)
Pb U_{iso} (Å ²)	0.010(1)	0.012(1)
Pd/Li U_{iso} (Å ²)	0.005(2)	0.004(2)
O U_{iso} (Å ²)	0.010(1)	0.014(1)
O–O–O (deg)	102.5(2)	101.9(3)
R_{wp} (%)	3.9	3.5

^aOrthorhombic space group $Imma$ (#74). The sites are Pb 4e (0, $1/4$, z), Pd 4c ($1/4$, $1/4$, $1/4$), and O 8f (x , 0, 0).

Refinements with the Li on the Pb site were conducted but did not improve the fits, supporting the substitution of Li at the Pd site.

In further support for substitution of Li for the Pd, the bond valence sums (BVS) for Li on both the Pd and Pb sites were calculated.³⁶ Li on the Pd site with a Li–O bond distance of 2.029 Å gives a BVS of 0.87. On the Pb site, the Li–O distance is 2.339 Å, giving a BVS of 0.38. While both sites leave Li underbonded, Li on the Pd site is more favored as the BVS is closer to the BVS ideal value of 1 for Li^+ .

For the nominally 8 mol % Li substitution, PbO impurities were observed by diffraction prior to SPS. No PbO phase is observed after SPS possibly because of the reducing

atmosphere of the SPS process that can result in Pb being reduced and melted into the graphite die. In addition to densifying the material, SPS appears to introduce approximately 6% Pb vacancies into the samples, while no oxygen vacancies were observed.

The change in the lattice parameters with Li substitution was monitored to improve our understanding of structural and compositional changes. Figure 3 shows the room-temperature

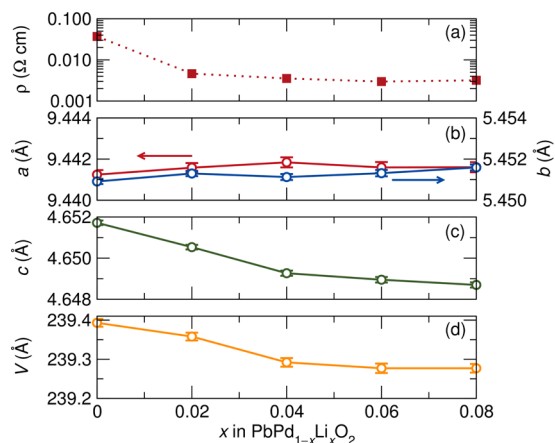


Figure 3. Room-temperature resistivity, lattice parameter, and unit cell volume changes as a function of Li substitution in PbPdO_2 . Only the c parameter changes significantly up to 4 mol % Li. The constant values above 4 mol % suggest a solubility limit of Li in the structure. Error bars indicate one standard deviation.

resistivity, lattice parameters, and unit cell volume as a function of substitution. The room-temperature resistivity drops below the Mott metallic limit of $10^{-2} \Omega \text{ cm}$ with as little 2% Li substitution and decreases only slightly with further substitution. Upon substitution, the a and b lattice parameters remain relatively constant, while the c axis contracts with a Li content of ≤ 4 mol %. A lattice contraction is expected due to the smaller Li ion as well as the necessary oxidation of Pd^{2+} to Pd^{3+} to maintain neutrality. The c lattice parameter remains constant after 4% Li substitution, which suggests a solubility limit of Li into the structure further supporting the refined Li occupancy values from neutron diffraction of the nominal 8 mol % sample. This also explains the PbO impurity phase in the more substituted samples. The small solubility limit of Li potentially arises from steric resistance to further lattice contraction from the Pb lone pairs, and resistance of Pd to further oxidize.

Ozawa et al. have reported that the angle of the Pd square planes can affect the electrical properties.¹⁹ The difference in this angle with Li substitution [$\text{O}-\text{O}-\text{O}$ (deg) in Table 1] is only 0.6° . Thus, a slight change in orbital overlap is not likely to significantly affect the electrical properties relative to the increased charge carriers from hole doping.

Electrical Transport and Seebeck Coefficient. The electrical properties of PbPdO_2 with substitution are shown in Figure 4. Stoichiometric PbPdO_2 shows a room-temperature resistivity of $0.037 \Omega \text{ cm}$, which is considerably lower than the value of $0.75 \Omega \text{ cm}$ reported by Ozawa and co-workers.¹² The difference can be attributed to the densification of the material through SPS. Upon substitution with 4 mol % Li, the room-temperature resistivity drops to $3.5 \times 10^{-3} \Omega \text{ cm}$. The Seebeck coefficient is $215 \mu\text{V/K}$ at room temperature for PbPdO_2 . This is also substantially higher than values from previous reports,

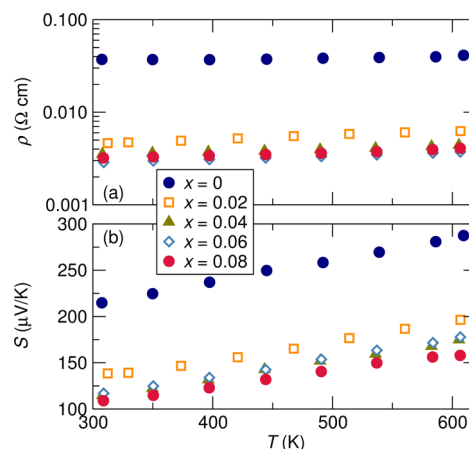


Figure 4. (a) Resistivity and (b) Seebeck coefficient for $\text{PbPd}_{1-x}\text{Li}_x\text{O}_2$. The resistivity drops by 1 order of magnitude with 2 mol % substitution, while the Seebeck coefficient drops by $100 \mu\text{V/K}$. The Seebeck coefficients of the Li-substituted samples increase with temperature and approach $200 \mu\text{V/K}$ at 600 K.

possibly because of densification from SPS. It is unusual for both the resistivity and Seebeck coefficient to change favorably, highlighting the importance of dense pellets not only for their robustness but also for optimal performance. Upon substitution with Li, the Seebeck coefficient drops, but the room-temperature value is still greater than $100 \mu\text{V/K}$ for all substitutions and increases with temperature. Because of instrumental constraints requiring a He atmosphere for sample measurements, it was not possible to reliably measure samples at higher temperatures because of surface reduction. Therefore, peak Seebeck coefficients are not reached for the temperatures measured and approach $200 \mu\text{V/K}$ at 600 K. However, the materials are stable in air to temperatures of 1000 K at which even higher Seebeck coefficients would be expected.

Hall measurements on the stoichiometric and 8 mol % Li-substituted samples suggested carrier concentrations of 1.88×10^{18} and $3.72 \times 10^{18} \text{ cm}^{-3}$, respectively, at room temperature. These concentrations are 1 order of magnitude higher than the value of $1.8 \times 10^{17} \text{ cm}^{-3}$ reported by Ozawa and co-workers,¹² which in turn explains why we observe a 1 order of magnitude difference in resistivity (lower in the samples measured here). It is expected that given a 1 order of magnitude decrease in the resistivity with Li substitution, we would see a corresponding increase in the carrier concentration. We see only a slight increase.

The resistivity and Seebeck coefficient values obtained for the polycrystalline Li-substituted PbPdO_2 materials are almost identical to those of polycrystalline $\text{Na}_x\text{CoO}_{2-\delta}$, which has a Seebeck coefficient of $100 \mu\text{V/K}$ and a resistivity of $2 \times 10^{-3} \Omega \text{ cm}$ at 300 K.³⁷ Single crystals of some complex cobalt oxide are the best performing oxide thermoelectric materials, and many different compositions have been explored since the discovery of high thermopower in NaCoO_2 .^{38,39} Central to the thermoelectric performance of these cobaltate compounds is the high Seebeck coefficient with metallic resistivities. When the unexpected thermopower was first observed, the Heikes formula⁴⁰ was unable to explain it at high temperatures. Koshibae and co-workers proposed a generalized Heikes formula for these compounds that explained the high thermopower at elevated temperatures,^{41,42} by accounting for the spin and orbital degeneracies associated with Co^{3+} and Co^{4+}

in various spin states, supported by the observed reduction in the Seebeck coefficient with applied magnetic fields.⁴³ Other explanations point to unique band structures for this class of materials.^{44–46}

Interestingly, Li-substituted PbPdO_2 consists of almost entirely diamagnetic square-planar Pd^{2+} , except for the small number of holes that dope into the Pd–O conduction band. This implies that the relatively high Seebeck coefficient must arise for reasons distinct from what is observed in the complex cobalt oxides.

Electronic Structure and Boltzmann Transport Analysis. The electronic structure of PbPdO_2 was calculated to better understand the electronic properties and is shown in Figure 5. The GGA-PBE band structure suggests a semimetal

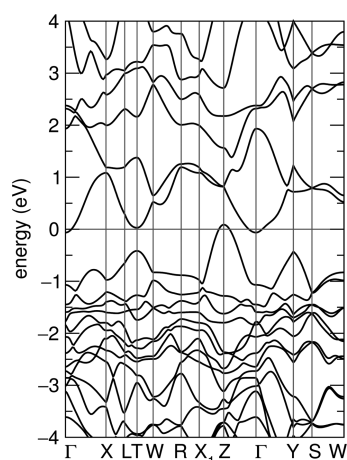


Figure 5. Band structure PbPdO_2 using the GGA-PBE functional, which predicts a semimetal with regions of flat and disperse bands below the Fermi level.

with the valence band maximum at the Z point and the conduction band minimum at the Γ point. On either side of the valence band maximum are flat regions that then disperse toward peaks at the T and Y points. The presence of both flat and disperse bands just under the Fermi level may explain the high Seebeck coefficient, in conjunction with moderately high mobility in the hole-doped compound. GGA-PBE is known to underestimate the band gap in PbPbO_2 ¹⁶ and leads to the semimetal prediction.

Hybrid functionals such as HSE06³² usually yield more realistic band gaps as seen from the corresponding density of states of PbPdO_2 shown in Figure 6a. It is seen that the valence band comprises mostly the Pd d state and the filled O p states, while the conduction band has components of Pd d and Pb s and p states. Because a dense mesh of k -points are necessary to obtain acceptable accuracy for Boltzmann transport calculations, we did not continue with the computationally expensive HSE06 calculations, which were limited to a comparatively small k -point mesh of 83 in the full Brillouin zone. Instead, we used the GGA + U scheme in the rotationally invariant scheme of Dudarev et al.,⁴⁷ where we invoked a Hubbard U term on the Pd- d states to correct for static correlations, using a value of U between 2.65 and 5.65 eV. J was fixed to 0.65 eV in both cases. Calculations of the band structure were performed with and without SOC (which is computationally expensive), and it was verified that the valence band structure, which is relevant to the hole doping studied here, is largely unchanged upon ignoring SOC effects; therefore SOC was not employed for the

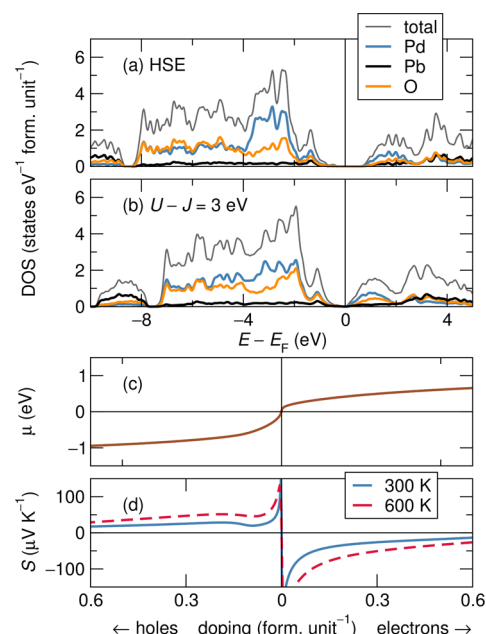


Figure 6. Element-resolved electronic density of states of PbPdO_2 from (a) HSE06 hybrid functional calculations and (b) GGA + U calculations with $U_{\text{eff}} = 3$ eV. The two bottom panels (c and d) display the chemical potential μ and the trace of the Seebeck coefficient tensor S as a function of doping, respectively, as obtained from Boltzmann transport calculations.

transport calculations. The computationally simpler scheme allowed us to employ 31^3 k -points (i.e., 29791 k -points) in the full Brillouin zone, which in combination with the standard settings for BoltzTraP provided sufficiently converged transport properties in the prior, similar case of PtCoO_2 .⁴⁸ Starting approximately from $U_{\text{eff}} = U - J = 3$ eV, a band gap opens, which is significantly smaller than the gap obtained with the hybrid functional as seen in Figure 6b. However, the absolute position of the peaks, the overall shape of the DOS, and character and hybridization of states are rather similar for the valence band, for HSE06 calculation, and for the $U_{\text{eff}} = U - J = 3$ eV calculation.

Panels c and d of Figure 6 display the chemical potential μ and the trace of the Seebeck coefficient tensor, respectively, as a function of filling in terms of doping of holes or electrons per formula unit, as obtained from the Boltzmann transport calculations. As one removes electrons from PbPdO_2 and dopes holes into the valence band, it is seen that the chemical potential varies smoothly to a small extent, even for quite substantial doping (Figure 6c). The Seebeck tensor is essentially isotropic, and therefore, only the trace of the Seebeck tensor \bar{S} is displayed here. \bar{S} rapidly drops as one introduces holes into PbPdO_2 , with the values ranging from 150 to 30 $\mu\text{V K}^{-1}$ at 300 K for small hole doping levels. In addition, as seen in the experimental data, that values at 600 K are substantially larger than those at 300 K. The trend and the magnitude of the values encourage the comparison with experiment and suggest that Boltzmann transport theory captures the relevant physics in this system. To ensure that the results presented here are not particularly sensitive to the value of the Hubbard U that was selected, we also performed calculations using a U_{eff} of 5 eV and found results substantially similar to those found for a U_{eff} of 3 eV.

Thermal Conductivity and Thermoelectric Figure of Merit. The thermal conductivities of stoichiometric PbPdO_2 and $\text{PbPd}_{0.96}\text{Li}_{0.04}\text{O}_2$ were measured from room temperature to 973 K. At the highest measured temperature of 973 K, the values for both samples approach $2.5 \text{ W m}^{-1} \text{ K}^{-1}$. Low thermal conductivity is expected from the crystal structure, which consists of a layered arrangement of heavy Pb atoms and, potentially, lattice anharmonicity due to the lone pairs in an asymmetric coordination environment.⁴⁹ However, the measured values of the thermal conductivity are somewhat high for an effective thermoelectric. Applying the Wiedemann–Franz law, $\kappa_{\text{el}} = LT/\rho$, where κ_{el} is the electronic contribution to thermal conductivity and L is $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, we obtain a κ_{el} of $\sim 0.36 \text{ W m}^{-1} \text{ K}^{-1}$ for the Li-substituted sample at the highest temperature, leading to lattice thermal conductivities just greater than $2 \text{ W m}^{-1} \text{ K}^{-1}$. For example, at temperatures near 700 K, the widely used thermoelectrics have lattice thermal conductivity values below $1 \text{ W m}^{-1} \text{ K}^{-1}$.⁴ The thermal conductivity can be combined with the electrical properties to give the thermoelectric figure of merit [$zT = S^2T/(\rho\kappa)$]. Figure 7 shows the measured thermal conductivity and the resulting

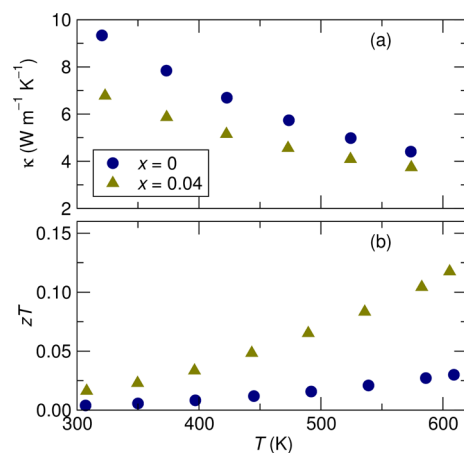


Figure 7. (a) Thermal conductivity and (b) zT of $\text{PbPd}_{1-x}\text{Li}_x\text{O}_2$ samples obtained from the electrical and thermal transport measurements. The thermal conductivity of $4 \text{ W m}^{-1} \text{ K}^{-1}$ gives Li-substituted PbPdO_2 a $zT = 0.12$ at 600 K. Higher zT values are anticipated as the temperature is further increased.

zT . The Li-substituted sample of PbPdO_2 has a zT of 0.12 at 600 K. It is clear that the peak zT has not been reached, and electrical measurements at higher temperatures would yield even higher zT values because of smaller thermal conductivities and larger Seebeck coefficients. In addition, single crystals of Li-substituted PbPdO_2 could show markedly decreased resistivities similar to what is seen in Na_xCoO_2 in which the resistivity at 800 K drops from 3.6×10^{-3} to $5.2 \times 10^{-4} \text{ } \Omega \text{ cm}$,³⁷ without significant effects on the Seebeck coefficient or thermal conductivity, and therefore yet higher values of zT .

CONCLUSION

Li has been substituted for Pd in PbPdO_2 , corresponding to hole doping. The Li substitution site and level of substitution have been established through Rietveld refinement of neutron diffraction data. The substitution limit appears to be close to 4 mol % Li substitution, beyond which evidence of further substitution is not observed. Metallic resistivities are reached with as little as 2% Li substitution for Pd. The Seebeck

coefficient of the substituted samples remains high, at $>100 \text{ } \mu\text{V/K}$ at room temperature, and approaches $200 \text{ } \mu\text{V/K}$ at 600 K. Despite the relatively high lattice thermal conductivity of the compound, a zT of 0.12 is measured at 600 K. Similar electrical properties are observed in the high-performing complex cobalt oxide compounds, arising from spin and orbital degeneracy, which are not present in Li-substituted PbPdO_2 . Our findings suggest potentially new avenues to achieving high-performing oxide thermoelectric materials and encourage the search for such properties in oxides of metals more earth-abundant than the ones studied here.

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Notes

The authors declare no competing financial interest.

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ADDITIONAL NOTE

^aCertain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best.

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