Double Perovskite Pr₂CoFeO₆ Thermoelectric Oxide: Roles of Sr-doping and Micro/Nanostructuring

Hao Wu, Xiao-Lei Shi, Wei-Di Liu, Meng Li, Han Gao, Wei Zhou, Zongping Shao, Yifeng Wang, Qingfeng Liu, Zhi-Gang Chen

PII:	S1385-8947(21)02254-3
DOI:	https://doi.org/10.1016/j.cej.2021.130668
Reference:	CEJ 130668
To appear in:	Chemical Engineering Journal
Received Date:	24 March 2021
Revised Date:	9 May 2021
Accepted Date:	31 May 2021



Please cite this article as: H. Wu, X-L. Shi, W-D. Liu, M. Li, H. Gao, W. Zhou, Z. Shao, Y. Wang, Q. Liu, Z-G. Chen, Double Perovskite Pr₂CoFeO₆ Thermoelectric Oxide: Roles of Sr-doping and Micro/Nanostructuring, *Chemical Engineering Journal* (2021), doi: https://doi.org/10.1016/j.cej.2021.130668

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Elsevier B.V. All rights reserved.

Double Perovskite Pr₂CoFeO₆ Thermoelectric Oxide: Roles of

Sr-doping and Micro/Nanostructuring

Hao Wu,^{1,a} Xiao-Lei Shi,^{2,3,a} Wei-Di Liu,^{2,3} Meng Li,³ Han Gao,⁴ Wei Zhou,¹ Zongping Shao,¹ Yifeng Wang,^{5,6} Qingfeng Liu,^{1,*} and Zhi-Gang Chen^{2,3,*}

¹ State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, China;

² Centre for Future Materials, University of Southern Queensland, Springfield Central, QLD 4300, Australia;

³ School of Mechanical and Mining Engineering, University of Queensland, Brisbane, QLD 4072, Australia;

⁴ Key Laboratory of Material Physics of Ministry of Education, School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450052, China;

⁵ College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China;

⁶ Jiangsu Collaborative Innovation Center for Advanced Inorganic Function Composites, Nanjing Tech University, Nanjing 210009, China;

^{*a*} These authors contribute equally to this work.

Corresponding Author

* Qingfeng Liu: <u>qfliu@njtech.edu.cn;</u>

* Zhi-Gang Chen: zhigang.chen@usq.edu.au

Abstract

Owing to their excellent thermal stability, non-toxicity, and low cost, oxide-based thermoelectric materials have considerably expanded research interests and industrial application. Here, we, for the first time, report a new-type Pr_2CoFeO_6 oxide-based thermoelectric materials from both theoretical and experimental aspects. Our first-principles calculation results indicate that Pr_2CoFeO_6 is a p-type semiconductor with narrow bandgap. The experimental thermoelectric evaluation shows that pristine Pr_2CoFeO_6 , synthesized by a combination of sol-gel method and conventional sintering, has a peak figure of merit, *ZT* of 0.015 at 773 K with a high positive Seebeck coefficient of 250 μ V K⁻¹ and very low thermal conductivity of 0.7 W m⁻¹ K⁻¹ at this temperature. Further Sr^{2+} doping on Pr-sites (Pr^{3+}) enhances the carrier concentration from 4.03×10^{14} cm⁻³ to 5.22×10^{17} cm⁻³, contributing to an improved power factor up to 46 μ W m⁻¹ K⁻². Besides, Sr-doping induces point defects in the matrix and further suppresses the thermal conductivity to 0.58 W m⁻¹ K⁻¹, leading to a promising *ZT* up to 0.05 at 673 K in $Pr_{1.8}Sr_{0.2}CoFeO_6$, which is significantly improved by 233 % compared to pristine Pr_2CoFeO_6 . We also predict that a high *ZT* of >0.2 can be achieved by the optimization of carrier density, band engineering, and energy filtering, which is comparable to many other oxide-based thermoelectric materials.

Keywords: thermoelectric; double perovskite; Pr₂CoFeO₆; band structure; nanostructure; calculation.

1. Introduction

With the depletion of carbon-based fossil fuels, it is urgent to improve the efficiency of the currently used fossil fuels or find alternative energy sources [1, 2]. Thermoelectrics can be directly used for solid-state cooling and power generation [3], and the thermoelectric conversion does not produce noise, vibration, or other pollution, therefore providing a potential solution for the reuse of waste heat and solid-state refrigeration [4]. The thermoelectric conversion efficiency can be evaluated by a dimensionless figure-of-merit ZT by $ZT = S^2 \sigma T / \kappa$ [5], where S, σ , κ , and T are the Seebeck coefficient, electrical conductivity, total thermal conductivity, and absolute temperature, respectively. The total thermal conductivity κ is composed of electronic thermal conductivity κ_e and lattice thermal conductivity κ_l [6]. Generally, achieving high thermoelectric power factor ($S^2\sigma$) and low κ are two keys to achieve an ideal ZT [7]. However, because of the coupling between S, σ , and κ_e , it is challenging to achieve high $S^2\sigma$ and low κ at the same time [8]. So far, on the basis of understanding the basic mechanism of thermoelectricity, researchers have made great efforts to improve $S^2\sigma$ and reduce κ (mainly κ_l). A variety of strategies such as band engineering [9] and energy filtering [10] have been applied to enhance $S^2\sigma$, and rational structure/lattice imperfection designs including point defects, dislocations, interfaces, nanoinclusions, and porosity have been employed to suppress κ_l by strengthening multi-wavelength phonon scattering [11].

With the development of advanced thermoelectric design, the *ZT* values of thermoelectric materials have been significantly improved, and new thermoelectric materials are continuously being discovered [4, 12, 13]. Currently, high-performance thermoelectric materials, including $Bi_{2-x}Sb_xTe_3$ [14], GeTe [15, 16], PbTe [17], SnTe [18], SnSe [19, 20], Cu_{2-x}Se [21], skutterudite [22], and half-Heusler [23], have been considered to be the most promising materials with high *ZTs* >1.5. Especially, the *ZTs* of PbTe [24], SnSe [25], GeTe [26], and Cu_{2-x}Se [27] have exceeded 2 and are approaching to 3. However, many of these materials are toxic, unstable at high temperatures, and high-cost, which considerably limit their large-scale commercialization [4]. Therefore, it is needed to explore

thermoelectric materials with high-temperature stability, environmental friendliness, and low cost [13]. To meet these requirements, oxide-based thermoelectric materials have been developed [28]. The current thermoelectric oxides with good thermoelectric potential include p-type Ca₃Co₄O₉ [29-31], Na_xCoO₂/Na_xCo₂O₄ [32-34], BiCuSeO [35-39], and n-type SrTiO₃ [28], CaMnO₃ [40-42], In₂O₃ [43-45], and ZnO [46, 47]. The p-type BiCuSeO shows a maximum *ZT* value of ~1.6 in Bi_{0.94}Pb_{0.06}CuSe_{1.01}O_{0.99} at 873 K [48], and the n-type SrTiO₃ ceramic co-doped with La and Nb represents the highest *ZT* of 0.65 at 1100 K [49]. Till now, researchers are continually exploring new types of oxide thermoelectric materials with both high thermoelectric performance and high practical value to meet various demands.

Double perovskites, such as Sr₂HoNbO₆ [50] and Sr₂TiCoO₆ [51], are attracting considerable attention as potential thermoelectric oxides. Double perovskite oxides possess two conventional formulas, namely AA'B₂O_{5+d} (A represents the alkaline-earth metal, A' represents the rare-earth metal, and B represents the transition metal) and A₂BB'O₆ (A represents the alkaline earth elements and B/B' represent the transition metal) and A₂BB'O₆ (A represents the alkaline earth elements and B/B' represent the transition metals), and show great potentials in thermoelectric application due to their intrinsic low κ and high electrical transport properties [52]. Recently, 3D-metal-based double perovskites such as La₂CuMnO₆, Ba₂FeMoO₆, Sr₂TiFeO₆, and Ba₂MnTaO₆ [12, 50, 53-58], were reported to have considerable thermoelectric properties. La₂CuMnO₆ showed a theoretical *ZT* of 0.39 at 800 K, derived from its extremely high $S^2\sigma$ (~60 µV cm⁻¹ K⁻²) [57], while theoretical study indicated that Ba₂FeMoO₆ showed promising cryogenic thermoelectric performance with a high *ZT* of ~1 at 200 K [53]. Besides, Ba-doping in Sr₂TiFeO₆ can effectively enhance $S^2\sigma$ and a high *S* of ~800 µV K⁻¹ was obtained for Ba_{0.25}Sr_{1.75}TiFeO₆ at 1123 K [54]. Furthermore, first-principles calculations indicated that Sr₂HoNbO₆ may possess a maximum *ZT* of 0.98 at 250 K, which is promising for low-temperature thermoelectric application [50].

 Pr_2CoFeO_6 is a recently discovered new double perovskite that possesses unique physical properties such as dielectric behavior [59], exchange bias [60], spin-phonon coupling [61], Griffiths

phase [60], and re-entrant cluster glass [60], therefore have attracted significant attention in recent years. However, their thermoelectric properties have never been evaluated. It was reported that Pr_2CoFeO_6 has a space group of orthorhombic Pnma (No. 62) with typical lattice parameters a = 5.466Å, b = 7.702 Å, c = 5.443 Å, and unit-cell volume V of 229.170 Å³ [62]; while other studies indicated that Pr_2CoFeO_6 shows a monoclinic structure with a space group of $P2_1/n$ [59], which is a typical anisotropic material. Fig. 1a illustrates its orthorhombic Pnma crystal structure. In our preliminary studies, we performed first-principles density functional theory (DFT) calculations on pristine orthorhombic Pr₂CoFeO₆ and found that Pr₂CoFeO₆ possesses a pseudo-like energy gap of ~0.23 eV, indicating a typical p-type semiconducting feature [63], as shown in Fig. 1b. Such a narrow energy gap indicates that Pr₂CoFeO₆ may act as a narrow-gap thermoelectric material, which is similar to some other famous narrow-gap thermoelectric materials such as SnTe (0.23eV) [64] and Bi₂Te₃ (0.17 eV) [65]. Besides, we also experimentally evaluated the thermoelectric performance of pristine Pr₂CoFeO₆ synthesized by a combination of sol-gel method and conventional sintering, and the results show that pristine Pr₂CoFeO₆ possesses an ultrahigh positive S of 674 µV K⁻¹ at 473 K and a relatively low κ of 0.7 W m⁻¹ K⁻¹ at 673 K, which is very competitive compared to other oxide-based thermoelectric materials as shown in Fig. 1c and 1d, respectively. The high S and low κ indicate considerable p-type thermoelectric potential in such a unique material, therefore we need further investigation on their thermoelectric behaviors.



Fig. 1. (a) Orthorhombic crystal structure and (b) calculated electronic band structure of double perovskites Pr_2CoFeO_6 based on its orthorhombic structure, and comparison of (c) maximum experimental absolute Seebeck coefficient |S| and (d) minimum experimental thermal conductivity κ_{min} between Pr_2CoFeO_6 and other oxide-based thermoelectric materials including $MTiO_3$ (M = Sr, Ba, Ca) [49, 66-68], CaMnO_3 [40-42], LaCoO_3 [69, 70], Na_xCo₂O₄ [32-34], Ca₃Co₄O₉ [29-31], BiCuSeO [35-39], In₂O₃ [43-45], and ZnO [46, 47].

In order to fully evaluate the thermoelectric potential of Pr_2CoFeO_6 , in this work, we, for the first time, employed Sr as a potentially effective dopant to further tune the thermoelectric properties of pristine Pr_2CoFeO_6 . We perform first-principles DFT calculations to confirm that rationally doping

Sr²⁺ on Pr-sites (Pr³⁺) can lower the Fermi level down into the valence bands, which provide more holes in the system and in turn, significantly enhance the carrier concentration n_p and contribute to improved σ and $S^2\sigma$. Besides, we performed comprehensive structural and morphological investigations including x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS) on our as-fabricated Sr-doped Pr₂CoFeO₆, which confirm that the polycrystalline Pr₂CoFeO₆ exhibits uniform nanograins derived from the nanocrystals synthesized by a sol-gel method (refer to **Fig. S1** in Supporting Information), while Sr-doping induces point defects in the matrix and further suppresses κ by effectively scattering the long- and short-wavelength phonons, leading to a promising *ZT* up to 0.05 at 673 K in Pr_{1.8}Sr_{0.2}CoFeO₆, which is competitive to most of the other oxide-based thermoelectric materials such as LaCoO₃ (*ZT* = 0.008 at 573 K) [72]. Furthermore, it is predicted that a high *ZT* of >0.2 can be further achieved by rational structural manipulation and band engineering, which is comparable to many other oxide-based thermoelectric materials such as CaTiO₃ [67], CaMnO₃ [41], and Ca₃Co₄O₉ [73].

2. Results and discussion

For pristine Pr_2CoFeO_6 , the most challenging issue is its low σ derived from its low n_p , which is only 4.03×10^{14} cm⁻³ as measured. To further tune n_p and in turn the thermoelectric properties of pristine Pr_2CoFeO_6 , in this work, we employed Sr as a potentially effective dopant. In most Sr-based compounds, Sr exhibits a stable Sr²⁺ valence state [28]. Considering that the common valence state of Pr is Pr³⁺ and Pr⁴⁺ in most Pr-based compounds [74], by doping Sr²⁺ on Pr-sites in Pr_2CoFeO₆, there will be more hole carriers produced in the system to considerably improve n_p of Pr_2CoFeO₆. At the same time, the atomic radius of Sr (2.19 Å) is close to that of Pr (2.49 Å), the similar atomic radius represents a small mismatch of dopant and host atoms, which is beneficial for the high solubility of the doping element [75]. In addition to this theoretical analysis, the doping of Sr in Pr_2CoFeO₆ can also cause changes in the electronic band structure of Pr_2CoFeO₆. Fig. 2a and 2b show the calculated

band structures of Pr₂CoFeO₆ and Pr_{1.5}Sr_{0.5}CoFeO₆, and corresponding density-of-states (DOS) of Pr₂CoFeO₆ and Pr_{1.5}Sr_{0.5}CoFeO₆ are shown in Fig. 2c and 2d, respectively. After doping with Sr on Pr-sites, the pseudo-like energy gap is slightly narrowed from 0.23 eV to 0.22 eV, and Sr-doping can lower the Fermi level down into the valence bands, which can provide more holes in the system and in turn significantly enhance n_p . As shown in Fig. 2c and 2d, the p-type semiconducting behavior of Pr₂CoFeO₆ is reflected by the DOS near the Fermi level, which is mainly determined by Fe_d orbital, and then O p and Co d orbitals. However, after magnifying the partial DOS (PDOS) of Pr and Sr for Pr_{1.5}Sr_{0.5}CoFeO₆ (Fig. 2e and 2f), we found that both Pr and Sr contribute to the p-type semiconducting. For Pr, the Pr d orbital mainly determines the PDOS of Pr near the Fermi level, while after doping with Sr, both Sr p and Sr d strengthen the PDOS near the Fermi level. Therefore, doping Sr can benefit the p-type semiconducting performance of Pr₂CoFeO₆ to some extent. However, it should be noted that the dominant contribution of Sr-doping in Pr₂CoFeO₆ is tuning the carrier density since the variations in the band structure and DOS are not so obvious by Sr-doping. We also performed the ultraviolet-visible absorption spectroscopy characterization on Pr_2CoFeO_6 . The wavelength λ of the absorption peak of Pr_2CoFeO_6 is 2267 nm (refer to Fig. S2), and the optical bandgap E_g of 0.55 eV can be calculated by $E_g = 1240/\lambda$. Considering that DFT calculations are well known for the underestimation of bandgaps such as BiCuSeO [48], CoSb₃ [76], and SnSe [77], the accuracy of DFT calculations are acceptable.



Fig. 2. Calculated band structures of (a) Pr_2CoFeO_6 and (b) $Pr_{1.5}Sr_{0.5}CoFeO_6$, and corresponding DOS of (c) Pr_2CoFeO_6 and (d) $Pr_{1.5}Sr_{0.5}CoFeO_6$. Magnified PDOS of (e) Pr and (f) Sr for $Pr_{1.5}Sr_{0.5}CoFeO_6$.

Sr-doped Pr_2CoFeO_6 ($Pr_{2-x}Sr_xCoFeO_6$, x = 0, 0.2, and 0.4) products were fabricated by a combination of sol-gel method and conventional sintering technique. To verify the phase and valence state information of as-fabricated materials, XRD and XPS characteristics were investigated. Fig. 3a shows the XRD patterns of $Pr_{2-x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4). Because double perovskite Pr_2CoFeO_6 is a newly found material, and there is no XRD standard card for this material, therefore we tried to use the standard card of Pr(Co_{0.5}Fe_{0.5})O₃ (ICSD-244742) [62] to index the XRD patterns of Pr₂CoFeO₆. The results show that all diffraction peaks from Pr₂CoFeO₆ samples can be indexed as a typical singlephase orthorhombic Pnma structure, similar to that of $Pr(Co_{0.5}Fe_{0.5})O_3$. The Rietveld refinement results of Pr₂CoFeO₆ based on the standard card of Pr(Co_{0.5}Fe_{0.5})O₃ (refer to Fig. S3 in Supporting Information) indicate that most peaks of Pr_2CoFeO_6 can well fit the standard card of $Pr(Co_{0.5}Fe_{0.5})O_3$, even though there is still some mismatches (such as peak intensities) due to the structural differences between Pr_2CoFeO_6 and $Pr(Co_{0.5}Fe_{0.5})O_3$ (such as the atomic positions and facets) [78]. On this basis, we consider that the achieved Pr₂CoFeO₆ should have typical orthorhombic Pnma structure, which fits well with the previous work fabricated by solid-state high-temperature techniques [62]. The intensity of 121* diffraction peak is the strongest in all samples, indicating that all products possess significant (121) surfaces. Fig. 3b shows the full-spectrum XPS result of Pr_{1.8}Sr_{0.2}CoFeO₆ and Fig. 3c-3f show magnified XPS results for Co, Fe, Pr, and Sr, respectively. We correct the binding energies of the Co and Fe elements by referencing the C1s line at 284.55 eV to eliminate the charging effect [79]. Satellite peaks can be observed at positions ~718.8 eV, as shown in Fig. 3d and 3e. Co possesses two different valence states in Sr-doped Pr₂CoFeO₆, namely Co²⁺ and Co³⁺, respectively, while Fe also possesses two different valence states in Sr-doped Pr₂CoFeO₆, namely Fe³⁺ and Fe⁴⁺, respectively. Table 1 lists the binding energy and area ratio under the XPS peaks corresponding with Co and Fe cations with different oxidation states and spin-orbits. Both of the Co 2p and Fe 2p regions exhibit spin-orbit splitting peaks centered at ~780 eV (Co $2p_{3/2}$), ~795 eV (Co $2p_{1/2}$), and ~711 eV (Fe $2p_{3/2}$) and ~725 eV (Fe $2p_{1/2}$), respectively. Such an interesting result may cause the disorder of Fe and Co in the lattice

of Pr_2CoFeO_6 , which was supported by the DFT calculations by previous work [62]. However, different from Co and Fe, Pr possesses a stable valence state of Pr^{3+} , while Sr possesses a stable valence state of Sr^{2+} , suggesting that Sr doping on Pr-sites can improve n_p of Pr_2CoFeO_6 . The XPS results of pristine Pr_2CoFeO_6 can be referred to **Fig. S4** in Supporting Information.

Table 1. Binding energy and percentage area obtained by deconvolution of XPS spectra for different oxidation states of Fe and Co.

Composition	Oxidation state	Area (%)	Spin orbit	Binding energy (eV)
Pr ₂ CoFeO ₆	Co ²⁺	57.44	Co 2p _{3/2}	780.06
			Co 2p _{1/2}	788.53
	Co ³⁺	42.56	Co 2p _{3/2}	782.58
			Co 2p _{1/2}	795.33
	Fe ²⁺	22.89	Fe 2p _{3/2}	710.09
			Fe 2p _{1/2}	/
	Fe ³⁺	41.53	Fe 2p _{3/2}	711.75
			Fe 2p _{1/2}	723.85
	Fe ⁴⁺	38.58	Fe 2p _{3/2}	714.86
			Fe 2p _{1/2}	724.40
Pr _{1.8} Sr _{0.2} CoFeO ₆	Co ²⁺	48.27	Co 2p _{3/2}	778.00
			Co 2p _{1/2}	788.44
	Co ³⁺	51.73	Co 2p _{3/2}	782.84
			Co 2p _{1/2}	795.24
	Fe ²⁺	/	Fe 2p _{3/2}	/
			Fe 2p _{1/2}	/
	Fe ³⁺	50.98	Fe 2p _{3/2}	710.47
			Fe 2p _{1/2}	723.50
	Fe ⁴⁺	49.02	Fe 2p _{3/2}	712.29
			Fe 2p _{1/2}	725.52



Fig. 3. (a) XRD patterns of $Pr_{2-x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4), and XPS results of $Pr_{1.8}Sr_{0.2}CoFeO_6$ for (b) full spectrum, (c) Co 2p, (d) Fe 2p, (e) Pr 3d, and (f) Sr 3d.

Comprehensive SEM, EDS, and TEM tools were performed to investigate the structural, compositional, and morphological characteristics of Sr-doped Pr₂CoFeO₆. Fig. 4a and 4b show the low- and high-magnification FE-SEM images of Pr_{1.8}Sr_{0.2}CoFeO₆ powders synthesized by a sol-gel method. It is clearly seen that the as-synthesized powders possess rough crystal surfaces and an average size of ~200 nm, which are typical nanocrystals that benefited from the high-efficiency sol-gel method. Fig. 4c shows a SEM image of a fractured Pr_{1.8}Sr_{0.2}CoFeO₆ bulk fabricated by conventionally sintering, from which typical nanograins with uniform grain sizes of ~200 nm on average can be clearly observed. Compared to the SEM images of un-doped Pr₂CoFeO₆ with larger grain sizes of >500 nm (refer to Fig. S5 in Supporting Information), the high-density grain boundaries in Pr_{1.8}Sr_{0.2}CoFeO₆ can effectively scatter the low- and medium-wavelength phonons during thermal transport, leading to lower κ_l . Fig. 4d shows the EDS map of overlap of Pr, Sr, Co, Fe, and O elements for a polished Pr_{1.8}Sr_{0.2}CoFeO₆ bulk, and Fig. 4e-4i show EDS maps of Pr, Fe, Co, O, and Sr, respectively. All EDS maps are taken from the SEM image of a polished Pr_{1.8}Sr_{0.2}CoFeO₆ bulk as an inset in Fig. 4d. It is clearly seen that all elements including Sr are uniform in the scanning area, indicating homogeneous doping without forming any agglomerate. In terms of the nanostructural feature of the as-fabricated Sr-doped Pr₂CoFeO₆, Fig. 4j shows a TEM image of the sample sliced from the bulk, and Fig. 4k shows a corresponding high-resolution TEM (HRTEM) image, from which typical nanograins can be observed with sizes range from 5 nm to 10 nm. At the same time, significant lattice distortion can be observed. Fig. 4l shows the corresponding selected area electron diffraction (SAED) pattern taken from Fig. 4k, in which the typical polycrystalline rings confirm the polycrystalline feature of these nanograins. Such intensive nanograins and lattice distortions can effectively scatter the phonons with various wavelengths and in turn, suppress κ_l . The characterizations on repeated Pr_{1.8}Sr_{0.2}CoFeO₆ samples can be referred to Fig. S6 in Supporting Information, which shows similar micro/nanostructural features.



Fig. 4. (a) Low- and (b) high-magnification FE-SEM images of $Pr_{1.8}Sr_{0.2}CoFeO_6$ powders, (c) SEM image of fractured $Pr_{1.8}Sr_{0.2}CoFeO_6$ bulk, and EDS maps of polished $Pr_{1.8}Sr_{0.2}CoFeO_6$ bulk for (d) overlap of Pr, Sr, Co, Fe, and O, (e) Pr, (f) Fe, (g) Co, (h) O, and (i) Sr. All EDS maps are taken from the SEM image of polished $Pr_{1.8}Sr_{0.2}CoFeO_6$ bulk as an inset in (d). (j) TEM image, (k) HRTEM image, and (l) corresponding SAED pattern of sliced $Pr_{1.8}Sr_{0.2}CoFeO_6$ bulk.

To evaluate the thermoelectric performance of double perovskite Pr₂CoFeO₆ before and after Srdoping, the main properties including σ , S, n_p , $S^2\sigma$, κ , κ_e , and κ_l within the temperature range between 300 K and 723 K were measured. Considering that Pr₂CoFeO₆ is an anisotropic material (indicated by its orthorhombic Pnma crystal structure), we measured all properties along the same direction perpendicular to the sintering pressure. Fig. 5a shows the measured σ of Pr_{2-x}Sr_xCoFeO₆ (x = 0, 0.2, 0.2) and 0.4). With increasing the temperature, σ of all samples is increased, suggesting obvious semiconductor characteristics. As well, with increasing the Sr-doping concentration (x), σ of Pr₂CoFeO₆ is significantly enhanced within the entire temperature range. Oppositely, S of Pr₂CoFeO₆ is considerably reduced, as indicated by Fig. 5b. S of all compositions exhibit positive values within the entire temperature range, indicating the presence of *p*-type semiconducting behavior. It should be noted that because of the low σ of pristine Pr₂CoFeO₆ at low temperatures (only 9.06×10⁻⁵ S cm⁻¹, exhibiting the characteristics of insulators [59]), it cannot observe the S value before 400 K, and the first measurable data for S is from 473 K, which is also the highest value of 674 μ V K⁻¹. These results indicate that Sr-doping can significantly improve the electrical transport, benefiting from the significantly enhanced room-temperature n_p from 4.03×10^{14} cm⁻³ to 5.44×10^{19} cm⁻³, as shown in Fig. **5c**. It should be noted that the calculated theoretical n_p of Pr_{1.6}Sr_{0.4}CoFeO₆ is ~3.49×10²¹ cm⁻³, which is higher than the as-measured value of 5.44×10^{19} cm⁻³. However, considering that the theoretical value is derived from an ideal Pr_{1.6}Sr_{0.4}CoFeO₆ crystal without any imperfection in its structure and compositional error, such a difference is understandable. Table 2 summarizes the measured properties including density ρ , n_p , σ , S, and $S^2 \sigma$ of $Pr_{2-x}Sr_xCoFeO_6$ at room temperature.

Table 2. The measured room-temperature ρ , n_p , σ , S, and $S^2\sigma$ of $Pr_{2-x}Sr_xCoFeO_6$ for x = 0, 0.2, and 0.4.

Composition	ρ (g cm ⁻³)	n_p (cm ⁻³)	σ (S cm ⁻¹)	S (µV K ⁻¹)	$S^{2}\sigma$ (μ W m ⁻¹ K ⁻²)
Pr ₂ CoFeO ₆	4.78	4.03×10^{14}	9.06×10 ⁻⁵	-	-
$Pr_{1.8}Sr_{0.2}CoFeO_6$	4.55	5.52×10^{17}	4.48	206.11	19.01
$Pr_{1.6}Sr_{0.4}CoFeO_6$	4.70	5.44×10 ¹⁹	9.08	125.27	14.24

Considering the unique electrical transport behavior of double perovskite oxide found in recent years, it is particularly important to deeply explore the carrier transport mechanism in the Pr_2CoFeO_6 . Generally, the electrical transport mechanism in double perovskite oxides mainly includes two types: the electrical conduction predominantly happens by the thermally-excited small polaron hopping (SPH) conduction, but occasionally happens by the Mott variable-range hopping (VRH) conduction [80]. The VRH conduction mechanism is especially rational in compounds that possess disordered structures such as in Sr_2CoSbO_6 [81] and A_2MnRuO_6 (A = Sr and La) [82]. Our XRD results show that the Pr_2CoFeO_6 system possesses an orthorhombic structure. Furthermore, more typical thermally-excited conductivity can dominate at a higher temperature. Therefore, we only consider the small polaron transition conduction mechanism. The SPH conduction model can be represented as follows:

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_{HOP}}{k_B T}\right) \tag{1}$$

where k_B represents the Boltzmann's constant and E_{HOP} represents the activation energy for SPH, σ_o is a constant [83]. Because of the lattice imperfections the double perovskite oxides as observed by our characterizations shown in **Fig. 4**, carriers can interact with these imperfections to form small polarons with greater effective mass m^* , which prevents these polarons from moving as freely as carriers in traditional degenerate semiconductors [84]. Moreover, carriers are more or less confined to a particular location because the energy is insufficient to overcome the barriers [52]. Compared with traditional degenerate semiconductors, this makes the motion of carriers rather difficult. **Fig. 5d** shows $1/K_BT$ dependent $\ln(\sigma T)$ of $Pr_{2-x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4) fitting with the SPH model. As shown in **Fig. 5d**, the observed data of linear fitting with the SPH conduction model represent the energy required for the carriers to overcome the energy barrier. Activation energies E_{HOP} for the carriers to overcome these energy barriers in $Pr_{2-x}Sr_xCoFeO_6$ were calculated using the slope of the linear fit with **Equation (1)**. The activation energy E_{HOP} was found to be ~0.65 eV for the Pr_2CoFeO_6 , while Sr-doping into the matrix can sharply decrease the activation energy to ~0.12 eV in $Pr_{1.8}Sr_{0.2}CoFeO_6$, indicating that Srdoping makes the restricted carriers roam like free ones.

It is important to study the variation of effective carrier density in the materials for a comprehensive understanding of σ of the materials. In complex double perovskites, their *S* values are dominantly interpreted by the SPH conduction, given by the SPH model [85]. The Heikes formula, modified by Chaikin and Beni [86], is conventionally used to depict the relationship between *S* and n_p :

$$S = \frac{k_B}{e} In(\frac{2-c}{c}) \tag{2}$$

where *c* is the fractional polaron concentration and *e* is the electronic charge. The calculated values of *c* for all samples are listed in **Table 3**. It can be concluded that the polaron concentration of Pr_2CoFeO_6 is almost negligible. However, with increasing the dopant concentration, the polaron concentration significantly increases. These results have the same trend as the influence of Sr-doping on n_p of the system shown by the Hall measurement. Great decrement in the activation energy barrier for SPH coupled with the improvement in fractional polaron concentration *via* Sr-doping cause a significant promotion of σ and therefore enhance the $S^2\sigma$ of Pr_2CoFeO_6 , as shown in both **Table 2** and **Fig. 5e**. Although *S* is reduced by Sr-doping, benefiting from the greatly enhanced σ , the high maximum $S^2\sigma$ of $\sim 46 \,\mu$ W m⁻¹ K⁻² at 573 K was obtained in $Pr_{1.8}Sr_{0.2}CoFeO_6$.

Table 3. Fractional polaron concentration and activation energy for SPH conduction model for all compositions.

Composition	Fractional polaron concentration (c)	Activation energy for SPH (E_{HOP})		
	at room temperature			
Pr ₂ CoFeO ₆	0.04	0.65		
$Pr_{1.8}Sr_{0.2}CoFeO_6$	0.17	0.12		
$Pr_{1.6}Sr_{0.4}CoFeO_6$	0.38	0.14		

To explore the room for further improving the $S^2\sigma$ of as-fabricated Pr₂CoFeO₆ materials, a single parabolic band (SPB) model was employed to study the relation between n_p and $S^2\sigma$. Detailed calculations can be referred to the experimental section in Supporting Information. **Fig. 5f** shows the n_p -dependent $S^2\sigma$ of Pr_{2-x}Sr_xCoFeO₆ (x = 0, 0.2, and 0.4) calculated by the SPB model. With increasing the doping concentration, the theoretical peak $S^2\sigma$ is also increased. Therefore, an optimized n_p between $\sim 10^{17}$ cm⁻³ and $\sim 10^{19}$ cm⁻³ can contribute to high $S^2\sigma$ for Sr-doped Pr₂CoFeO₆, which fits well with the experimental results shown in **Fig. 5e**.



Fig. 5. Temperature-dependent (a) electrical conductivity σ and (b) Seebeck coefficient *S* of Pr_{2-x}Sr_xCoFeO₆ (x = 0, 0.2, and 0.4). (c) *x*-dependent room-temperature carrier concentration n_p of Pr_{2-x}Sr_xCoFeO₆. (d) $1/K_BT$ -dependent $\ln(\sigma T)$ of Pr_{2-x}Sr_xCoFeO₆ (x = 0, 0.2, and 0.4) fitting with the SPH model. Here K_B is Boltzmann's constant and E_{HOP} is the activation energy for small-polaron hopping. (e) Temperature-dependent thermoelectric power factor $S^2\sigma$ of Pr_{2-x}Sr_xCoFeO₆ (x = 0, 0.2, and 0.4). (f) n_p -dependent $S^2\sigma$ of Pr_{2-x}Sr_xCoFeO₆ (x = 0, 0.2, and 0.4) calculated by SPB model.

Fig. 6a shows the measured temperature-dependent thermal diffusivity D of $Pr_{2-x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4). Combined with the measured mass densities ρ shown in Table 2 and specific heat C_p shown in Fig. S7 (Supporting Information), Fig. 6b shows that the determined κ by $\kappa = D \cdot \rho \cdot C_p$.

 Pr_2CoFeO_6 exhibits intrinsic low κ , and the κ values within the entire temperature range are less than 1 W m⁻¹ K⁻¹, which is smaller than 80 % of the thermoelectric oxides [28]. With increasing the doping concentration from x = 0 to x = 0.2, the κ value is significantly reduced within the entire temperature range. However, with further increasing the doping concentration up to x = 0.4, the κ value is increased again, partially resulted from the significantly enhanced κ_e , as shown in Fig. 6c. The κ_e was calculated using the Wiedemann-Franz law [87]: $\kappa_e = L \cdot T \cdot \sigma$, where L is the Lorentz number calculated by using the formula $L = 1.5 + \exp\left[-\frac{|S|}{116}\right]$ [88], and $\kappa_l = \kappa - \kappa_e$. As a result, $\Pr_{1.8} Sr_{0.2} CoFeO_6$ exhibits the lowest κ_l of <0.6 W m⁻¹ K⁻¹ between 500 K and 700 K, as shown in **Fig. 6d**. Such low κ_l value is mainly derived from the effective multi-wavelength phonon scattering at hierarchical crystal/lattice imperfections in Pr_{1.8}Sr_{0.2}CoFeO₆ including high-density grain boundaries, significant lattice distortions, and point defects by Sr-doping. Besides, double perovskite oxides possess multivalent cations, a plethora of defects may be introduced during materials synthesis, which further act as phonon scattering centers [52]. As well, for x = 0 and 0.2, the linear decrement of κ_l indicates that the phonon scattering is dominated by Umklapp phonon scattering [89]; while for x = 0.4, with increasing the temperature, the κ_l was increased, and the underlying reason of this phenomenon need further investigation. Fig. 6e shows determined temperature-dependent ZT of $Pr_{2-x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4), from which a peak ZT of ~0.05 can be achieved at 673 K in $Pr_{1.8}Sr_{0.2}CoFeO_6$, which is significantly improved by 233 % compared to pristine Pr₂CoFeO₆. Such a promising ZT is competitive to some other oxide-based thermoelectric materials such as $LaCoO_3$ (ZT = 0.048 at 300 K) [71] and BaTiO₃ (ZT = 0.008 at 573 K) [72]. Fig. 6f also exhibits n_p -dependent ZT of Pr_{2-x}Sr_xCoFeO₆ (x = 0, 0.2, and 0.4) calculated by the SPB model. Interestingly, the as-achieved n_p of 5.52×10^{17} cm⁻³ is very close to an optimized value of $\sim 10^{18}$ cm⁻³ to achieve a peak ZT. Besides, we further study the magnetic state of $Pr_{2-x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4) to explore the potential relationship between their magnetic and thermoelectric properties. The results show that all samples exhibit a typical paramagnetic state (as shown in Fig. S8-S9), indicating that there is a weak relationship between the magnetic and

thermoelectric performance for $Pr_{2-x}Sr_xCoFeO_6$ [4, 90]. Detailed discussions are provided in the Supporting Information.



Fig. 6. Temperature-dependent (a) thermal diffusivity D, (b) thermal conductivity κ , (c) electronic thermal conductivity κ_e , (d) lattice thermal conductivity κ_l , and (e) thermoelectric figure-of-merit ZT of $Pr_{2-x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4). (f) n_p -dependent ZT of $Pr_{2-x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4) calculated by the SPB model.

It should be noticed that the as-achieved ZT of 0.05 is not the upper limit ZT value for the Pr_2CoFeO_6 system since the entire experimental is based on single Sr-doping, which is only a preliminary attempt. Generally, there are still many strategies to further improve the thermoelectric performance of Pr_2CoFeO_6 . For example, for many oxide-based thermoelectric materials, multiple dopants were commonly used to finely tune the band structures of materials to ensure a high $S^2\sigma$. Taking n-type SrTiO₃ as a typical case, La³⁺ was used to dope Sr²⁺ sites and Nb⁵⁺ was used to dope Ti⁴⁺ sites for the same time, which can simultaneously improve the electron carrier concentration n_e

(by co-doping) and m^* (mainly by Nb-doping) [28]. At the same time, multiple-doping can result in distorted lattice and multiple point defects, which can significantly scatter the short-wavelength phonons and in turn, suppress κ_l . Pure SrTiO₃ was reported to show relatively low ZTs from 0 to ~0.05 due to their low σ (close to 0) and high κ (~12 W m⁻¹ K⁻¹ at 300 K) [28, 91]. After multiple-doping by La and Nb, their ZTs were significantly improved up to 0.43 at ~1000 K [28, 66], benefited from both the enhanced σ and suppressed κ_l . Since Pr₂CoFeO₆ is a typical double perovskite, in addition to Prsites, the Co- and Fe-sites can also be doped by rational dopants with smaller valence states to further tune n_p and strengthen the lattice distortions/point defects at the same time, leading to higher σ and lower κ_l . Another effective route to further improve the thermoelectric performance of Pr₂CoFeO₆ is introducing rational nanoinclusions. The nanoinclusions can result in modulation doping or trigger a strong energy filtering effect at the interfaces between Pr₂CoFeO₆ matrix and nanoinclusions, which can significantly improve S without obviously damaging σ , leading to significantly enhanced $S^2\sigma$ [28]. At the same time, the introduced nanoinclusions, as well as the high-density phase boundaries, can also strongly scatter the medium- and long-wavelength phonons, further suppressing the κ_l . It was reported that based on La/Nb co-doped SrTiO₃, by introducing TiO₂ nanoinclusions as secondary phases, an effective modulation doping was triggered and a further suppressed κ_l was realized, leading to an enhanced ZT up to ~0.65 at 1100 K [49]. Compared with the pure SrTiO₃, the ZT value is improved by 12 times. Therefore, by employing the multi-strategies discussed above, it can be predicted that a high ZT of >0.2 can be further achieved in Pr_2CoFeO_6 , which is comparable to many other oxide-based thermoelectric materials such as CaTiO₃ [67], CaMnO₃ [41], and Ca₃Co₄O₉ [73]. Therefore, more studies are needed to further explore the thermoelectric potential and mechanism of Pr₂CoFeO₆-based double perovskites.

3. Conclusions

In this work, we, for the first time, evaluate the thermoelectric potential of double perovskite Pr_2CoFeO_6 . A series of $Pr_{2,x}Sr_xCoFeO_6$ (x = 0, 0.2, and 0.4) samples were fabricated by combining a sol-gel method and conventional sintering to study their structural characteristics and thermoelectric properties. The as-fabricated $Pr_{2,x}Sr_xCoFeO_6$ exhibits a single-phase polycrystalline feature, and the dopant Sr is uniform in $Pr_{2,x}Sr_xCoFeO_6$ dense bulks. Sr^{2+} -doping on Pr^{3+} -sites significantly improves the carrier density and in turn, the electrical transport performance and thermoelectric power factor, while Sr-doping also considerably suppresses the activation energy for SPH, benefiting the high electrical transport properties. Combining with the further reduction of inherent low κ_l by sol-gelsynthesis induced nanograins and Sr-doping induced lattice distortions and point defects, the highest *ZT* of 0.05 is achieved in $Pr_{1.8}Sr_{0.2}CoFeO_6$ at 673 K. It should be noted that a higher *ZT* of >0.2 can be further realized by the optimization of carrier density, band engineering, and energy filtering, which is comparable to many other oxide-based thermoelectric materials.

4. Experimental details

The experimental details can be referred to Supporting Information.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 51972170), the State Key Laboratory of Materials-Oriented Chemical Engineering (No. ZK201812), the CAS Key Laboratory of Carbon Materials (No. KLCMKFJJ2002), the Priority Academic Program

Development of Jiangsu Higher Education Institutions (PAPD), the Jiangsu Specially-Appointed Professor Program, Australian Research Council, Innovation Centre for Sustainable Steel (ICSS), and USQ strategic research grant.

Appendix A. Supplementary data

Supplementary data to this article can be found online.

References

- [1] Y. Xiao and L.-D. Zhao, Science 367 (2020) 1196.
- [2] X. Shi and L. Chen, Nat. Mater. 15 (2016) 691-692.
- [3] G.J. Snyder and E.S. Toberer, Nat. Mater. 7 (2008) 105-114.
- [4] X.-L. Shi, J. Zou, and Z.-G. Chen, Chem. Rev. 120 (2020) 7399-7515.
- [5] Y. Wang, L. Yang, X. Shi, X. Shi, L. Chen, M. Dargusch, J. Zou, and Z.-G. Chen, Adv. Mater.
 31 (2019) 1807916.
- [6] X.-L. Shi, W.-Y. Chen, T. Zhang, J. Zou, and Z.-G. Chen, Energy Environ. Sci. 14 (2021) 729 764.
- [7] C. Gayner and K.K. Kar, Prog. Mater. Sci. 83 (2016) 330-382.
- [8] J. He and T.M. Tritt, Science 357 (2017) eaak9997.
- [9] Y. Pei, X. Shi, A. LaLonde, H. Wang, L. Chen, and G.J. Snyder, Nature 473 (2011) 66-69.
- [10] Y.-X. Chen, X.-L. Shi, Z.-H. Zheng, F. Li, W.-D. Liu, W.-Y. Chen, X.-R. Li, G.-X. Liang, J.-
- T. Luo, P. Fan, and Z.-G. Chen, Mater. Today Phys. 16 (2021) 100306.
- [11] X.-L. Shi, W.-Y. Chen, X. Tao, J. Zou, and Z.-G. Chen, Mater. Horiz. 7 (2020) 3065-3096.
- [12] S.A. Khandy and J.-D. Chai, J. Phys. Chem. Solids 154 (2021) 110098.
- [13] W.-D. Liu, Y. Yu, M. Dargusch, Q. Liu, and Z.-G. Chen, Renew. Sust. Energ. Rev. 141 (2021)110800.

- [14] J. Pei, B. Cai, H.-L. Zhuang, and J.-F. Li, Natl. Sci. Rev. 7 (2020) 1856-1858.
- [15] X. Zhang, Z. Bu, S. Lin, Z. Chen, W. Li, and Y. Pei, Joule 4 (2020) 986-1003.
- [16] W.-D. Liu, D.-Z. Wang, Q. Liu, W. Zhou, Z. Shao, and Z.-G. Chen, Adv. Energy Mater. 10(2020) 2000367.
- [17] H. Wu, L.-D. Zhao, F. Zheng, D. Wu, Y. Pei, X. Tong, M.G. Kanatzidis, and J. He, Nat. Commun. 5 (2014) 4515.
- [18] R. Moshwan, L. Yang, J. Zou, and Z.-G. Chen, Adv. Funct. Mater. 27 (2017) 1703278.
- [19] X.-L. Shi, X. Tao, J. Zou, and Z.-G. Chen, Adv. Sci. 7 (2020) 1902923.
- [20] X. Lou, S. Li, X. Chen, Q. Zhang, H. Deng, J. Zhang, D. Li, X. Zhang, Y. Zhang, H. Zeng, and
- G. Tang, ACS Nano (2021).
- [21] W. Liu, L. Yang, Z.-G. Chen, and J. Zou, Adv. Mater. 32 (2020) 1905703.
- [22] Z.-Y. Liu, J.-L. Zhu, X. Tong, S. Niu, and W.-Y. Zhao, J. Adv. Ceram. 9 (2020) 647-673.
- [23] C. Fu, S. Bai, Y. Liu, Y. Tang, L. Chen, X. Zhao, and T. Zhu, Nat. Commun. 6 (2015) 8144.
- [24] Y. Wu, Z. Chen, P. Nan, F. Xiong, S. Lin, X. Zhang, Y. Chen, L. Chen, B. Ge, and Y. Pei, Joule 3 (2019) 1276-1288.
- [25] C. Chang, M. Wu, D. He, Y. Pei, C.-F. Wu, X. Wu, H. Yu, F. Zhu, K. Wang, and Y. Chen, Science 360 (2018) 778-783.
- [26] M. Hong, K. Zheng, W. Lyv, M. Li, X. Qu, Q. Sun, S. Xu, J. Zou, and Z.-G. Chen, Energy Environ. Sci. 13 (2020) 1856-1864.
- [27] D. Yang, X. Su, J. Li, H. Bai, S. Wang, Z. Li, H. Tang, K. Tang, T. Luo, Y. Yan, J. Wu, J. Yang, Q. Zhang, C. Uher, M.G. Kanatzidis, and X. Tang, Adv. Mater. 32 (2020) 2003730.
- [28] X.-L. Shi, H. Wu, Q. Liu, W. Zhou, S. Lu, Z. Shao, M. Dargusch, and Z.-G. Chen, Nano Energy 78 (2020) 105195.
- [29] D. Wang, L. Chen, Q. Yao, and J. Li, Solid State Commun. 129 (2004) 615-618.

- [30] W. Li, J. Wang, B. Poudel, H.B. Kang, S. Huxtable, A. Nozariasbmarz, U. Saparamadu, andS. Priva, ACS Appl. Mater. Interfaces 11 (2019) 42131-42138.
- [31] Z. Shi, C. Zhang, T. Su, J. Xu, J. Zhu, H. Chen, T. Gao, M. Qin, P. Zhang, Y. Zhang, H. Yan, and F. Gao, ACS Appl. Mater. Interfaces 12 (2020) 21623-21632.
- [32] M. Ito, T. Nagira, D. Furumoto, S. Katsuyama, and H. Nagai, Scripta Mater. 48 (2003) 403-408.
- [33] M. Ito and D. Furumoto, Scripta Mater. 55 (2006) 533-536.
- [34] M. Ito and D. Furumoto, J. Alloys Compd. 450 (2008) 517-520.
- [35] J. Li, J. Sui, Y. Pei, C. Barreteau, D. Berardan, N. Dragoe, W. Cai, J. He, and L.-D. Zhao, Energy Environ. Sci. 5 (2012) 8543-8547.
- [36] Y. Liu, L.-D. Zhao, Y. Liu, J. Lan, W. Xu, F. Li, B.-P. Zhang, D. Berardan, N. Dragoe, and Y.-H. Lin, J. Am. Chem. Soc. 133 (2011) 20112-20115.
- [37] J.L. Lan, Y.C. Liu, B. Zhan, Y.H. Lin, B. Zhang, X. Yuan, W. Zhang, W. Xu, and C.W. Nan, Adv. Mater. 25 (2013) 5086-5090.
- [38] Y.-L. Pei, H. Wu, D. Wu, F. Zheng, and J. He, J. Am. Chem. Soc. 136 (2014) 13902-13908.
- [39] F. Li, J.-F. Li, L.-D. Zhao, K. Xiang, Y. Liu, B.-P. Zhang, Y.-H. Lin, C.-W. Nan, and H.-M.
- Zhu, Energy Environ. Sci. 5 (2012) 7188-7195.
- [40] L. Bocher, M.H. Aguirre, D. Logvinovich, A. Shkabko, R. Robert, M. Trottmann, and A. Weidenkaff, Inorg. Chem. 47 (2008) 8077-8085.
- [41] Y. Wang, Y. Sui, and W. Su, J. Appl. Phys. 104 (2008) 093703.
- [42] K.K. Liu, Z.Y. Liu, F.P. Zhang, J.X. Zhang, X.Y. Yang, J.W. Zhang, J.L. Shi, G. Ren, T.W.
- He, and J.J. Duan, J. Alloys Compd. 808 (2019) 151476.
- [43] D. Bérardan, E. Guilmeau, A. Maignan, and B. Raveau, Solid State Commun. 146 (2008) 97-101.
- [44] J. Lan, Y.-H. Lin, Y. Liu, S. Xu, and C.-W. Nan, J. Am. Ceram. Soc. 95 (2012) 2465-2469.

- [45] J.-L. Lan, Y. Liu, Y.-H. Lin, C.-W. Nan, Q. Cai, and X. Yang, Sci. Rep. 5 (2015) 7783.
- [46] M. Ohtaki, K. Araki, and K. Yamamoto, J. Electron. Mater. 38 (2009) 1234-1238.
- [47] P. Jood, R.J. Mehta, Y. Zhang, G. Peleckis, X. Wang, R.W. Siegel, T. Borca-Tasciuc, S.X.

Dou, and G. Ramanath, Nano Lett. 11 (2011) 4337-4342.

- [48] Y. Gu, X.-L. Shi, L. Pan, W.-D. Liu, Q. Sun, X. Tang, L.-Z. Kou, Q.-F. Liu, Y.-F. Wang, and
- Z.-G. Chen, Adv. Funct. Mater. (2021) 2101289. DOI: 10.1002/adfm.202101289.
- [49] J. Wang, B.-Y. Zhang, H.-J. Kang, Y. Li, X. Yaer, J.-F. Li, Q. Tan, S. Zhang, G.-H. Fan, C.-
- Y. Liu, L. Miao, D. Nan, T.-M. Wang, and L.-D. Zhao, Nano Energy 35 (2017) 387-395.
- [50] S.A. Khandy and D.C. Gupta, J. Magn. Magn. Mater. 458 (2018) 176-182.
- [51] P. Roy, I. Bose, and T. Maiti, Integr. Ferroelectr. 174 (2016) 34-42.
- [52] K. Tanwar, D.S. Gyan, S. Bhattacharya, S. Vitta, A. Dwivedi, and T. Maiti, Phys. Rev. B 99 (2019) 174105.
- [53] O. Sahnoun, H. Bouhani-Benziane, M. Sahnoun, and M. Driz, J. Alloys Compd. 714 (2017) 704-708.
- [54] P. Roy, V. Waghmare, and T. Maiti, RSC Adv. 6 (2016) 54636-54643.
- [55] M. Nabi, T.M. Bhat, and D.C. Gupta, Int. J. Energ. Res. 43 (2019) 4229-4242.
- [56] S.A. Mir and D.C. Gupta, J. Alloys Compd. 854 (2021) 156000.
- [57] S.A. Mir and D.C. Gupta, Int. J. Energ. Res. 43 (2019) 4783-4796.
- [58] S.A. Mir and D.C. Gupta, Sci. Rep. (2021). DOI: 10.21203/rs.3.rs-206716/v1.
- [59] A. Pal, A. Singh, V.K. Gangwar, and S. Chatterjee, AIP Conf. Proc. 1942 (2018) 110002.
- [60] A. Pal, P. Singh, V.K. Gangwar, S. Ghosh, P. Prakash, S.K. Saha, A. Das, M. Kumar, A.K.
- Ghosh, and S. Chatterjee, Appl. Phys. Lett. 114 (2019) 252403.
- [61] A. Pal, S. Ghosh, A.G. Joshi, S. Kumar, S. Patil, P.K. Gupta, P. Singh, V.K. Gangwar, P.
- Prakash, R.K. Singh, E.F. Schwier, M. Sawada, K. Shimada, A.K. Ghosh, A. Das, and S. Chatterjee,

J. Phys. Condens. Mat. 31 (2019) 275802.

- [62] W. Wong-Ng, G. Liu, I. Levin, I. Williamson, P. Ackerman, K.R. Talley, J. Martin, K. AlHamdan, W. Badegaish, J.A. Kaduk, and L. Li, Powder Diffr. 31 (2016) 259-266.
- [63] S.A. Khandy and D.C. Gupta, J. Magn. Magn. Mater. 441 (2017) 166-173.
- [64] R. Moshwan, W.-D. Liu, X.-L. Shi, Y.-P. Wang, J. Zou, and Z.-G. Chen, Nano Energy 65 (2019) 104056.
- [65] P. Larson, V.A. Greanya, W.C. Tonjes, R. Liu, S.D. Mahanti, and C.G. Olson, Phys. Rev. B65 (2002) 085108.
- [66] J.-B. Li, J. Wang, J.-F. Li, Y. Li, H. Yang, H.-Y. Yu, X.-B. Ma, X. Yaer, L. Liu, and L. Miao,J. Mater. Chem. C 6 (2018) 7594-7603.
- [67] H. Muta, A. Ieda, K. Kurosaki, and S. Yamanaka, Mater. Lett. 58 (2004) 3868-3871.
- [68] J. Suchanicz, P. Czaja, K. Kluczewska, H. Czternastek, M. Sokolowski, and A. Węgrzyn, Phase.Transit. 91 (2018) 1036-1043.
- [69] J. Androulakis, P. Migiakis, and J. Giapintzakis, Appl. Phys. Lett. 84 (2004) 1099-1101.
- [70] Y. Wang, Y. Sui, P. Ren, L. Wang, X. Wang, W. Su, and H.J. Fan, Inorg. Chem. 49 (2010)3216-3223.
- [71] K. Iwasaki, T. Ito, T. Nagasaki, Y. Arita, M. Yoshino, and T. Matsui, J. Solid State Chem. 181(2008) 3145-3150.
- [72] C. Mallada, J.L. Menéndez, O.J. Dura, M.A. López de la Torre, R. Menéndez, and R. Santamaría, J. Eur. Ceram. Soc. 37 (2017) 3741-3746.
- [73] Y. Liu, Y. Lin, Z. Shi, C.-W. Nan, and Z. Shen, J. Am. Ceram. Soc. 88 (2005) 1337-1340.
- [74] E. Pinel, P. Boutinaud, and R. Mahiou, J. Alloys Compd. 380 (2004) 225-229.
- [75] T. Zhu, L. Hu, X. Zhao, and J. He, Adv. Sci. 3 (2016) 1600004.
- [76] Z.-H. Zheng, X.-L. Shi, D.-W. Ao, W.-D. Liu, Y.-X. Chen, F. Li, S. Chen, X.-Q. Tian, X.-R.

Li, J.-Y. Duan, H.-L. Ma, X.-H. Zhang, G.-X. Liang, P. Fan, and Z.-G. Chen, Nano Energy 81 (2021) 105683.

- [77] M. Jin, X.-L. Shi, T. Feng, W. Liu, H. Feng, S.T. Pantelides, J. Jiang, Y. Chen, Y. Du, J. Zou, and Z.-G. Chen, ACS Appl. Mater. Interfaces 11 (2019) 8051-8059.
- [78] I. Islam, S.A. Khandy, M.B. Zaman, A.K. Hafiz, A.M. Siddiqui, and J.-D. Chai, J. Alloys Compd. 867 (2021) 158900.
- [79] I. Palchan, M. Crespin, H. Estrade-Szwarckopf, and B. Rousseau, Chem. Phys. Lett. 157 (1989)321-327.
- [80] S. Vasala and M. Karppinen, Prog. Solid State Ch. 43 (2015) 1-36.
- [81] H. Wei, Y. Chen, G. Huo, H. Zhang, and J. Ma, Physica. B 405 (2010) 1369-1373.
- [82] P.M. Woodward, J. Goldberger, M.W. Stoltzfus, H.W. Eng, R.A. Ricciardo, P.N. Santhosh, P.

Karen, and A.R. Moodenbaugh, J. Am. Ceram. Soc. 91 (2008) 1796-1806.

- [83] E. Gorham-Bergeron and D. Emin, Phys. Rev. B 15 (1977) 3667-3680.
- [84] S.J.L. Billinge, R.G. DiFrancesco, G.H. Kwei, J.J. Neumeier, and J.D. Thompson, Phys. Rev. Lett. 77 (1996) 715-718.
- [85] S. Lee, R.H.T. Wilke, S. Trolier-McKinstry, S. Zhang, and C.A. Randall, Appl. Phys. Lett. 96 (2010) 031910.
- [86] P.M. Chaikin and G. Beni, Phys. Rev. B 13 (1976) 647-651.
- [87] X.-L. Shi, W.-D. Liu, A.-Y. Wu, V.T. Nguyen, H. Gao, Q. Sun, R. Moshwan, J. Zou, and Z.-G. Chen, InfoMat 2 (2020) 1201-1215.
- [88] H.-S. Kim, Z.M. Gibbs, Y. Tang, H. Wang, and G.J. Snyder, APL Mater. 3 (2015) 041506.
- [89] X. Shi, Z.-G. Chen, W. Liu, L. Yang, M. Hong, R. Moshwan, L. Huang, and J. Zou, Energy Storage Mater. 10 (2018) 130-138.
- [90] W. Zhao, Z. Liu, P. Wei, Q. Zhang, W. Zhu, X. Su, X. Tang, J. Yang, Y. Liu, and J. Shi, Nat. Nano. 12 (2017) 55-60.
- [91] J.U. Rahman, W.H. Nam, N. Van Du, G. Rahman, A.U. Rahman, W.H. Shin, W.-S. Seo, M.H.Kim, and S. Lee, J. Eur. Ceram. Soc. 39 (2019) 358-365.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Double perovskite Pr_2CoFeO_6 has developed as a new thermoelectric oxide.
- Sr-doping lowers the Fermi level into the valence band of Pr₂CoFeO₆.
- Unique micro/nanostructures suppress lattice thermal conductivity to 0.58 W m⁻¹ K⁻¹.
- Carrier concentration is optimized to induce a power factor of ~46 μ W m⁻¹ K⁻².
- A ZT of 0.05 is experimentally obtained and a high ZT of >0.2 is predicted.



Graphical Abstract