Enhanced Charge Transport in Ca$_2$MnO$_4$-Layered Perovskites by Point Defect Engineering

Amram Azulay, Marwan Wahabi, Yuriy Natanzon, Yaron Kauffmann, and Yaron Amouyal*

1. INTRODUCTION

Coupling between thermal and electronic transport in crystalline materials, as expressed by the Wiedemann–Franz relation, has always been one of the greatest challenges in understanding the underlying physics of thermoelectric materials. In this sense, CaO(CaMnO$_3$)$_m$ Ruddlesden–Popper layered perovskites, comprising $m$ perovskite subcells separated by CaO planes, exhibit intriguing thermal and electronic transport properties that can be tuned by altering their crystal periodicities. Applying the well-established phonon glass electron crystal (PGEC) concept enables us to increase the transparency of these CaO planes to electron transport at the same time while preserving their opacity to phonon transport. First-principles calculations indicate that the total local potential at CaO planes, where Y substitutes for Ca, is lower by ca. 50% compared to La substitution. Measurements of the electrical conductivity and Seebeck coefficients for Ca$_{2−x}$R$_x$MnO$_4$ (R = La or Y; $x = 0.01, 0.05, 0.1,$ and 0.15) bulk materials in the range of 300–1000 K confirm that compounds doped with Y exhibit higher electrical conductivity values than their La-doped counterparts. We attribute this to lower polaron hopping energy values (up to 23%) evaluated using the small polaron hopping model. This study introduces an original way to employ the PGEC approach for thermoelectric oxides.

KEYWORDS: thermoelectricity, perovskites, charge transport, polarons, density functional theory

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employing point defect engineering. Whereas the effects of the CaO planes on thermal planes have been addressed with remarkable achievements, their deleterious effects on charge carrier transport are still an unresolved issue and the focus of the present study.

Herein, we hypothesize that the CaO planes act as energy barriers for electron transport and we apply selective doping to reduce the barrier heights, thereby facilitating thermal activation of charge carriers and enhancing their mobility. To this end, we consider the Ca$_3$MnO$_7$ lattice, having $m = 1$ periodicity, to be the most appropriate case study for tuning electrical conductivity by selective doping of the Ca sites since it comprises the most highly packed CaO stacking. Performing first-principles calculations of the electron charge density along [001] the direction of the Ca$_3$MnO$_7$ lattice, we find that A-site substitution of Y for Ca reduces the local electrostatic potential of electrons at the vicinity of the CaO planes compared to La substitution. This implies that Y doping should enhance electrical conductivity to a greater extent with respect to La doping. We validate this prediction by synthesizing both La- and Y-doped Ca$_3$MnO$_7$ compounds and measuring their electrical conductivity and Seebeck coefficients. The Y-doped compounds, indeed, exhibit higher conductivities compared to the La-doped ones, and this enhancement is associated with the lower activation energy for polaron hopping. This study demonstrates a combination of computational and experimental aspects for optimizing electron transport in crystals using point defect engineering. Such an approach could aid in improving the TE conversion efficiency of oxides, which are attractive for their natural abundance, nontoxicity, low cost, and chemical and structural stability at elevated temperatures.

2. EXPERIMENTAL SECTION

2.1. Computational Procedures. First-principles calculations are performed applying the density functional theory (DFT), implementing the VASP code with a planar basis set of wave functions and the projector augmented wave (PAW) method, utilizing the MedeA computational environment. An antiferromagnetic Ca$_3$MnO$_7$ ($m = 1$) compound of the $\mathbf{I}_4/\mathbf{a}$d space group with spin-polarized electron density is chosen for the calculations, applying plane-wave expansion up to an energy cutoff of 400 eV. To simulate the exchange–correlation component, we apply the generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Ernzerhof (PBE). Additionally, the Hubbard U-correction is applied for the 3d orbitals of Mn ions, and the parameters are calibrated to correctly describe the electronic structure of transition-metal oxides: $U = 4.3$ eV, $J = 0.8$ eV. Calculations are performed for a supercell of 224 atoms, where one Ca atom is substituted by either La or Y, resulting in $x = 0.03125$. Such a supercell is large enough to predict the effect of one dopant atom only, without interfering with neighboring dopants due to periodic boundary conditions. Equilibrium values of lattice parameters are found by allowing relaxation of the cell geometry and atomic positions using a threshold force of 0.02 eV Å$^{-1}$. Finally, we calculate the local electrostatic potential comprising Coulombic and Hartree–Fock exchange interactions of an electron with its neighboring ions and consider it as the potential energy of an electron throughout the lattice.

2.2. Material Synthesis. We apply a standard solid-state reaction (SSR) routine to synthesize Ca$_3$R$_{m}$MnO$_7$ compounds with $x = 0.01, 0.05, 0.10, 0.15, 0.2$, where $R = Y$ or La. The pure oxide powders, CaCO$_3$ (Reag. Ph Eur, Merck), MnO$_2$ ($\geq 99\%$, Sigma-Aldrich), and Y$_2$O$_3$ (99.99%, Strem Chemicals) or La$_2$O$_3$ (99.99%, Sigma-Aldrich), are weighed in the proper stoichiometric ratios and milled by a mortar and pestle. Finally, the powder mixtures undergo four 24 h SSR steps, with increasing temperatures applying a 100 K h$^{-1}$ heating rate at 1273, 1373, 1473, and 1573 K. Prior to each step, the powders are thoroughly milled to increase the surface area for the reaction. Subsequently, disk-shaped specimens are prepared for each compound by uniaxial pressing of the powder at 700 MPa and sintering of the green body at 1573 K in air for 24 h.

2.3. Material Characterization. X-ray diffraction (XRD) is used to analyze the crystal structure and the confirm single-phase purity of the samples. Crystal structure analysis of the specimens is carried out using a Rigaku MiniFlex II X-ray diffractometer for the 20 angular range of 10–90° with a 0.01° resolution, applying a 0.4° min$^{-1}$ scanning speed. Microstructure characterization is carried out for the surface of the as-sintered samples using a Zeiss Ultra Plus scanning electron microscope (SEM) applying a 4 kV acceleration voltage; secondary electron (SE) signals are recorded for imaging. Chemical analysis is conducted employing energy-dispersive X-ray spectroscopy (EDS) using an Oxford Instruments X-Max 80 mm$^2$ SDD detector. Crystal lattice imaging and chemical identification of atoms are carried out using a double-corrected high-resolution scanning/transmission electron microscope (HR-S/TEM) Titan Themis G$^2$ 60-300 (FEI/Thermo Fisher) operated at 200 keV and equipped with a Dual-X detector (Bruker Corporation) for EDS mapping. The chemical maps are postprocessed (by background correction and Radial Wiener filter), quantified, and analyzed using Velox software. Electrical conductivity and Seebeck coefficients are measured at temperatures ranging from 300 to 1000 K in air using a Nemesis SBA-458 apparatus (Netzsch GmbH, Selb, Germany), providing instrumental accuracies of ±5 and ±7%, respectively.

Figure 1. Schematic illustration of the CaO(CaMnO$_3$)$_m$ Ruddlesden–Popper series showing $m = 1, 2, 3$, and $\infty$ structures, consisting of $m$ CaMnO$_3$ perovskite subcells residing between two adjacent CaO planes. The CaO planes act as scattering centers for both charge and heat carriers.
3. RESULTS AND DISCUSSION

The Ca$_2$MnO$_4$ phase has been reported to possess a tetragonal crystal structure of the $I_{4}/1/acd$ (#139) and $I_{4}/mmm$ (#142) space groups. In a first-principles study, Baranovskiy et al. showed that the difference between the total energies of these polymorphs is relatively small, so that both may coexist.\(^{18,19}\) In this work, we consider the latter.

Figure 2 shows the XRD patterns acquired from powders of the Ca$_{2-x}$R$_x$MnO$_4$ samples ($x = 0.01, 0.05, 0.10$, and $0.15$), matching the tetragonal crystal structure of the $I_{4}/ac$ space group, JCPDS # 040093922.

![Figure 2. X-ray powder diffraction patterns acquired from (a) Y- and (b) La-doped Ca$_{2-x}$R$_x$MnO$_4$ samples ($x = 0.01, 0.05, 0.10$, and $0.15$), matching the tetragonal crystal structure of the $I_{4}/ac$ space group, JCPDS # 040093922.](image)

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Figure 2 shows the XRD patterns acquired from powders of the Ca$_{2-x}$R$_x$MnO$_4$ samples ($R = Y$ or La; $x = 0.01, 0.05, 0.10$, and $0.15$), matching the tetragonal crystal structure of the $I_{4}/ac$ space group, JCPDS # 040093922.

Figure 3 displays the atomically resolved elemental mapping of a Y-doped Ca$_2$MnO$_4$ specimen, clearly indicating the CaO and CaMnO$_3$ subcells and the substitution of Y for Ca sites. La is a well-known A-site rare-earth element substituting for Ca sites in calcium manganite perovskites,\(^{34-40}\) as observed experimentally as well as from first-principles calculations of the substitutional formation energies.\(^{15}\) Doping these compounds with electron donors favoring the $+3$ valence state and substituting for the A-site Ca$^{2+}$ ions, such as Y and La, produces Mn$^{3+}$ ionic defects ($3d^4$, $t_2g^3e_g^1$) in the Mn$^{4+}$ matrix ($3d^3$, $t_2g^3e_g^0$).\(^{38,41,42}\) Electron transport in manganites takes place along Mn$^{3+}$–O–Mn$^{4+}$ chains by thermally activated hopping;\(^{43-45}\) therefore, the CaO planes separating between adjacent CaMnO$_3$ subcells may be considered as energy barriers, impeding electron transport. Based on this picture, we implement selective doping of the Ca sublattice sites to reduce these energy barrier heights.

Figure 4a schematically illustrates the Ca$_2$MnO$_4$ crystal structure showing the periodicity of CaO and MnO$_2$ atomic planes along the c-axis; the CaO plane between perovskite CaMnO$_3$ subcells, lacking a Mn ion, promotes electrically resistive behavior. Figure 4b shows the total local potential averaged over the a–b planes along the c-axis of the Ca$_2$MnO$_4$ structure, where Y or La substitutes for Ca. It is indicated that Y substitution reduces the potential well with respect to La by about 50%; such a difference is expected to affect charge localization and transport. It should be noted that the $I_{4}/1/acd$ structure holds a single Ca site; therefore, the substitution of the Ca atom on the perovskite subcell or on the CaO plane is crystallographically equivalent. To illustrate charge localization, we calculate the electron localization function (ELF) derived from the conditional probability of finding a second electron at position B, given that a first electron of the same spin is located with certainty at position A. The ELF is a dimensionless quantity varying from 0 (no localization) to 1 (full localization), while ELF = 1/2 corresponds to a uniform electron gas of an electron pair.\(^{46,47}\) Figure 4c displays the ELF maps plotted across the (200) planes of the Ca$_2$MnO$_4$ structure, where Y or La substitutes for Ca with $x = 0.03125$. We expect that the lower degree of electron localization in Y-substituted lattices, as well as the lower local electrostatic potential, should reduce the energy barrier for charge transport and enhance electron mobility, with little or no effect on charge carrier concentrations. We, however, emphasize that the values should
be considered only to realize trends with respect to transport rather than characterize actual values of activation barriers since these simulations reflect an electrostatic state.

Notably, although the electronegativity of Y is slightly higher than that of La, viz., 1.2 and 1.1 on the Pauling scale, respectively, it is shown that electrons are localized in the immediate vicinity of La atoms, as opposed to the case of Y doping. This apparent discrepancy may be elucidated based on the effective nuclear charge in terms of orbital exponents, for which La and Y attain values of 1.55 and 1.25 for the 6s^2 and 5s^2 electrons, respectively. Furthermore, larger ELF values were reported for the less electronegative atoms in other systems, as well. We note that the electronegativity scale may be applied for rough estimates only and for individual systems, as well.

Because the latter involve many-body considerations such as charge screening and orbital shapes.

The electrical conductivity of the Ca_{2−x}R_{x}MnO_4 samples (R = Y or La; x = 0.01, 0.05, 0.10, and 0.15) is measured for the temperature range 300−1000 K. In agreement with our computational expectation, the Y-doped samples exhibit higher electrical conductivity values than their La-doped counterparts for most of the temperature range. For example, the electrical conductivity of the x = 0.05 Y sample at 300 K is about twice as large as its x = 0.05 La counterpart. Seebeck coefficient measurements confirm that all samples are n-type semiconductors, as implied by their negative S values.

Interestingly, although the x = 0.01 La sample exhibits a lower S value than the x = 0.01 Y does, implying higher n, it is still less conductive. Remarkably, we note that the x = 0.10 samples (both Y- and La-doped ones) are slightly more conductive than their x = 0.15 counterparts despite their significantly lower doping levels. As will be shown by electron transport analysis, these findings can be explained in terms of activation energies for conduction. We note that all samples exhibit similar microstructure, grain size, and morphology, as shown for the x = 0.05 and 0.10 couples in SEM micrographs, see Figure 6. These microstructural features, in any case, should insignificantly affect electronic transport in Ca_{2−x}MnO_4 since it is dominated by scattering on the boundaries between CaMnO_3 and CaO sublattices, i.e., by the density of CaO planes. Such length scales (several Å) are much smaller than the characteristic grain size (several μm).

As will be shown, we fit our electrical conductivity and Seebeck coefficient data to the small polaron hopping model and extract the S values at the high-temperature limit from the linear regression analysis. Then, using the Heikes formula:

$$S_{\text{Heikes}}(T \to \infty) = -\frac{k_B}{\mu e} \ln \left( \frac{g}{c} \right)$$  \hspace{1cm} (1)$$

we evaluate c, which is the fraction of Mn^{3+} ions of the total number of Mn sites. Here, k_B is the Boltzmann constant, e is an electron charge, and g is a factor combining spin and orbital degeneracy. The degeneracy factor for the mixed-valence Mn^{3+}/Mn^{4+} system considering strong Hund's coupling and high spin state reads g = 4/10.53 To estimate charge carrier density in cm^{-3} from c, we use the molecular volume (i.e., the unit cell volume normalized to one formula unit, Z = 1) as a constant-size occupation site of the electron (polaron), neglecting minor variations of this volume associated with doping and heating. The results are shown in Figure 7 and Table 1; markedly, each couple of samples (i.e., the same dopant amount, x) attains almost identical charge carrier concentrations, and these are close to the nominal values calculated based on dopant amount assuming each substitution produces one Mn^{3+} ionic defect in the Mn^{4+} matrix.

Further validation for similar doping levels of each couple of samples is given by the chemical analysis of x = 0.05, 0.10, and 0.15 samples using EDS, see Figure 8. A clear indication for a similar elemental concentration of the dopants (Y or La) and proximity to the nominal amount is observed for each couple. These results adhere to the S values and charge carrier concentration similarities seen in Figures 5b and 7.
Charge transport analysis of manganites at temperatures above $T_C$ is usually performed in terms of the small polaron hopping model.\textsuperscript{33,35,58,62} To extract the activation energy for electron transport from the experimental data, we fit the temperature-dependent electrical conductivity and Seebeck coefficient values to the small polaron hopping model:\textsuperscript{63-67}

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{k_B T}\right)$$

$$S = \frac{k_B}{\mu e} \left(\frac{E_S}{k_B T} + \alpha'\right)$$

where $\sigma_0$ is a constant determined by the optical phonon frequency, hopping distance, and polaron concentration; $E_a$ is the conduction activation energy; $E_S$ is the charge carrier generation energy; and $\alpha'$ is a constant matching the Heikes expression at the limit of high temperatures. Table 1 summarizes the conduction activation energies and charge carrier generation energies obtained by linear regression of the data in the temperature ranges of 300–700 and 400–1000 K, respectively. The Seebeck coefficient values for the $x = 0.01$ pair were analyzed in the temperature range of 300–1000 K.

Figure S1 depicts the inverse temperature dependence of $\ln(\sigma T)$ and Seebeck coefficient, demonstrating the linear fits, and Table S1 indicates the $R$-squared values. All samples are found to obey the small polaron conduction mechanism since $E_a > E_S$.\textsuperscript{59,68-70} As expected from isovalent electron donors having similar electronegativities, our charge transport analysis accurately reveals that the charge carrier generation energies ($E_g$) are independent of the dopant chemical identity, and all pairs possess essentially the same value. Conversely, the activation energies for conduction ($E_a$) are higher for samples doped with La, in agreement with the higher potential barrier and ELF calculated for the La-substituted lattice (Figure 4). Using the values obtained for $E_a$ and $E_g$, we derive the polaron hopping energy, $W_H = E_a - E_S$. Evidently, polaron hopping requires lower activation energy for Y-doped compounds than for the La-doped ones, showing up to 23% reduction. This result further implies that the polaron binding energy, $E_B = 2W_H$, correlates with the electrostatic potential well depth (Figure 4b). Since $E_B$ of La-doped compounds is larger, it could be stated that the potential well, which was found to be greater for La-substituted Ca$_2$MnO$_4$, reflects, to a certain extent, the binding energy of small polarons. It is also indicated that the $x = 0.10$ samples feature significantly lower $W_H$-values than their $x = 0.15$ counterparts, elucidating their greater electrical conductivity despite having smaller dopant amounts and lower charge carrier concentrations. This finding verifies the effect of polaron hopping activation energy on mobility. Since the conductivity ($\sigma$) depends on both charge carrier concentration and mobility ($\mu$), so that $\sigma = \mu n$, we can associate the difference in $\sigma$ observed in Figure 5a between couples with the difference in their conduction kinetics, i.e., the mobility term, rather than with their charge carrier concentration. To support this statement on a quantitative basis, we estimate the electron mobility from the measured $\sigma$ values and the calculated $n$ values, and their room-temperature values are listed in Table 1. It is clearly indicated that the Y-doped samples exhibit higher mobilities with respect to the La-doped ones for all dopant concentrations, as predicted by our DFT calculations.

4. CONCLUSIONS

In this work, we correlate DFT simulations with experimental charge transport in Ca$_{2-x}$R$_x$MnO$_4$ ($R = Y$ or La; $x = 0.01, 0.05$, 0.10, and 0.15) bulk materials. We find that La substitution for Ca generates a deeper electrostatic energy barrier on CaO.

Figure 5. Temperature-dependent (a) electrical conductivity and (b) Seebeck coefficient values of the Ca$_{2-x}$R$_x$MnO$_4$ samples ($R = Y$ or La; $x = 0.01, 0.05$, 0.10, and 0.15) measured between 300 and 1000 K. For all compositions and in most of the temperature range, enhanced electrical conductivity is observed for the Y-doped samples compared to their La-doped counterparts, while Seebeck coefficients are approximately equal.
planes compared to Y substitution, and correspondingly, we show that Y-doped samples exhibit higher electrical conductivity. Analysis of the temperature-dependent Seebeck coefficient data using the Heikes formula indicates that the charge carrier concentrations of each couple of samples (same \( x \)) is nearly identical, implying that Y doping yields significantly larger electron mobility than La doping does. The charge carrier generation energy is found to be nearly identical for samples which are doped equally with either Y or La; conversely, all La-doped samples exhibit higher conduction activation energies. Using both values, we derive the polaron hopping and binding energies, consistently showing higher values in La-doped samples, suggesting that the dopants uniquely affect the hopping energy term. This study highlights the fundamental correlation between structure and charge transport in layered perovskites, and proves that a fundamental understanding of this relationship should offer new ways to improve the electrical conductivity of AB(ABO\(_3\))\(_{m}\)-based materials. A striking implication for this relationship is the capability to tune (or enhance) the electrical conductivity of the Ca\(_2\)MnO\(_4\) structure by selective doping while preserving its inherently low thermal conductivity, as shown for La doping. This PGEC-based approach is universal and can be further tested for other crystalline materials.

Figure 6. Scanning electron microscopy (SEM) micrographs taken from the surface of the as-sintered Ca\(_{2-x}\)R\(_x\)MnO\(_4\) samples, showing similar microstructure, grain size, and morphology for specimens of the following compositions: (a) R = La, \( x = 0.05 \); (b) R = La, \( x = 0.10 \); (c) R = Y, \( x = 0.05 \); and (d) R = Y, \( x = 0.10 \).

Figure 7. Ratio of Mn\(^{3+}\) to Mn ions and charge carrier concentrations of the Ca\(_{2-x}\)R\(_x\)MnO\(_4\) samples (R = Y or La; \( x = 0.01, 0.05, 0.10, \) and 0.15) evaluated using the Heikes formula. Samples of the same doping level (same \( x \)) obtain approximately equal charge carrier concentration, as expected.
Table 1. Values of Conduction Activation Energy ($E_a$), Charge Carrier Generation Energy ($E_g$), Polaron Hopping Energy ($W_H$), Charge Carrier Concentration ($n$), and Room-Temperature Electron Mobility ($\mu$), Evaluated for the Ca$_{3-x}$R$_x$MnO$_4$ Samples ($R = Y$ or La; $x = 0.01, 0.05, 0.10$, and $0.15$) Based on the Small Polaron Hopping Model and the Heikes Formula

| Sample ($x$) | $E_a$ (meV) | $E_g$ (meV) | $W_H$ (meV) | $n$ ($\times 10^{20}$ cm$^{-3}$) | $\mu$ ($\times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) |
|-------------|-------------|-------------|-------------|----------------|------------------|
| Y           | Y           | Y           | Y           | Y                      | Y                |
| 0.01        | 114 ± 4     | 123 ± 4     | 22 ± 1      | 1.3 1.6 0.7 0.43      |                   |
| 0.05        | 95 ± 2      | 106 ± 6     | 35 ± 3      | 5.8 6.4 1.9 0.74      |                   |
| 0.10        | 86 ± 3      | 100 ± 3     | 26 ± 3      | 10.9 10.8 3.6 2.4     |                   |
| 0.15        | 94 ± 2      | 114 ± 2     | 20 ± 1      | 14.5 14.5 2.3 1.4     |                   |

Notes

The authors declare no competing financial interest.

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