Oxide materials are of current interest as high-temperature energy-harvesting thermoelectrics in the automotive and manufacturing sectors due to their low cost, low toxicity and high chemical robustness. The phonon-glass electron crystal (PGEC) concept which has been successfully used to optimise the thermoelectric figure of merit (ZT) in clathrates and skutterudites by combining the high electronic conduction of a crystal with the low thermal conduction of a glass is an approach which has not yet been realised in oxides due to the strong coupling between electronic and thermal transport. Through crystal chemistry engineering of the ABO$_3$ perovskite based around a combined experimental and computational understanding of the mechanisms responsible, PGEC behaviour has been achieved for the first time in oxide thermoelectrics by decoupling thermal and electronic transport. By targeting the lattice component of the thermal conductivity ($\kappa_{\text{latt}}$), we have induced a glass-like $\kappa_{\text{tot}}$ through the introduction of large mass disorder on the perovskite A site whilst retaining ABO$_3$ stoichiometry and avoiding vacancy defects that severely compromise electronic transport. Substitution at the perovskite B site with a donor cation allows for independent tuning of the electronic transport, producing a significant power factor. This high mass disorder approach will enable the PGEC concept to be applied experimentally to a wide range of materials, and the computational results which support our observations can be used to generate descriptors towards theoretical screening of new high-performance PGEC thermoelectrics.

Phonon-glass electron-crystal (PGEC) behaviour is realised in La$_{0.5}$Na$_{0.5}$Ti$_{1-x}$Nb$_x$O$_3$ thermoelectric oxides. The vibrational disorder imposed by the presence of both La$^{3+}$ and Na$^+$ cations on the A site of the ABO$_3$ perovskite oxide La$_{0.5}$Na$_{0.5}$Ti$_3$O$_3$ produces a phonon-glass with a thermal conductivity, $\kappa$, 80% lower than that of SrTiO$_3$ at room temperature. Unlike other state-of-the-art thermoelectric oxides, where there is strong coupling of $\kappa$ to the electronic power factor, the electronic transport of these materials can be optimised independently of the thermal transport through cation substitution at the octahedral B site. The low $\kappa$ of the phonon-glass parent is retained across the La$_{0.5}$Na$_{0.5}$Ti$_{1-x}$Nb$_x$O$_3$ series without disrupting the electronic conductivity, affording PGEC behaviour in oxides.

Thermoelectric generators offer enhanced energy efficiency across the industrial and automotive sectors through the conversion of waste heat into electricity. Materials performance is assessed by the dimensionless figure of merit $ZT = (S^2a/\kappa)T$, combining the thermal conductivity ($\kappa$), absolute temperature ($T$), the Seebeck coefficient ($S$) and electrical conductivity ($a$), which together define the power factor ($SF^2a$). One strategy to optimise $ZT$ is the phonon-glass electron-crystal (PGEC) concept proposed by Slack$^6$, which aims to decouple the quantities governed by the Boltzmann transport equation in an "electronic-crystal", by maximising $S$ and $a$, from the quantity governed by phonon transport processes in a "phonon-glass" (PG) by minimising $\kappa$. Through the introduction of large mass disorder on the perovskite A site, we have induced a glass-like $\kappa_{\text{tot}}$ through the introduction of large mass disorder on the perovskite A site whilst retaining ABO$_3$ stoichiometry and avoiding vacancy defects that severely compromise electronic transport. Substitution at the perovskite B site with a donor cation allows for independent tuning of the electronic transport, producing a significant power factor. This high mass disorder approach will enable the PGEC concept to be applied experimentally to a wide range of materials, and the computational results which support our observations can be used to generate descriptors towards theoretical screening of new high-performance PGEC thermoelectrics.
acoustic phonons interacting through anharmonic phonon-phonon Umklapp processes (Equation S6, ESI†) that is characteristic of PCs. The identification of the phonon-scattering processes that limit heat conduction in a material has led to a panoptic approach to reduce κ for PC materials. Here κ remains above the minimum thermal conductivity (κ\text{min}) expected for a PG, where the thermal conductivity is described by a coupled lattice of harmonic oscillators vibrating with the same frequency but with random phases, and κ\text{min} can be calculated using Cahill’s model (Equation S9, ESI†) from the number density of atoms (N) and \( \theta_b \). The phonon MFP of a PG is much smaller than a PC and remains constant as a function of temperature as all vibrations are localised over interatomic distances. Through Equation 1, \( \kappa_{\text{min}} \) of a PG exhibits a characteristic temperature dependence which follows the heat capacity above \( \theta_b \), in contrast to \( \kappa(T) \) of a PC which asymptotically approaches this lower \( \kappa_{\text{min}} \) limit from above at high temperature. PG behaviour of \( \kappa \) was observed in amorphous and disordered insulating materials,7, 8 and realised in high performance thermoelectrics such as skutterudites and clathrates which behave as PGECS through the incorporation of “rattling” effects produced by extensive low-frequency ion displacements within large cages in the framework structures of these systems.9, 10 Recently, ultralow thermal conductivities of 0.4–0.5 W m\text{-1} K\text{-1} resulting from bonding anharmonicity where weakly bound cations act as rattlers were observed in metal tellurides.11, 12

As part of the search for materials based on less toxic and/or scarce components13, 14 that can operate under more demanding conditions including the broad temperature ranges required for some applications (automotive exhaust waste heat recovery: 350–700 K, industrial furnace waste heat recovery: 700–1100 K),15, 16 there is growing interest in thermoelectric oxide materials.17, 18 However, the strategies used to design high-performance thermoelectric materials based on small band gap, broad-band semiconductors and intermetallics cannot be translated directly to oxide materials.19 Transition metal oxides are often narrow-band semiconductors with electronic transport properties that are not governed by the Boltzmann equation, and typically have poor mobilities and conductivities compared to classical semiconductors. Therefore, considerable effort has been focused on finding oxide materials with large power factors by optimising \( \sigma \) and \( S \), which has led to reasonably high performance in p-type layered cobaltate oxides, \( \text{Ca}_2\text{CoO}_3 \) and \( \text{Na}_2\text{CoO}_3 \), with ZT values of ≈0.4 and ≈0.6 at 700 K, respectively.20, 21 Both p- and n-type semiconductors are needed for device fabrication, and it has been more difficult to achieve comparable performance in n-type oxides. By exploiting the band structure of the perovskite oxide \( \text{SrTiO}_3 \) (STO), which has contributions from both light and heavy electrons at the Fermi level,22 it is possible to achieve large power factors of 28–36 \( \mu \text{W K}^{-1} \text{cm}^{-2} \) at 300 K in n-type \( \text{Sr}_1-x\text{La}_x\text{TiO}_3 \) (\( x \approx 0.015\)–0.1) single crystals, however, the performance is negated by the large \( \kappa \) of \( \approx 12 \text{Wm}^{-1} \text{K}^{-1} \) in STO. The nanostructuring approaches used to reduce \( \kappa \) in classical compound semiconductors and intermetallics by increasing grain boundary scattering are inefficient in titanate perovskites as the phonon MFP of \( \text{SrTiO}_3 \) is 2–3 nm, requiring nanometer-sized grains for any noticeable effect on \( \kappa \).24 Because of this inherently small phonon MFP, the best strategy to reduce \( \kappa_{\text{min}} \) through the introduction of point defect scattering achieved by substitution. The scattering time for point defects (\( \tau_{\text{Di}} \)) is added to the other scattering processes according to the Matthiessen rule,25 and is influenced heavily by the disorder scattering parameter, \( \Gamma = \Gamma_{\text{MF}} + \Gamma_{\text{SF}} \), where \( \Gamma_{\text{MF}} \) is the mass fluctuation arising from the mass contrast introduced by the defect and \( \Gamma_{\text{SF}} \) the strain field induced by ionic radius variance of the defect (Equation S5, ESI†). Calculation of \( \Gamma \) predicts the effect of substitution on \( \kappa \), and the calculated contributions to \( \Gamma \) for several previously-reported titanate perovskites, substituted with different rare-earth cations and/or vacancies, are given in Table 1. Therefore, \( \kappa_{\text{min}} \) can be expected to increase 20% (\( \approx 0.6 \)) significantly increasing \( \Gamma_{\text{MF}} \) (Table 1) and resulting in a \( \kappa \) close to \( \kappa_{\text{min}} \) from Cahill’s model, was rather encouraging.27 However, the complex defect chemistry of these materials did not allow for electronic doping whilst simultaneously retaining the PG behaviour, as compositions with carrier concentrations sufficient for good thermoelectric response displayed PC thermal conductivity. In order to realise PGECS in titanates, a strategy required that combines an equivalent \( \Gamma \) to those achieved by cation vacancy-containing materials with a structural chemistry that permits electronic doping.

Table 1 Calculated dimensionless disorder scattering parameters (\( \Gamma \)), including mass fluctuation (\( \Gamma_{\text{MF}} \)) and strain field (\( \Gamma_{\text{SF}} \)) terms, for doped titanate perovskites. The nature (phonon-glass or –crystal) of the heat transport are shown.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \Gamma )</th>
<th>( \Gamma_{\text{MF}} )</th>
<th>( \Gamma_{\text{SF}} )</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Sr}_1-x\text{La}_x\text{TiO}_3</td>
<td>3.02×10^{-2}</td>
<td>1.93×10^{-2}</td>
<td>3.00×10^{-2}</td>
<td>PC</td>
</tr>
<tr>
<td>\text{Sr}_2\text{Y}_1\text{TiO}_5</td>
<td>5.59×10^{-2}</td>
<td>5.58×10^{-2}</td>
<td>2.80×10^{-2}</td>
<td>PC</td>
</tr>
<tr>
<td>\text{Sr}_2\text{Dy}_0.1\text{TiO}_3</td>
<td>0.213</td>
<td>0.212</td>
<td>5.92×10^{-4}</td>
<td>PC</td>
</tr>
<tr>
<td>\text{Sr}<em>2\text{La}</em>{0.3}\text{TiO}_3</td>
<td>0.405</td>
<td>0.404</td>
<td>1.88×10^{-4}</td>
<td>PG</td>
</tr>
<tr>
<td>\text{Nd}<em>{0.6}\text{La}</em>{0.4}\text{La}_{0.2}\text{TiO}_3</td>
<td>0.701</td>
<td>0.694</td>
<td>6.84×10^{-4}</td>
<td>PG</td>
</tr>
</tbody>
</table>

The A site substitution of two Sr\text{Ti} cations in STO for the charge-balancing cation pair \( \text{La}^{3+} \) and \( \text{Na}^{+} \) preserves the overall stoichiometry of the parent structure,30 while introducing charge, size and mass disorder. Structural characterisation of \( \text{La}_2\text{Sr}_2\text{NiO}_3 \) (LTONO) with synchrotron powder X-ray and neutron diffraction gave good agreement with the reported rhombohedral structure (Fig. S1, Table S2, ESI†),21 most importantly highlighting that \( \text{La}^{3+} \) and \( \text{Na}^{+} \) are fully disordered at the A site. Despite this, the anisotropic displacement parameters do not indicate a strong local deviation away from the average structure with a root mean square displacement of 0.078(9) Å for the A site at 300 K, showing that

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LNTO is a crystalline solid with disordered A site cation distribution. The incorporation of both La$^{3+}$ and Na$^{+}$ on the A site in LNTO achieves a higher $\Gamma$ (0.513) than that observed for PG Sr$_{1-x}$La$_{0.67}x$Na$_{0.33}$TiO$_3$ where $x = 0.8$, with $\Gamma_{MF}$ contributing 99.9% of this value. Both STO and LNTO measured in this study are electronically insulating with $\sigma < 3 \times 10^{-12}$ S cm$^{-1}$ at 300 K, thus $x$ corresponds to $\kappa_{latt}$. The thermal conductivity of LNTO (2.29±0.12 W m$^{-1}$K$^{-1}$ at 700 K) is dramatically reduced by 66 % from that of STO (6.83±0.35 W m$^{-1}$K$^{-1}$ at 700 K) in Fig. 1d, and follows the temperature dependence of the heat capacity, a distinguishing feature of a PG. As a result it is not possible to use the Debye-Callaway model for PCs to describe the evolution of $\kappa(T)$ of LNTO. Instead, both the magnitude and temperature dependence of $\kappa$ compare closely to the $\kappa_{min}$ expected for STO if it displayed PG heat transport, calculated with the Cahill model (Equation S9, ESI†), using the cutoff frequencies $\theta_i$ calculated from the measured longitudinal and transverse velocities of sound for STO crystals. Despite the crystalline nature of LNTO, at high temperature the heat transport is no longer mediated by coherent and long-distance propagation of phonons through the lattice, but rather occurs via hops of elementary lattice excitations in a diffusional manner. Spectral phonon analysis on the low temperature thermal conductivity shows that the dominant scattering mechanism is due to the point defects introduced by the increased A site charge and mass disorder (Fig. S2, ESI†). To confirm this concept, we have performed phonon calculations for STO and LNTO at density functional theory (DFT) level using the finite-displacement method (ESI†). We also computed the average separation ($d_{average}$) between the 10 atoms exhibiting the largest phonon displacement amplitudes for each individual phonon mode across the spectrum (Fig. 2a). This quantity is a qualitative indicator of the phonon “localisation” (inset of Fig. 2a). The $d_{average}$ of STO across the spectrum is close to 11 Å, which is the maximum value permitted from the size of the cell used for the calculations, confirming the “delocalised” nature of the phonons. In the case of LNTO, a 20% decrease in $d_{average}$ is observed that suggests increased phonon localisation in the disordered crystal. The random distribution of high mass-contrast La$^{3+}$ and Na$^{+}$ cations can be envisaged as producing locally decoupled oscillators with dramatically different vibrational frequencies (Fig. 1e), which efficiently disrupt the coherent phonon transport that was Fig. 1 Measured $\kappa_{MF}$ for phonon-crystals SrTiO$_3$ and Sr$_{0.67}$La$_{0.33}$TiO$_3$ are shown in a) and are compared against the Debye-Callaway model for crystalline solids (solid lines), alongside example spring models b) and c), illustrating phonon coupling between nearest-neighbours in the crystal structure with identical force constants. The theoretical $\kappa_{MF}$ of STO is calculated from Cahill’s model for disordered crystalline solids, and is compared against the experimental data in a) and d). The $\kappa_{MF}$ of Sr$_{1-x}$La$_{0.67}x$Na$_{0.33}$TiO$_3$ (LNTO) shown in d) cannot be modelled as a phonon-crystal using the Callaway model, and compares much more closely to $\kappa_{latt}$ of a phonon-glass, with a temperature dependence that follows the contribution of the heat capacity ($C_p$) shown on the right-hand axis of d). The vibrational disorder of LNTO resulting from phonon interactions between randomly distributed A site cations with high mass contrast and the rest of the structure is illustrated through the spring model in e). Phonon mean free paths shown in f) are extracted using the measured $\kappa_{MF}$, $C_p$, and speed of sound $v_s$ in Equation 1, where $v_s$ is calculated from Equation 2 using $\theta_i$ obtained by fitting $C_p$ data. Error bars representing the uncertainty in numerical values in a), d) and f) are smaller than the symbols except for the high-temperature $\kappa_{latt}$ and $\theta_i$ for STO.

Fig. 2. Localisation of phonons a) in STO (blue, downward triangle) and LNTO (black, upward triangle) from static DFT calculations; for each individual phonon mode, $d_{average}$ is calculated as the mean distance between the 10 atoms that participate to the greatest extent in a given phonon mode as defined by their displacement amplitudes. The schematic insert illustrates a localised (black circle) and a delocalised (blue circle) phonon mode. b) Energy dispersion of selected electronic bands at the band edges of undoped STO (in a rhombohedral cell with R3c space group symmetry) with different degrees of octahedral tilting $\phi$ (see the inset for definition of tilt angle). All the bands have been aligned to the Fermi level, and the splitting of the $t_2g$ states at the bottom of the conduction band into dispersive and dispersion-less bands is highlighted in yellow. The full band structure of cubic STO (with zero tilting) is shown in Fig. S17, ESI†.
previously well-established by the periodic nearest-neighbour couplings in STO (Fig. 1b). As a result of this vibrational glassiness, the phonon MFP of $s=5$ Å for LNTO (evaluated with Equation 1 from the measured heat capacity, lattice thermal conductivity and mean velocity of sound $\nu = \theta_0 \nu_0 / \sqrt{\kappa_{\text{lat}} N}$ (Equation 2)), where $\theta_0 = 605$ K is extracted from the heat capacity (Fig. S3, Table S3, ESI†) remains constant over a wide temperature range (Fig. 1f) from 80K to 1000K. Glass-like thermal conductivity is established in $\text{La}_{0.8}\text{Na}_{0.2}\text{Ti}_2\text{O}_5$ through phonon engineering by utilizing mass, size and charge disorder of the A site cations.

This complete A site replacement of Sr$^{2+}$ with La$^{3+}$ and Na$^{+}$ in $\text{La}_{0.8}\text{Na}_{0.2}\text{Ti}_2\text{O}_5$ retains the flexible B site substitution chemistry of STO, and allows the introduction of electronic dopant cations into PG LNTO to produce a significant power factor. Synthesis of $\text{La}_{0.5}\text{Na}_{0.5}\text{Ti}_2\text{O}_5\text{Nb}_3\text{O}_9$ at 1623 K under $\text{H}_2/\text{N}_2$ (5%) atmosphere utilising sacrificial powder to prevent the loss of sodium from cold-pressed pellets afforded substitution of Nb$^{5+}$ in phase pure materials to $x=0.2$ (Fig. S4, ESI†). The unit cell parameters increase with $x$ (Fig. 3a) consistent with substitution of Nb$^{5+}$ forming Ti$^{4+}$, both of which are larger than Ti$^{4+}$ ($r_{\text{Ti}^{4+}} = 0.64$ Å, $r_{\text{Ti}^{3+}} = 0.67$ Å and $r_{\text{Nb}^{5+}} = 0.605$ Å). The octahedral tilt angle, $\phi$, decreases from 7.9142(7)* at $x=0$ to 7.2219(18)* for $x=0.2$ (Fig. S5, Table S5, ESI†) as the structure tends more towards cubic symmetry with increasing $x$, and both the mean B–O and A–O distances increase following the expansion of the unit cell. The distortion observed in the crystal structure of LNTO compared to STO could be detrimental to the achievement of a high power factor, due to a change of band dispersion with octahedral tilt angle (Fig. 2b). However, by calculating the electronic structure of STO for different tilt angles (ESI†) we found that the coexistence of dispersive and dispersion-less bands at the bottom of the conduction band is retained for the range of tilt angles observed in the Nb-doped LNTO series, and the ratio of effective electronic mass for the two bands remains $s=5$ for all tilt angles examined, which is similar to the values reported for cubic STO previously.

Tauc plots from diffuse reflectance data show that the parent and doped compositions of LNTO have band gaps of $\approx 3.2$ eV, which is similar to STO (Fig. S8, Table S9, ESI†). The electronic conductivity at 500 K increases as a function of $x$ in $\text{La}_{1-x}\text{Sr}_x\text{Ti}_2\text{O}_5$ from $\sigma = 1200 \pm 6$ S cm$^{-1}$ at $x = 0.05$ to $360 \pm 18$ S cm$^{-1}$ at $x = 0.2$ (Fig. 3b). This is consistent with the linear increase of the carrier concentration (from $7 \times 10^{20}$ cm$^{-3}$ for $x=0.05$ to $3.2 \times 10^{21}$ cm$^{-3}$ for $x=0.2$) obtained from the temperature dependence of the Seebeck coefficient and a mobility $\approx 1$ cm$^2$ V$^{-1}$ s$^{-1}$ (Fig. S9, Table S4, ESI†). The increase in $\sigma$ with $T$ below 500 K is ascribed to the formation of resistive depletion layers of acceptor-based dopants segregated to the grain boundaries (Fig. S9, ESI†). Above this temperature, $\sigma$ decreases with increasing $T$ as carrier mobility is reduced with a $\sigma$ for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Ti}_2\text{O}_5\text{Nb}_3\text{O}_9$ comparable to that of $\text{Sr}_{0.5}\text{Dy}_{0.5}\text{Ti}_2\text{O}_5$ measured in this study. Observation of negative thermopowers indicates that the carriers are predominantly n-type in nature, and the absolute magnitudes of $S_{500}$ decrease from $-222 \pm 11$ to $-127 \pm 6$ $\mu$V K$^{-1}$ from $x = 0.05$ to 0.2 as a result of increasing carrier concentration $n$ (Fig. 3c). The observed magnitudes and temperature dependencies exhibited by both $\sigma$ and $S$ (Fig. S9, ESI†) are comparable to many of the titanates reported previously, which were doped on either the A or B sites. The observation of high $S$ and $\sigma$ suggests that the unique band structure of STO, consisting of heavy and light electrons, that allows for high power factors is retained in $\text{La}_{0.8}\text{Na}_{0.2}\text{Ti}_2\text{O}_5\text{Nb}_3\text{O}_9$ despite the slight distortion of the structure away from cubic symmetry, consistent with the DFT calculations. A maximum power factor of $0.62 \pm 0.07$ mW m$^{-1}$ K$^{-2}$ was obtained for $\text{La}_{0.8}\text{Na}_{0.2}\text{Ti}_2\text{O}_5\text{Nb}_3\text{O}_9$ at $\approx 700$ K (Fig. S10, ESI†). A linear dependence of power factor upon $x$ is observed at 900 K which is different to other Nb-doped titanates, where peak
values are typically achieved at $x \approx 0.1$. In contrast to the strong doping dependence of $\sigma$ and $S$ (Fig. 3b and 3c), the magnitudes of total thermal conductivity ($k_{\text{total}}$), in the range of 2.34±0.12-2.59±0.13 W m$^{-1}$ K$^{-1}$, are only 2 to 10% higher than undoped La$_{0.4}$Na$_{0.6}$TiO$_3$ and thus almost independent of B-site substitution (Fig. 3d). All of the electronically-conducting La$_{0.4}$Na$_{0.6}$Ti$_{1-x}$Nb$_x$O$_3$ compositions exhibit the same glass-like temperature dependence of $\kappa$ that was observed for LNTO, meaning that $k_{\text{total}} \propto k_{\text{total}}$ for all $x$ (Fig. 4a). The lattice contribution to the thermal conductivity ($k_{\text{lat}}$) decreases as the electronic contribution ($k_{\text{elec}}$) increases from 6.5 at $x = 0.05$ to 19% at $x = 0.2$ at 500 K (Fig. 3d, Fig. S1, and S1f). The retention of PG temperature dependences and magnitudes of $\kappa$ in electronically-conducting La$_{0.4}$Na$_{0.6}$Ti$_{1-x}$Nb$_x$O$_3$ (Fig. 4a) reflects decoupling of thermal and electronic transport, which has not previously been reported in an oxide thermoelectric family.

The La$_{0.5}$Na$_{0.5}$Ti$_{1-x}$Nb$_x$O$_3$ compositions produce ZT temperature dependences with peak values around 0.2 above 900 K (Fig. 4b) which are comparable with the values obtained for Sr$_{0.5}$Dy$_{0.5}$TiO$_3$-5 in this study. The increase in $\sigma$ and reduction of $\kappa$ in the intermediate temperature range (400-800 K) for PGE La$_{0.5}$Na$_{0.5}$Ti$_{1-x}$Nb$_x$O$_3$ results in an improved ZT over SDTO up to 550 K. As a result, the average energy-conversion efficiencies ($\varepsilon_{\text{ave}}$, Equation 3) of the new PGE La$_{0.5}$Na$_{0.5}$Ti$_{1-x}$Nb$_x$O$_3$ materials (1.93%) are slightly higher than Sr$_{0.5}$Dy$_{0.5}$TiO$_3$-5 (1.91%):

$$
\varepsilon_{\text{ave}} = \frac{T_H-T_C}{T_H} \frac{\varepsilon_{\text{eff}}}{\sigma + \kappa} \frac{T_H}{T_H + T_C} (1 - \frac{T_R}{T_H})
$$

where $T_H$ and $T_C$ are the hot- and cold-end temperatures of the material, and are set to 700 and 350 K, respectively, temperatures which are applicable to automotive exhaust waste heat recovery.16

**Conclusions**

Phonon engineering of SrTiO$_3$ by complete substitution of the A site cations to enhance charge and mass disorder in La$_{0.5}$Na$_{0.5}$TiO$_3$ produces an 80% reduction of the thermal conductivity which has the temperature dependence of a PG. The glass-like thermal conductivity is retained upon B site substitution with the donor Nb, which enhances electronic transport to afford a PGE oxide thermoelectric. By fixing the disordered A site composition to achieve the glassy $\kappa$, it is possible to independently tune the carrier concentration via B site chemistry analogous to that established in STO itself, allowing decoupling of the usually strongly covarying thermal and electronic transport properties. It is worthwhile to note that such substitutions may control thermal conductivity across a range of current thermoelectrics, and should be considered as a route to improving ZT further.

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**Notes and references**