Improved High-Temperature Thermoelectric Properties of Dual-Doped Ca$_3$Co$_4$O$_9$

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**ABSTRACT:** Layered structured Ca$_3$Co$_4$O$_9$ has displayed great potential for thermoelectric (TE) renewable energy applications, as it is nontoxic and contains abundantly available constituent elements. In this work, we study the crystal structure and high-temperature TE properties of Ca$_{3-y}$Na$_y$Co$_{2+y}$Mo$_y$O$_9$ (0 ≤ $y$ ≤ 0.10) polycrystalline materials. Powder X-ray diffraction (XRD) analysis shows that all samples are single-phase samples and without any noticeable amount of the secondary phase. X-ray photoelectron spectroscopic (XPS) measurements depict the presence of a mixture of Co$^{3+}$ and Co$^{4+}$ valence states in these materials. The Seebeck coefficient (S) of dual-doped materials is significantly enhanced, and electrical resistivities ($\rho$) and thermal conductivities ($\kappa$) are decreased compared to the pristine compound. The maximum thermoelectric power factor (PF = $S^2/\rho$) and dimensionless figure of merit ($zT$) obtained for the $y = 0.025$ sample at 1000 K temperature are $\sim 3.2 \times 10^{-4}$ W m$^{-1}$ K$^{-2}$ and 0.27, respectively. The $zT$ value for Ca$_{2.95}$Na$_{0.05}$Co$_{3.975}$Mo$_{0.025}$O$_9$ is about 2.5 times higher than that of the parent Ca$_3$Co$_4$O$_9$ compound. These results demonstrate that dual doping of Na and Mo cations is a promising strategy for improving the high-temperature thermoelectric properties of Ca$_3$Co$_4$O$_9$.

1. **INTRODUCTION**

Environmental issues associated with the use of fossil fuels and continuously rising demand of energy have challenged the scientific community to search for alternative energy sources for the future energy mix. Thermoelectric (TE) materials offer an eco-friendly sustainable source of energy and a promising method for scavenging the unused heat/thermal energy from industrial procedures, vehicle emission, and incinerator plants, converting it into electric power. Conventional TE materials require inexpensive and effective TE technologies for large-scale production, which are critically dependent on the TE properties of candidate materials. For efficiently transforming waste heat into electrical power, we need to design new thermoelectric materials with a high value of the dimensionless thermoelectric figure of merit ($zT$) parameter, which is defined as

$$zT = \frac{S^2 \rho}{\kappa} = \frac{\text{PF}}{\kappa}$$

(1)

where $S$ (V/K) is the Seebeck coefficient, $\rho$ (Ω m) is the electrical resistivity, $\kappa$ (W m$^{-1}$ K$^{-2}$) is the thermal conductivity, PF (W m$^{-1}$ K$^{-2}$) is the power factor, and $T$ (K) is the absolute temperature.

The essential prerequisite for practical TE applications is the value of $zT \geq 1$, which can be obtained by increasing the power factor ($\text{PF} = S^2/\rho$) and decreasing the thermal conductivity. Conventional TE alloys such as PbTe and Bi$_2$Te$_3$ have $zT \geq 1$, but they are poisonous and unstable at high operating temperatures. However, transition metal oxides usually show stability at high operating temperatures and can be manufactured from nonpoisonous and low-cost precursors with lower production cost and can be joined with nonoxide materials in TE devices to increase their efficiency rate. Therefore, noteworthy research endeavors have been dedicated recently to the improvement of high-temperature TE oxide materials for renewable green energy technologies. Presently, SrTiO$_3$ is considered as an interesting $n$-type material for TE applications due to its inherently high Seebeck coefficient and consequently large PF value, whereas layered structured oxides such as Na$_x$CoO$_2$, Ca$_3$Co$_4$O$_9$, Bi$_2$Sr$_2$Co$_2$O$_8$, and BiCuSeO are $p$-type materials and are of importance owing to their inherently lower thermal conductivities. Though their thermoelectric properties can be enhanced further through band engineering or element substitution, there are some intrinsic restrictions. For example, BiCuSeO...
oxidizes at a temperature of 573 K and then decomposes at a temperature of 773 K; these limitations must be resolved before using any of these materials for practical high-temperature TE applications.\textsuperscript{13} The practical advantages of using the Na\textsubscript{x}Co\textsubscript{2}O\textsubscript{4} material are hindered by its hygroscopic nature in air and the volatilite nature of Na at high operating temperatures.\textsuperscript{10} In comparison, Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9} (denoted C-349 in this article) is generally considered as a promising p-type oxide material and it has high chemical and thermal stabilities in air at temperatures up to 1199 K. The best values of $zT$ reported so far are around 0.87 for a single crystal of Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9} (973 K),\textsuperscript{14} 0.74 at 800 K for Ca\textsubscript{3−x}Tb\textsubscript{x}Co\textsubscript{4}O\textsubscript{9} (x = 0.5),\textsuperscript{15} and 0.64 for heavily doped Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9−δ} (1073 K) polycrystalline samples with metallic nano-inclusions.\textsuperscript{16}

The Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9−δ} compound can also be represented as [Ca\textsubscript{2}Co\textsubscript{O\textsubscript{2}}\textsubscript{1/2}][Co\textsubscript{O\textsubscript{2}}\textsubscript{1/2}]\textsubscript{1.61} and it has an intricate incommensurate monoclinic crystal structure with (X2/m(2b0)8) superspace group symmetry. The crystal structure of the C-349 system and high thermoelectric performance of this material are associated with its layered structure,\textsuperscript{17} which comprises two subsystems: a Ca\textsubscript{2}Co\textsubscript{O\textsubscript{2}} rocksalt (RS)-type [subsystem 1] layer packed in between two hexagonal CdI\textsubscript{2} (H)-type CoO\textsubscript{2} layers [subsystem 2].\textsuperscript{17} These two subsystems arrange alternately alongside the $c$-axis and have similar $a$ and $c$ lattice parameters for both layers. The incompatibility of these two unit cells results from different unit cell lattice parameters along the $b$-axis, i.e., $b_1$ (subsystem 1) and $b_2$ (subsystem 2) with a $b_1$($RS$)/$b_2$($H$) ratio of $\sim$1.61. The CoO\textsubscript{2} ($H$) layer is conducting and the Ca\textsubscript{2}CoO\textsubscript{3} (RS) layer is insulating and considered to be a charge reservoir.\textsuperscript{18}

Besides interesting TE properties, the misfit layered structure C-349 cobaltite material has become a subject of promising research in many other areas due to its interesting physical properties such as ferromagnetic transition, spin density wave transition, and spin–lattice coupling.\textsuperscript{19} These properties are associated with its strong electronic correlation nature and complicated crystal structure and suggest its possible uses in solid oxide fuel cells (SOFC), magnetoresistance modules, and water splitting.\textsuperscript{20−22} The bulk C-349 polycrystalline form has a smaller value of $zT$ than a single crystal, and consequently, it is still not used in thermoelectric devices for TE renewable energy technologies.\textsuperscript{23} Several research efforts have been made over the last two decades to improve the thermoelectric performance of C-349 materials using various manufacturing methods such as hot-pressing (HP), cold high-pressure pressing (CPP), magnetic alignment (MA), templated grain growth (TGG), spark plasma sintering (SPS), sol–gel-based electrospinning, and the auto-combustion production method with the SPS process.\textsuperscript{24−30} Kanas et al. reported the influence of processing including solid-state sintering, SPS, and postcalcination on the stability, microstructure, and TE properties of Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9−δ} materials. They obtained a phase-pure C-349 material from starting precursors to the final dense product in a single step with a $zT$ value of around 0.11 at 800 °C using a new postcalcination method.\textsuperscript{31} The work of Miyazawa et al. reported hybrid microwave sintering of Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9} TE materials, which increased the densification and grain texturing of bulk Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9} ceramics, resulting in a prominent increase in electrical conductivity, while the Seebeck coefficient and thermal conductivities were reported to remain unaffected by microstructural variations.\textsuperscript{32} Song et al. used the nanostructuring approach to increase the TE performance of Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9} materials through nanoscale platelets and Ag inclusions. They observed that the nano-scale texturing method improves thermoelectric performance with a significant decrease in thermal conductivity.\textsuperscript{33} These fabrication and processing procedures have certain drawbacks such as comparatively extensive processing time, high expenses linked with the appliances and reliance of TE properties on growth, and texturing speed. However, there is a possibility to enhance and improve the TE performance of Ca\textsubscript{3}Co\textsubscript{4}O\textsubscript{9} polycrystalline materials through the chemical substitution approach with metal ions at both Ca and Co sites, which can actually modify the carrier concentration and thus improve the electrical transport and thermal conductivities of these materials. The previous research work reported include the partial replacement of Na, Nd, Bi, Y, Ag, Sr, Pb, etc., at the Ca site,\textsuperscript{27,24−40} and these cation substitutions modify the carrier concentration ($n$) without fluctuating the band structure of the material. The substitution of Mn, Fe, Cu, Ti, Cr, Ga, Mo, In, etc., at the Co site\textsuperscript{41−46} causes prominent variations in the band structure and electrical transport properties of the C-349 system. Substitution of Na\textsuperscript{+} at the Ca site has previously been published, which increases the carrier concentrations and thus results in an increase in electrical conductivity values and consequently an enhancement of the thermoelectric power factor of $\sim$5.5 $\times$ 10$^{-4}$ W m$^{-1}$ K$^{-2}$ at a temperature of 1000 K. However, thermal conductivities of these materials are quite high, i.e., around 4.0 W m$^{-1}$ K$^{-1}$, which has a detrimental effect on $zT$ values.\textsuperscript{27,44} In the case of 4d and 5d transition metal cations with higher valences, doping in C-349-based materials displayed much lower thermal conductivities with reasonably good $zT$ values.\textsuperscript{47,48} However, there are only a few examples in the literature on simultaneous substitution of two different metal ions at both Ca and Co sites in the C-349 system with noteworthy advances in thermoelectric properties with $zT$ values ($\sim$0.20 to 0.25).\textsuperscript{48−50}

We reported previously that dual doping of Na and W in the C-349 system significantly improves the thermoelectric properties of these oxide materials.\textsuperscript{49} This inspired us to synthesize Ca$_{3−2y}$Na$_y$Co$_{4−x}$Mo$_x$O$_{9}$ (0 $\leq$ $y$ $\leq$ 0.10) polycrystalline samples with the traditional solid-state chemistry process and thoroughly investigate the crystal structure and high-temperature thermoelectric properties of Na and Mo dual-doped materials. We anticipated that this dual doping would simultaneously improve the electrical conductivity and Seebeck coefficient values of these studied polycrystalline materials. Thus, the dual doping approach would possibly result in the improvement of the figure of merit of the C-349 system. The thermoelectric properties of these materials may further be enhanced in the future using alternate manufacturing procedures and structure modification techniques.

2. RESULTS AND DISCUSSION

2.1. Structural Study. The room-temperature crystal structures of Ca$_{3−2y}$Na$_y$Co$_{4−x}$Mo$_x$O$_{9}$ (0 $\leq$ $y$ $\leq$ 0.10) polycrystalline materials were inspected by collecting powder X-ray diffraction (XRD) data. The XRD patterns (Figure 1) show that all samples are phase pure, without any noticeable quantity of the secondary phase and/or impurity. All XRD reflection peaks match well with the previously published patterns can be indexed with the traditional monoclinic crystal structure of the C-349 material and diffraction patterns can be indexed with the reported standard (JCPDS card no. 21-139).\textsuperscript{11,12,45} The zoomed-in (0040) diffraction peaks of all investigated materials are displayed in the inset of Figure 1 to elucidate the effect of
Na and Mo dual doping. It is observed that diffraction peaks shift/move toward lower 2θ values with increasing doping content (y). The XRD data were Rietveld-analyzed in the monoclinic crystal structure within [X2/m(060)0] superspace group symmetry using JANA2006 software. The refined crystallographic structural parameters are listed in Table 1. It can be seen from Table 1 that the lattice parameters a, b1, and c and unit cell volumes (V1 and V2) all increase with increasing Na, Mo dual doping content (y), which is in agreement with the experimental shifting of XRD peaks to a lower 2θ values. However, the b2 values reduce with increasing dual doping contents, which depicts that there is an increase of crystallographic structural distortion in the C-349 material. This trend in the unit cell lattice parameters with doping contents (y) is in agreement with the observation that Shannon ionic radii of Na+ [1.02 Å] and MoO43− [0.59 Å] ions are larger than those of the corresponding Ca2+ [1.0 Å] and Co3+/Co4+ [0.53 Å] cations within (VI) coordination number, respectively. To investigate the microdimensional anisotropic behavior in dual-doped C-349 materials, scanning electron microscopic (SEM) morphological images (Figure 2) were investigated in both parallel ([|p]) and perpendicular (⊥p) directions of the pellet pressure axis. The grain morphological features in both parallel ([|p]) and perpendicular (⊥p) directions of the applied pressure axis are almost similar, which suggests that there are no or insignificant anisotropic features at the micrometer range. Anisotropy was also observed by taking XRD data for the pellet, bar, and powder forms of all samples, and no variation was detected in peak intensities. The SEM micrographs reveal a plate-like morphology of crystal grains, which is a specific nature of layered cobaltite materials, which are synthesized by the traditional solid-state chemistry route. A detailed examination of SEM images depicts that the average crystal grain size increases from y = 0.0 (0.83 μm) to y = 0.10 (4.10 μm) samples with an increase in doping amounts (y), which is in agreement with the lower melting point (m.p.) of precursor sodium molybdate dehydrate (Na2MoO4·2H2O) and expectedly higher diffusion rates during the annealing process and thus formation of larger grain sizes. The measured bulk density values were also measured and observed in the range (~86 to 92%) of the theoretical density for the studied samples, as listed in Table 1. The binding energies (BEs) of Co 2p and Mo 3d subshells for selected compositions were investigated with the high-resolution X-ray photoelectron spectroscopy (XPS) technique, as displayed in Figure 3. As reported elsewhere, the XPS spectrum of Co 2p divides into two peaks of Co 2p3/2 and 2p1/2 with an intensity ratio of ~1:2 due to the spin–orbital interactions.

![Figure 1](https://pubs.acs.org/acsomega/6581). X-ray diffraction (XRD) data of Ca3−x+Na2xNa2MoO4−δ (0 ≤ y ≤ 0.10) samples. The inset shows the shift of (0040) reflections.

| Composition | y = 0.0 | y = 0.025 | y = 0.05 | y = 0.10 |
|-------------|---------|-----------|----------|----------|
| a (Å)       | 4.8229(12) | 4.8239(10) | 4.8258(10) | 4.8272(7) |
| b1 (Å)      | 4.5453(17) | 4.5560(16) | 4.5620(9)  | 4.5640(12)|
| b2 (Å)      | 2.8215(11) | 2.8200(5)  | 2.8169(6)  | 2.8170(3) |
| c (Å)       | 10.8327(12) | 10.8359(16) | 10.8370(18) | 10.8390(4) |
| (Vd1) Å3    | 234.7(4)  | 236.9(3)   | 237.1(3)   | 238.7(4)  |
| (Vd2) Å3    | 145.2(5)  | 147.2(4)   | 148.3(3)   | 149.7(2)  |
| CoO4 layer (Co–O) | 1.8210 | 1.8123 | 1.8416 | 1.8670 |
| RS layer (CO–O) | 1.7559 | 1.7428 | 1.7828 | 1.8063 |
| Average grain size (μm) | 0.83 (±0.002) | 3.25 (±0.08) | 3.80 (±0.05) | 4.10 (±0.06) |
| Density (g cm−3) | 3.801 (±0.02) | 4.01 (±0.042) | 3.89 (±0.036) | 3.87 (±0.089) |
| Theoretical density (g cm−3) | 4.37 | 4.35 | 4.34 | 4.34 |
| Relative density (%) | 86.27 | 92.18 | 89.63 | 89.20 |
| Carrier conc. ×1035 | 5.09 | 6.39 | 5.23 | 5.22 |
| Carrier mob. | 1.02 | 0.963 | 0.940 |
| \(\rho_{\text{100K}} \times 10^{-6} \) (Ω m) | 23.98 | 10.57 | 12.82 | 14.02 |
| \(E_{\text{hop}}\) (eV) | 0.042 | 0.028 | 0.029 | 0.030 |
| \(S_{\text{T=100K}}\) (μV K−1) | 174.99 | 227.32 | 231.51 | 234.21 |
| \(P_{\text{T=100K}}\) (W m−1 K−2) | 1.27 | 3.22 | 2.87 | 2.75 |
| \(k_{\text{T=100K}}\) (W m−1 K−1) | 1.367 | 1.188 | 1.297 | 1.419 |
| \(\varepsilon_{\text{T=100K}}\) | 0.093 | 0.27 | 0.22 | 0.19 |

Table 1. Crystallographic/Structural Parameters, Average Grain Size, Bulk Densities, Carrier Mobility (\(\mu_{300K}\)), Carrier Concentration (n_{300K}), Activation Energies (\(E_{\text{hop}}\)), and Other Key Thermoelectric Parameters Are Summarized
The graphical shapes of both Co 2p1/2 and Co 2p3/2 are identical to the previously published results in the literature. Shake-up satellite peaks are also detected at higher BEs compared to the Co 2p1/2 and Co 2p3/2 main peaks due to metal-to-ligand charge transfer processes. The Co 2p3/2 peaks are detected at 779.69 and 780.47 eV for \( y = 0.0 \) and \( y = 0.05 \) compositions, respectively. This indicates that BEs increase with Na and Mo dual doping. We can consider three different oxidation states of Co ions, i.e., Co\(^{2+}\), Co\(^{3+}\), and Co\(^{4+}\), for the studied samples and perform a careful analysis of the XPS data. We believe that the average oxidation state of cobalt ions is most probably between 3+ and 4+, which is consistent with the reported results in the literature. The higher BE for the \( y = 0.05 \) sample indicates that the relative amount of Co\(^{4+}\) ions increases with an increase in doping.

Figure 3 also shows the characteristic Mo 3d spectrum for the \( y = 0.05 \) sample with two main peaks, i.e., Mo 3d\(_{3/2}\) and Mo 3d\(_{5/2}\). The observed peaks are fitted well by assigning them to Mo\(^{6+}\) cations, which is in agreement with the reported results in the literature. XPS analysis is also used to investigate the composition of \( y = 0.0, 0.05, \) and 0.10 samples. Elemental compositions are extracted from the survey spectra of native elements only and the values are an average of three measurements on different surface locations, as presented in Table 2. The compositions obtained from XPS versus expected compositions are also listed in Table 2. The XPS extracted values have been normalized to the expected Co contents. The expected compositions are close to XPS analysis, which shows that Na and Mo are present in the crystal structure.

### 2.2. Electrical Transport Properties

Figure 4a shows temperature-dependent electrical resistivity \( (\rho) \) for \( \text{Ca}_3_{-2y}\text{Na}_y\text{Co}_{4-y}\text{Mo}_y\text{O}_9 \ (0 \leq y \leq 0.10) \) samples. The \( \rho(T) \) initially decreases from room temperature to 500 K for the \( y = 0.0 \) sample with semiconducting behavior \( (d\rho/dT < 0) \) and then increases thereafter from 600 K temperature onward with...
around 10.5 mΩ cm, which is comparable to the highest reported value for the parent C-349 compound synthesized by other methods. For instance, the reported values of electrical resistivity for cobaltite compounds synthesized by solution-based and spark plasma sintering (SPS) processes are around 16 mΩ cm\(^2\) and in the range of 14–19 mΩ cm,\(^{63}\) respectively. In our case, the value of \(\rho\) for the \(y = 0.0\) sample is greater than the previously reported values, which suggests that there is still room for improvement by making more compact/dense samples using other manufacturing processes.

A small polaron hopping model was used to describe the electrical conduction mechanism at higher temperatures for the synthesized materials, which is given by eq 2\(^{54}\)

\[
\rho(T) = \rho_0 T \exp\left(\frac{E_{\text{hop}}}{k_B T}\right)
\]

where \(\rho_0\) is the residual resistivity, \(k_B\) is Boltzmann’s constant, \(T\) is the absolute temperature, and \(E_{\text{hop}}\) is the activation energy of small polaron hopping for electrical conduction. The linear fitting of \(\ln(\rho/T)\) versus \(1/T\) plots, as shown in Figure 4b, suggests that the “small polaron hopping conduction model” applies well to \(\rho\) data for all samples in the given temperature range. The slope of the straight line \((E_{\text{hop}}/k_B)\) was used to determine the activation energies of all studied materials and the obtained values of \(E_{\text{hop}}\) are listed in Table 1. The \(E_{\text{hop}}\) calculated for the pristine C-349 compound is similar to the reported value in the literature for this cobaltite.\(^{55}\) However, the values of \(E_{\text{hop}}\) for Na and Mo dual-doped samples are smaller than the parent C-349 compound owing to the increased carrier concentrations \((n)\) and carrier mobilities \((\mu)\), as presented in Figure 5. This shows that dual doping of Na and Mo results in the decrease of the energy barrier for carrier hopping from the top of the valance band to the bottom of the conduction band in these polycrystalline materials. As reported elsewhere, the ratio of Co\(^{3+}/Co^{4+}\) ions directly affects the hopping distance in these cobaltite compounds, as the carrier hopping takes place between Co\(^{3+}\) and Co\(^{4+}\) ions in the CoO\(_2\) subsystem.\(^{66}\) The higher doping levels are expected to increase the relative concentration of Co\(^{3+}\) cations as we substitute Mo\(^{6+}\) cations (high valence) at the Co sites, and therefore, hopping distance and consequently the values of \(E_{\text{hop}}\) are likely...
The room-temperature carrier concentration \( n_{300K} \) and carrier mobility \( \mu_{300K} \) measured in the van der Pauw geometry using the Hall effect (see the Experimental Details) as a function of dual doping content \( y \) are displayed in Figure 5. The \( y = 0.025 \) sample shows the highest values of \( n_{300K} \) and \( \mu_{300K} \) which is consistent with its lowest \( \rho_{300K} \) value out of all of the studied materials. We anticipate that as the concentration of Mo\(^{6+}\) cations in the CoO\(_2\) subsystem increases with an increase in dual doping, the structural distortions and/or creation of oxygen (O) vacancies in the lattice structure also increase. As a result, the absolute values of \( \rho_{300K} \) also start to increase when the doping content is further increased. The carrier mobilities follow the trend of carrier concentrations and their values decrease with an increase in doping after the \( y = 0.025 \) sample.

The competing effects of Na\(^{+}\) (hole-like doping) and Mo\(^{6+}\) (electron-like doping) cations on carrier mobility and carrier concentration do not support \( \rho_{300K} \) values to increase sharply with doping. Here, we have used the equation \( 1/\rho = ne\mu \) to relate the electrical resistivity with carrier concentration and carrier mobility. The structural distortions and the presence of small amounts of impurities may also play an important role in increasing the electrical resistivities of materials with an increase in doping content \( y \).

The temperature-dependent Seebeck coefficient \( S \) of Ca\(_3\)-Na\(_2\)-Co\(_4\)-MoO\(_9\) and Ag-doped (228 \( \mu \)V K\(^{-1}\)) samples is presented in Figure 6a. The positive values of the Seebeck coefficient \( S \) indicate that holes are the majority charge carriers in all these samples. It is further observed that the values of \( S \) increase with an increase in temperature, in the whole temperature range, for all studied samples. In addition, the Seebeck coefficient \( S \) values increase monotonically with the increasing content of dual doping \( y \), as shown in the inset of Figure 6a. The maximum Seebeck coefficient achieved in this work is \( \sim 234 \) \( \mu \)V K\(^{-1}\) at a temperature of 1000 K for the \( y = 0.10 \) sample, which is comparable to or slightly better than the published results for Na-substituted (187 \( \mu \)V K\(^{-1}\))\(^{34}\), Na, W-dual-doped (216 \( \mu \)V K\(^{-1}\))\(^{38}\), and La, Fe-dual-doped (227,63 \( \mu \)V K\(^{-1}\))\(^{39}\) C-349 materials at the same temperature. As discussed earlier, the doping of Na\(^+\) cations at Ca\(^{2+}\) cation sites should increase the hole-type carrier concentrations, as it will favor higher oxidation states for the transition metal cations, provided that the oxygen content remains the same. However, the substitution of Mo\(^{6+}\) cations at the Co sites should increase the relative concentration of Co\(^{3+}\) cations at the expense of Co\(^{4+}\) cations, and thus, it will decrease the hole carrier concentrations. The competing effects of dual doping on the electronic properties and the structural distortions induced by the cation size mismatch result in an increase of the carrier concentrations for the \( y = 0.025 \) sample, as it has the largest measured values of carrier concentrations and carrier mobilities (Table 1), and thereafter, the carrier concentration and carrier mobility values \( n_{300K} \) and \( \mu_{300K} \) start decreasing with further doping. This is in agreement with the previously reported results of Seebeck coefficients for doped C-349 materials.\(^{34,37}\) The relationship among the carrier concentrations \( n \), carrier mobilities \( \mu \), and Seebeck coefficients is given by the following Motts formula (devised from the Sommerfeld expansion)\(^{64}\)

\[
S(T) = \frac{\pi^2 k_B^2 T}{3e} \left[ \frac{\partial \ln(\sigma(\varepsilon))}{\partial \varepsilon} \right]_{\varepsilon = \varepsilon_f}
\]  

(3)

By substituting \( \sigma = en\mu(\varepsilon) \) in eq 3, we obtain

\[
S(T) = C_e \frac{n}{n} + \frac{\pi^2 k_B^2 T}{3e} \left[ \frac{\partial \ln(\mu(\varepsilon))}{\partial \varepsilon} \right]_{\varepsilon = \varepsilon_f}
\]

(4)

Here, \( C_e \) is given by

\[
C_e = (\pi^2 k_B^2 T/3e) \Psi(\varepsilon)
\]

(5)

where \( n \) is the carrier concentration, \( \mu(\varepsilon) \) is the energy-correlated carrier mobility, \( k_B \) is Boltzmann’s constant, \( C_e \) is the electrical specific heat, and \( \Psi(\varepsilon) \) is the density of states (DOSs). In general, the following possible interrelated justifications for the enhanced Seebeck coefficients of thermoelectric materials are presented: (i) eq 4 contains two terms...
and according to Drude’s model, the first term \( \frac{\xi}{n} \) is more dominant.\(^{65}\) As the carrier concentrations \( (n) \) decrease with an increase in dual doping content, the Seebeck coefficient values increase with doping. However, the electrical specific heat \( (C_v) \) and the second term of eq 4 are more dominant for the \( y = 0.0 \) sample, and therefore, it has a lower value of the Seebeck coefficient. Wang et al. reported that doping of iron (Fe) at the Co sites increases carrier concentration \( (n) \) and the electrical specific heat \( (C_v) \), but the effect of the \( C_v \) parameter is larger than that of the carrier concentration \( (n) \), and thus, it results in an increase of the Seebeck coefficient with doping.\(^{66}\) (ii) it has been reported earlier that \( \mu(e) \) changes with doping\(^{14,58}\) and the slope of DOS at the Fermi energy level is the key contributing factor to the second part of eq 4; and (iii) the partial substitution of Co\(^{3+} /\)Co\(^{4+}\) cations with Mo\(^{6+}\) cations decreases the hole carrier concentration, which results in an increase of the Seebeck coefficient. However, a more detailed analysis is required to exactly understand and explain the observed trends in the carrier concentration, carrier mobility, and Seebeck coefficients of these cobaltite materials.

Pisarenko’s relation for bulk-degenerated semiconducting materials is given by eq \(^{67}\)

\[
|S| = \frac{8\pi^2k_B^2T^3}{3\hbar^2m}\left(\frac{\pi}{3n}\right)^{2/3} 
\]

where, \( k_B \), \( T \), \( h \), and \( m^* \) are the Boltzman’s constant, absolute temperature, Plank’s constant, electrical unit charge, and the effective mass of polarons/carriers, respectively. The obtained value of \( m^*/m \) from the plot of room-temperature \( S \) versus \( n^{-2/3} \) is approximately equal to 0.9 for all samples, as presented in the inset of Figure 6b.

Using the measured carrier concentrations and the calculated \( m^* \) value, “a simple parabolic-band model” can be applied as given by the following equations\(^{67}\)

\[
F_{1/2}(\xi) = \int_0^\infty \frac{x^2dx}{1 + \exp(x - \xi)} 
\]

(7)

\[
S = -\frac{k_B}{q}\left\{\frac{(2 + \lambda)F_{1/2} + 1}{(1 + \lambda)F_{1/2}} - \xi\right\} 
\]

(8)

\[
n = 4\pi\left\{\frac{2m^*k_B^2T}{h^2}\right\}^{2/3}F_{1/2} \]

(9)

where \( F_{1/2}(\xi) \), \( \xi \), and \( \lambda \) are the Fermi integral, reduced electrochemical potential, and scattering factors, respectively. The value of \( \lambda \) can be associated with an (i) acoustic phonon scattering mechanism, (ii) optical phonon scattering mechanism, and (iii) ionized impurity scattering mechanism.\(^{67}\) The estimated room-temperature Seebeck coefficient \( S \) values as a function of carrier concentration \( (n) \) are displayed in Figure 6b. These dissimilar scattering mechanisms are represented by three different lines in the plot. The estimated and measured values of \( S \) are modeled well when \( \lambda = \text{mechanism (i)} \), which suggests that the acoustic phonon scattering is the main controlling scattering mechanism for all studied samples. The Seebeck coefficient and electrical resistivity data were used to estimate the thermoelectric power factor (PF = \( S^2/\rho \)) of all samples. Figure 7 shows the temperature-dependent PF for dual-doped C-349-based materials. It is evident that PF increases with an increase in temperature for all of the investigated compositions, mainly due to an increase in the Seebeck coefficient values with temperature. On the other hand, PF values initially increase with dual doping, with the maximum value for the \( y = 0.025 \) sample, and then decrease as dual doping is increased further. Moreover, all dual-doped compositions have considerably larger PF values than the pristine C-349 material. The observed power factor of \( \sim 3.2 \times 10^{-4} \) W m\(^{-1}\) K\(^{-2}\) at 1000 K for the \( y = 0.025 \) sample is \( \sim 2.5 \) times greater than that of the parent compound. Table 3 illustrates that the obtained PF values in this work are comparable to or better than the previously published PF values of C-349-based materials.

2.2.1. Thermal Conductivity. Figure 8a shows temperature-dependent total thermal conductivity (\( \kappa_{\text{Tot.}} \)) for Ca\(_{3-2y}\)Na\(_y\)Co\(_{1-y}\)Mo\(_6\)O\(_{19}\) (0 \( \leq y \leq 0.10 \)) samples. Total thermal conductivity for all samples decreases gradually with an increase in temperature in the given temperature range. The measured \( \kappa_{\text{Tot.}} \) at a temperature of 1000 K is around 1.36 W m\(^{-1}\) K\(^{-1}\) for the \( y = 0.0 \) sample and it reduces to \( \sim 1.18 \) W m\(^{-1}\) K\(^{-1}\) for the \( y = 0.025 \) sample at 1000 K. The \( \kappa_{\text{Tot.}} \) increases again with a further increase in dual doping and its value for the \( y = 0.10 \) sample is slightly higher than that for the pure C-349 sample (Figure 8b). To understand the observed variation in thermal conductivities, we have considered the individual contributions of lattice (\( \kappa_{\text{Lat.}} \)) and electrical (\( \kappa_{\text{el.}} \)) thermal conductivities. Figure 8c shows \( \kappa_{\text{Lat.}} \) values, which are obtained experimentally from the measured data of electrical resistivities using the “Wiedemann–Franz law” \( \kappa_{\text{el.}} = LT/\rho \), where \( L \) is Lorentz’s number and its value is around 2.44 \( \times 10^{-8} \) W K\(^{-2}\) for free electrons.\(^{2} \) The values of the lattice part of thermal conductivity were determined using the relation \( \kappa_{\text{Lat.}} = \kappa_{\text{Tot.}} - \kappa_{\text{el.}} \) and these are presented in Figure 8d. It is obvious from the plot that the contribution of \( \kappa_{\text{Lat.}} \) to \( \kappa_{\text{Tot.}} \) is quite small and that \( \kappa_{\text{Lat.}} \) is the major contributing factor to the total thermal conductivities in these samples. We can therefore conclude that the observed changes in \( \kappa_{\text{Tot.}} \) are the direct result of variations in \( \kappa_{\text{Lat.}} \) with an increase of dual doping content (\( y \)).\(^{41} \) We anticipate that dual doping of Na\(^+\) and Mo\(^{6+}\) cations with higher ionic radii than the corresponding Ca\(^{2+}\) and Co\(^{3+}/\)Co\(^{4+}\) cations will cause distortions in the crystal structure, which will ultimately result in an increase of phonon scattering and
therefore a decrease in the lattice contribution to thermal conductivity. On the other hand, an increase in carrier concentration and carrier mobility will increase the electrical contribution to total thermal conductivity. Moreover, it is generally known that substitution of heavy atoms leads to lower lattice thermal conductivity ($\kappa_{\text{Lat.}}$) because of the small group velocity of phonons and prominent Umklapp phonon−phonon scattering. However, the trend of ($\kappa_{\text{Lat.}}$) was opposite to the prediction for the $y = 0.05$ and $0.1$ samples. These changes in thermal conductivity can be explained by considering the relationship $\kappa_{\text{overall}} = \kappa_{\text{CoO}_2} + \kappa_{\text{RS}}$, where $\kappa_{\text{CoO}_2}$ and $\kappa_{\text{RS}}$ are the partial thermal conductivities of the CoO$_2$ and RS layers, respectively. This definition of partial thermal conductivity enables the analysis of the mechanisms of thermal conduction and control of thermal conductivity as a result of a more in-depth understanding of microscopic heat transport.

The Co−O bond lengths are obtained for both CoO$_2$ and RS layers from the Rietveld analysis of XRD data (see Table 1). The bond length value decreased for the $y = 0.025$ sample and then increased for $y = 0.05$ and $0.10$ samples. We can also expect small microstructural variations among doped samples as a result of the grinding, pelletizing, and sintering processes.

The most important conclusion is that the overall thermoelectric properties of doped samples have significantly improved despite subtle variations in transport properties from sample to sample.

2.2.2. Thermoelectric Figure of Merit, $zT$. Figure 9 displays temperature-dependent figure of merit ($zT = S^2/\kappa\rho$) for Ca$_{3-2y}$Na$_y$Co$_{4-y}$Mo$_y$O$_9$ ($0 \leq y \leq 0.10$) materials. It is evident from the plot that $zT$ values are considerably higher for all dual-doped samples compared to the pristine C-349 compound. Moreover, the dual doping of Na and Mo in the C-349 system appears to be a better strategy for improving the $zT$ values than single-ion substitution of either Na$^{27}$ or Mo$^{45}$. Among all of the investigated samples, the $y = 0.025$ sample has the highest $zT$ value of $\sim 0.27$ at 1000 K, which is about 2.5 times higher than the $zT$ value of the undoped C-349 compound. This improvement in the $zT$ value at high temperatures is due to simultaneous enhancement of electrical conductivity and Seebeck coefficient and the decrease of the thermal conductivity of this sample.

In a wider context, the $zT$ value of the Ca$_{2.95}$Na$_{0.05}$Co$_{3.975}$Mo$_{0.025}$O$_9$ composition is comparable to or better than most of the results published in the literature (see Table 3. Thermoelectric Power Factor (PF) and Figure of Merit ($zT$) of Different Cobaltite Materials).

| materials              | $T$/K | measuring direction | PF ($\sigma \cdot S^2$) $\times 10^{-4}$ /W m$^{-1}$ K$^{-2}$ | $zT$ | ref |
|------------------------|-------|---------------------|-------------------------------------------------------------|------|-----|
| Ca$_{2.95}$Ag$_{0.05}$Co$_{4.05}$O$_9$ | 973   |                     |                                                             |      | 19  |
| Ca$_{3.00}$Na$_{0.05}$Co$_{3.95}$W$_{0.05}$O$_9$ | 1000  | in-plane            | 4.50                                                          | 0.23 | 19  |
| Ca$_{3.00}$Ga$_{0.05}$Co$_{3.95}$O$_9$ | 973   |                     | 2.71                                                          | 0.21 | 48  |
| Ca$_{3.00}$Bi$_{0.05}$Co$_{3.95}$O$_9$ | 1073  |                     | 3.20                                                          |      | 68  |
| (Ca$_{3.00}$Bi$_{0.05}$)$_2$Co$_{4.05}$O$_9$ | 973   | in-plane            | 3.10                                                          |      | 69  |
| (Ca$_{3.00}$Bi$_{0.05}$)$_2$Co$_{4.05}$O$_9$ | 1000  |                     | 3.95                                                          | 0.25 | 70  |
| Ca$_{3.00}$Ga$_{1.05}$Co$_{3.95}$O$_9$ | 973   |                     |                                                               | 0.22 | 39  |
| Ca$_{3.00}$Ga$_{1.05}$Co$_{3.95}$O$_9$ | 1000  |                     | 3.56                                                          | 0.26 | 44  |
| Ca$_{3.00}$Co$_{3.95}$Ga$_{0.05}$O$_9$ | 773   |                     | 3.22                                                          | 0.20 | 72  |
| Ca$_{3.00}$Co$_{3.95}$Ga$_{0.05}$O$_9$ | 1073  | in-plane            | 4.57                                                          | 0.23 | 50  |
| Ca$_{3.00}$Co$_{3.95}$Fe$_{0.05}$O$_9$ | 1073  | in-plane            | 4.57                                                          |       | 73  |
| Ca$_{3.00}$Co$_{3.95}$Fe$_{0.05}$O$_9$ | 1073  | out-plane           | 0.35                                                          |       | 73  |

Figure 8. (a) Temperature dependence of the total thermal conductivity ($\kappa_{\text{Tot.}} = \kappa_{\text{el.}} + \kappa_{\text{Lat.}}$) for Ca$_{3-2y}$Na$_y$Co$_{4-y}$Mo$_y$O$_9$ ($0 \leq y \leq 0.10$) materials; (b) doping content ($y$) dependence of $\kappa_{\text{Tot.}}$ at 1000 K; (c) electrical part of thermal conductivity ($\kappa_{\text{el.}}$), and (d) lattice part of thermal conductivity ($\kappa_{\text{Lat.}}$).
It has been observed that dual doping of two different cations in the C-349 system provides us a promising strategy for improving the TE properties of cobaltite materials. We conclude that dual doping of Na and Mo cations in the C-349 system is a useful strategy for simultaneously improving the electrical conductivity and for reducing the thermal conductivity. The $y = 0.025$ sample exhibited the highest PF value of $\sim 0.025$ at a temperature of 973 K for 8 h to achieve partial or complete decomposition of CaCO$_3$. The preheated disks were crushed to the powder form and pressed again into disks and heated twice at a temperature of 1173 K for 8 h for the complete reaction, with crushing and pelleting at an applied pressure of $\sim$50 MPa in between the two steps, at a heating rate of $5^\circ$C/min in air and then cooled down gradually to room temperature.

Powder X-ray diffraction (XRD) patterns were obtained at room temperature using a high-resolution D8 Advanced powder diffractometer (Bruker, Germany) with monochromatic radiation (Cu Ka $\lambda = 1.54 \ \text{Å}$) for all samples. The XRD data were collected in a 2$\theta$ range of $5^\circ \leq 2\theta \leq 60^\circ$. Rietveld analysis was used to analyze XRD data using a computer program JANA2006.$^{54}$ Microstructural analysis was performed using an FEI Nova NanoSEM 450 scanning electron microscope. The X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Electron Ltd., Winsford, U.K.) technique was employed to study the oxidation/valance states of metal cations. XPS analysis was performed for all samples at room temperature using monochromatic X-ray radiation (Al Ka) with a takeoff angle of 90$^\circ$ from the plane of the surface. High-resolution XPS spectra for Co 2p and Mo 3d were recorded with a detector pass energy of 50 eV in 10 scans. Binding energies (BEs) were calculated using the reference peak (Au 4f) with 84.0 eV energy. The carrier density and carrier mobility were measured using the Hall measurements at room temperature in a Cryogenics setup. For these measurements, the square-shaped samples were connected from the corners using silver paste. The sheet resistance and the Hall coefficient were then measured following the van der Pauw procedure$^{55}$ in a magnetic field range of $-5$ to $5$ T. The Hall coefficient was linear with the magnetic field for all samples, and the slope was used to define the carrier density and carrier mobility.

The Seebeck coefficient ($S$) and electrical resistivities ($\rho$) were determined concurrently on a ZEM3 instrument (ULVAC-RIKO Inc.) under a low-pressure helium (He) environment from 300 to 1000 K. Furthermore, thermal conductivity was estimated using the equation $\kappa = \alpha_\rho C_p$, where $\alpha$ is the thermal diffusivity, $\rho$ is the mass density, and $C_p$ is the specific heat capacity. Thermal diffusivities ($\alpha$) were measured with an LFA-457 laser flash apparatus (NETZSCH) under vacuum. The $C_p$ of the samples was determined using the temperature-independent Dulong–Petit law. The bulk density ($\rho$) for all compositions was estimated with the Archimedes process and using a few drops of the surfactant in water.

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**Table 3**: The electrical resistivity of the $y = 0.025$ sample is higher than the previously reported results, which is probably due to low mass density and/or the presence of any trace quantity of impurity. We anticipate that the thermoelectric properties of these dual-doped C-349 materials can further be improved by preparing denser samples under optimized experimental conditions and using innovative synthesis techniques. We conclude that dual doping of Na and Mo cations in the C-349 system provides us a promising strategy for improving the TE properties of cobaltite materials.

**Figure 9**: Temperature dependence of the dimensionless thermoelectric figure of merit ($zT$) of Ca$_{1-y}$Na$_y$Co$_{4+y}$Mo$_y$O$_9$ ($0 \leq y \leq 0.10$) samples. The inset represents dual doping content ($y$) dependence of $zT$ at 1000 K.
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c05721

Notes
The authors declare no competing financial interest.

REFERENCES
(1) Bell, L. E. Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. Science 2008, 321, 1457–1461.
(2) Snyder, G. J.; Tobozer, E. S. Complex thermoelectric materials. Nat. Mater. 2008, 7, 105–110.
(3) Rowe, D. M. Thermoelectrics Handbook — Macro to Nano; CRC Press, Taylor & Francis Group: Boca Raton, Florida, 2006.
(4) Zhao, X. B.; Ji, X. H.; Zhang, Y. H.; Zhu, T. J.; Tu, J. P.; Zhang, X. B. Bismuth telluride nanotubes and the effects on the thermoelectric properties of nanotube-containing nanocomposites. Appl. Phys. Lett. 2005, 86, No. 062111.
(5) Pei, Y.; LaLonde, A.; Iwanaga, S.; Snyder, G. J. High thermoelectric figure of merit in heavy hole dominated PbTe. Energy Environ. Sci. 2011, 4, 2085.
(6) Fergus, J. W. Oxide materials for high temperature thermoelectric energy conversion. J. Eur. Ceram. Soc. 2012, 32, 525–540.
(7) Nigam, P. H.; Christensen, D. V.; Synder, G. J.; Hung, L. T.; Linderoth, S.; Nong, N. V.; Prysi, N. Towards high efficiency segmented thermoelectric unicomposites. Phys. Status Solidi A 2014, 211, 9–17.
(8) Shi, X.-L.; Wu, H.; Liu, Q.; Zhou, W.; Lu, S.; Shao, Z.; Dargusch, M.; Chen, Z.-G. SrTiO3-based thermoelectrics: Progress and challenges. Nano Energy 2020, 78, No. 105195.
(9) Shi, X.-L.; Zou, J.; Chen, Z.-G. Advanced Thermoelectric Design: From Materials and Structures to Devices. Chem. Rev. 2020, 120, 7399–7513.
(10) Jakubczyk, E. M.; Mapp, A.; Chung, C. C.; Sansom, C. L.; Jones, J. L.; Dorey, R. A. Enhancing thermoelectric properties of Na2CoO3 ceramics through Na pre-treatment induced nano-decoration. J. Alloys Compd. 2019, 788, 91–101.
(11) Masset, A. C.; Michel, C.; Maignan, A.; Hervieu, M.; Toulemonde, O.; Studer, F.; Raveau, B.; Jestmann, J. Misfit-layered cobaltite with an anisotropic giant magnetoresistance: Ca3Co4O9+. Phys. Rev. B 2000, 62, 166.
(12) Hira, U.; Prysi, N.; Shef. F. Thermoelectric properties of dual doped Bi2Sr2Co2O8-based ceramics. J. Electrochem. Mater. 2019, 48, 4618–4626.
(13) Li, F.; Wei, T.-R.; Kang, F.; Li, J.-F. Thermal stability and oxidation resistance of BiCuSeO based thermoelectric ceramics. J. Alloys Compd. 2014, 614, 394–400.

(14) Shikano, M.; Funahashi, R. Electrical and thermal properties of single-crystalline (Ca2Co3O5)δ-CaO2 with a Ca3Co4O9 structure. Appl. Phys. Lett. 2003, 82, 1851–1853.
(15) Saini, S.; Yaddapanu, H. S.; Tian, K.; Yin, Y.; Maggi, D.; Tiwari, A. Terbium ion doping in Ca3Co4O9: A step towards high-performance thermoelectric materials. Sci. Rep. 2017, 7, No. 44621.
(16) Van Nong, N.; Prysi, N.; Linderoth, S.; Ohtaki, M. Enhancement of the thermoelectric performance of p-type layered oxide Ca3Co4O9 through heavy doping and metallic nanoinclusions. Adv. Mater. 2011, 23, 2484–2490.
(17) Grebille, D.; Lambert, S.; Boreux, F.; Petricek, V. Contribution of powder diffraction for structure refinements of aperforisitic misfit cobalt oxides. J. Appl. Crystallogr. 2004, 37, 823–831.
(18) Yang, G.; Ramasse, Q.; Klie, D. Direct measurement of charge transfer in thermoelectric Ca3Co4O9. Phys. Rev. B 2008, 78, No. 153109.
(19) Zhang, F. P.; Zhang, X.; Lu, Q. M.; Zhang, J. X.; Liu, Y. Q.; Zhang, G. Z. Preparation and high temperature thermoelectric properties of Ca3−xAgxCo4O9+δ oxides. Solid State Ionics 2011, 201, 1–5.
(20) Nagasawa, K.; Daviero-Minaud, S.; Preux, N.; Rollé, A.; Roussel, P.; Nakatsugawa, H.; Mentre, O. Ca3Co4+δO9−δ: A thermoelectric material for SOFC cathode. Chem. Mater. 2009, 21, 4738–4745.
(21) Hira, U.; Grivel, J. C.; Christensen, D. V.; Prysi, N.; Shef. F. Electrical, magnetic and magnetotransport properties of Na and Mo doped Ca3Co4O9 materials. RSC Adv. 2019, 9, 31274–31283.
(22) Lim, C. S.; Chua, C. K.; Sofer, Z.; Jankovsky, O.; Pumera, M. Alternating misfit layered transition/alkaline earth metal chalcogenide Ca3Co4O9 as a new class of chalcogenide materials for hydrogen evolution. Chem. Mater. 2014, 26, 4130–4136.
(23) Prasotsopka, N.; Pintsoontorn, S.; Kamwanna, T.; Kurosaki, K.; Ohishi, Y.; Muta, H.; Yamana, S. Thermoelectric properties of Ca3Co4+δGa4O9+δ prepared by thermal hydro-decomposition. J. Electron. Mater. 2014, 43, 2064–2071.
(24) Garnier, V.; Caillard, R.; Sotelo, A.; Desgardin, G. Relationship among synthesis, microstructure and properties in sinter-forged Bi2212 ceramics. Physica C 1999, 319, 197–208.
(25) Wang, Y.; Su, Y.; Wang, X.; Su, W.; Liu, X. Enhanced high temperature thermoelectric characteristics of transition metals doped Ca3Co4O9+δ by cold high-pressure fabrication. J. Appl. Phys. 2010, 107, No. 033708.
(26) Zhou, Y.; Matsubara, I.; Horii, S.; Takeuchi, T.; Funahashi, R.; Shikano, M.; Shirmoyama, J.-I.; Kishio, K.; Shin, W.; Izu, N.; Murayama, N. Thermoelectric properties of highly grain-aligned and densified Co-based oxide ceramics. J. Appl. Phys. 2003, 93, 2653.
(27) Masuda, Y.; Nagahama, D.; Itahara, H.; Tani, T.; Oo, Y.; Komoto, K. Thermoelectric performance of Bi- and Na-substituted Ca3Co4O9+δ improved through ceramic texturizing. J. Mater. Chem. 2003, 13, 1094–1099.
(28) Noudem, J. G.; Kenfaui, D.; Chateigné, D.; Gomina, M. Granular and lamellar thermoelectric oxides consolidated by spark plasma sintering. J. Electron. Mater. 2011, 40, 1100–1106.
(29) Yin, T.; Liu, D.; Ou, Y.; Ma, F.; Xie, S.; Li, J. F.; Li, J. Nanocrystalline thermoelectric Ca3Co4O9 ceramics by sol–gel based electrospinning and spark plasma sintering. J. Phys. Chem. C 2010, 114, 10061–10065.
(30) Wu, N. Y.; Holgate, T. C.; Nong, N. V.; Prysi, N.; Linderoth, S. High temperature thermoelectric properties of Ca3Co4O9+δ by auto-combustion synthesis and spark plasma sintering. J. Eur. Ceram. Soc. 2014, 34, 925–931.
(31) Kanas, N.; Sing, S. P.; Rotan, M.; Saleemi, M.; Bittner, M.; Feldhoff, A.; Norby, T.; Wik, K.; Grande, T.; Einarsrud, M.-A. Influence of processing on stability, microstructure and thermoelectric properties of Ca3−δCo4+δO9−δ. J. Eur. Ceram. Soc. 2018, 38, 1592–1599.
(32) Miyazawa, K.; Amaral, F.; Kovalevsky, A. V.; Graça, M. P. F. Hybrid microwave processing of Ca3Co4O9 thermoelectrics. Ceram. Int. 2016, 42, 9482–9487.
(53) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. 1976, 32, 751–767.

(54) Li, S.; Funahashi, R.; Matsubara, I.; Ueno, K.; Sodeoka, S.; Yamada, H. Synthesis and thermoelectric properties of the new oxide materials Ca$_x$Bi$_2$Co$_{2}$(O$_2$)$_6$. (0.0 < x <0.75). Chem. Mater. 2000, 12, 2424–2427.

(55) Limelette, P.; Soret, J. C.; Muguerra, H.; Grebille, D. Magnetoresistance scaling in the layered cobaltate Ca$_3$Co$_4$O$_9$. Phys. Rev. B: Condens. Matter Mater. Phys. 2008, 77, No. 245123.

(56) Wakisaka, Y.; Hirata, S.; Mizokawa, T.; Suzuki, Y.; Miyazaki, Y.; Kajitani, T. Electronic structure of Ca$_3$Co$_4$O$_9$ studied by photoemission spectroscopy: Phase separation and charge localization. Phys. Rev. B: Condens. Matter Mater. Phys. 2008, 78, No. 255107.

(57) Mizokawa, T.; Tjong, L. H.; Lin, H.-J.; Chen, C. T.; Kitawaki, R.; Terasaki, I.; Lambert, S.; Michal, C. X-ray absorption study of layered oxides with a Co-O triangular lattice. Phys. Rev. B 2005, 71, No. 193107.

(58) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. Handbook of X-ray photoelectron spectroscopy: A reference book of standard spectra for identification and characterization of XPS Data, Waltham: int. J. Chastain Edn, Perkin Elmer Corporation (Physical Electronics), (1992).

(59) Huang, Y.; Zhao, B.; Hu, X.; Lin, S.; Ang, R.; Song, W.; Sun, Y. Enhanced electronic correlation and thermoelectric response by Cu-doping in Ca$_3$Co$_4$O$_9$ single crystals. Dalton Trans. 2012, 41, 11716–11887.

(60) Wu, T.; Tyson, T. A.; Chen, H.; Bai, J.; Wang, H.; Jaye, C. A structural change in Ca$_3$Co$_4$O$_9$ associated with enhanced thermoelectric properties. J. Phys.: Condens. Matter 2012, 24, No. 455602.

(61) Pinitsoontorn, S.; Lerdsongkram, N.; Keawpark, N.; Amornnakit, B. Thermoelectric properties of transition metals-doped Ca$_3$Co$_4$O$_9$ of M=Co, Cr, Fe, Ni, Cu and Zn. J. Mater. Sci: Mater. Electron. 2012, 23, 1050–1056.

(62) Sotelo, A.; Constantinescu, G.; Rasekh, S. H.; Torres, M. A.; Diez, J. C.; Madre, M. A. Improvement of thermoelectric properties of Ca$_3$Co$_4$O$_9$ using soft chemistry synthetic methods. J. Eur. Ceram. Soc. 2012, 32, 2415–2422.

(63) Kenfawi, D.; Bonnefont, G.; Chatteigner, D.; Fantozzi, G.; Gomina, M.; Noudem, J. G. Ca$_3$Co$_4$O$_9$ ceramics consolidated by SPS process: Optimisation of mechanical and thermoelectric properties. Mater. Res. Bull. 2010, 45, 1240–1249.

(64) Mott, N. F.; Davis, E. A. Electronic processes in non-crystalline materials; Clarendon Press: Oxford, 1971.

(65) Liu, Y.; Lin, Y.; Jiang, L.; Nan, C. W.; Shen, Z. Thermoelectric properties of Bi$_{2}$ substituted Co-based misfit-layered oxides. J. Electroceram. 2008, 21, 748–751.

(66) Wang, Y.; Sui, Y.; Wang, X.; Su, W.; Liu, X. Enhanced high temperature thermoelectric characteristics of transition metals doped Ca$_3$Co$_4$O$_9$ by cold high-pressure fabrication. J. Appl. Phys. 2010, 107, No. 033708.

(67) May, A. F.; Synder, G. J. Introduction to Modelling Thermoelectric Transport at High Temperatures. In Thermoelectrics and its Energy Harvesting; edn., Rowe, D. M., Ed.; CRC Press: Boca Raton, 2012.

(68) Constantinescu, G.; Madre, M. A.; Rasekh, S.; Torres, M. A.; Diez, J. C.; Sotelo, A. Effects of Ga addition on Ca-deficient Ca$_3$Co$_4$O$_9$ thermoelectric materials. Ceram. Int. 2014, 40, 6255–6260.

(69) Hao, H.; Zhao, L.; Hu, X. Microstructure and thermoelectric properties of Bi- and Cu-substituted Ca$_3$Co$_4$O$_9$ oxides. J. Mater. Sci. Technol. 2009, 25, 105–108.

(70) Liu, Y.; Lin, Y.; Jiang, L.; Nan, C. W.; Shen, Z. Thermoelectric properties of Bi$_{2}$ substituted Co-based misfit-layered oxides. J. Electroceram. 2008, 21, 748–751.

(71) Liu, H. Q.; Zhao, X. B.; Zhu, T. J.; Song, Y.; Wang, F. P. Thermoelectric properties of Gd Y co-doped Ca$_3$Co$_4$O$_9$.Curr. Appl. Phys. 2009, 9, 409–413.

(72) Ou, Y.; Peng, J.; Li, F.; Yu, Z. X.; Ma, F. Y.; Xie, S. H.; Li, J. F.; Li, J. Y. The effects of dual doping on the thermoelectric properties of...
Ca$_{3-x}$M$_x$Co$_{4-y}$Cu$_y$O$_9$ (M = Na, La). *J. Alloys Compd.* **2012**, *526*, 139–144.

(73) Bittner, M.; Kanas, N.; Hinterding, R.; Steinbach, F.; Groeneveld, D.; Wemhoff, P.; Wiik, K.; Einarsrud, M.-A.; Feldhoff, A. Triple-phase ceramic 2D nanocomposite with enhanced thermoelectric properties. *J. Eur. Ceram. Soc.* **2019**, *39*, 1237–1244.

(74) Takeuchi, T.; Nagasako, N.; Asahi, R.; Mizutani, U. Extremely small thermal conductivity of the Al-based Mackay-type -cubic approximants. *Phys. Rev. B* **2006**, *74*, No. 054206.