Nanoscale Texturing and Interfaces in Compositionally Modified Ca$_3$Co$_4$O$_9$ with Enhanced Thermoelectric Performance

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ABSTRACT: Oxide thermoelectric materials are nontoxic, chemically and thermally stable in oxidizing environments, cost-effective, and comparatively simpler to synthesize. However, thermoelectric oxides exhibit comparatively lower figure of merit (ZT) than that of metallic alloy counterparts. In this study, nanoscale texturing and interface engineering were utilized for enhancing the thermoelectric performance of oxide polycrystalline Ca$_3$Co$_4$O$_9$ materials, which were synthesized using conventional sintering and spark plasma sintering (SPS) techniques. Results demonstrated that nanoscale platelets (having layered structure with nanoscale spacing) and metallic inclusions provide effective scattering of phonons, resulting in lower thermal conductivity and higher ZT. Thermoelectric measurement direction was found to have a significant effect on the magnitude of ZT because of the strong anisotropy in the transport properties induced by the layered nanostructure. The peak ZT value for the Ca$_{2.85}$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ specimen measured along both perpendicular and parallel directions with respect to the SPS pressure axis is found be 0.16 at 630 °C and 0.04 at 580 °C, respectively. The peak ZT of 0.25 at 670 °C was observed for the spark plasma-sintered Ca$_{2.95}$Ag$_{0.05}$Co$_4$O$_9$ sample. The estimated output power of 2.15 W was obtained for the full size model, showing high-temperature thermoelectric applicability of this nanostructured material without significant oxidation.

1. INTRODUCTION

Thermoelectric (TE) modules are promising for generating electricity from wasted heat in industrial sectors and other electromechanical processes.1 In order to realize an efficient TE module, it is essential to find high-performance materials with excellent durability and robustness over high-temperature regime in air.2,3 Oxide TE materials are desirable for harvesting energy at high-temperature environments such as automobile exhaust, jet engines, and industrial plants.2,4 Most of the commercial TE materials based upon Bi–Te alloys are suitable for low-temperature applications (below 150 °C).3 Other materials being researched such as skutterudites and Pb–Te alloys are only suitable up to 400 °C or below in air.5,6 Half-Heusler alloy can operate up to 500 °C in air but for short time and challenge with respect to the long term thermal cycling.8 Moreover, volatile elements such as Bi and Pb in TE materials could come out of the lattice during prolonged high-temperature operation, which in turn may degrade their TE properties eventually. On the other hand, oxide materials are stable over temperatures exceeding 400–500 °C in air and thus provide a viable solution for high-temperature deployment.

The effectiveness of a TE material for power generation is determined by a dimensionless figure of merit, (ZT), given as

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$

where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ represents the thermal conductivity. From this relation, the TE material should have high Seebeck coefficient and electrical conductivity with low thermal conductivity. Therefore, an ideal TE material should have a narrow band gap and high mobility carriers behaving like a “phonon-glass/electron-crystal”,9 that is, it should have low thermal conductivity similar to that of an amorphous or glasslike material and high electrical conductivity of a crystalline material. In practice, TE parameters $\alpha$, $\sigma$, and $\kappa$ are closely interrelated, making it challenging to adjust the electrical and thermal properties independently.

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The oxide TE material NaCo$_2$O$_4$ has been shown to exhibit a high Seebeck coefficient and electrical conductivity. However, it has a poor thermal stability because of the presence of volatile Na ions. NaCo$_2$O$_4$ has been found to be sensitive to the humidity with increasing temperature.\textsuperscript{1,12} Out of other possibilities for oxide materials, Ca$_3$Co$_4$O$_9$ has emerged as a promising candidate for high-temperature (<900 °C) applications because of its reasonable TE performance and chemical stability. Additionally, it can be fabricated from inexpensive precursors using conventional ceramic fabrication process. The highest reported ZT value for a Ca$_3$Co$_4$O$_9$ single crystal was reported to be ∼0.87 at 700 °C,\textsuperscript{13} which was attributed to its unique layered structure consisting of stacks of a conductive layer [CoO$_2$] and an insulating layer [Ca$_2$CoO$_3$].\textsuperscript{14} The misfit layered structure and the weak connection between these two substructure layers were considered to result in significant phonon scattering which assisted in reducing the thermal conductivity.\textsuperscript{15} However, the single crystal material is expensive and has scalability challenges.

In order to fabricate a high-quality single-phase Ca$_3$Co$_4$O$_9$ material, Kang et al. suggested a postcalcination-based fabrication method; however, they did not report the ZT value.\textsuperscript{16} Alternative methods, such as hot pressing and spark plasma sintering (SPS), have also been used to synthesize high-density unmodified and doped Ca$_3$Co$_4$O$_9$. The substitution of heavier and smaller Lu\textsuperscript{17} ions on Ca sites has been shown to provide a ZT value of 0.36 at 800 °C through modification of NaCl-type [Ca$_3$Co$_4$O$_9$] layer of Ca$_3$Co$_4$O$_9$.\textsuperscript{18} The increased ZT was obtained because of the reduced thermal conductivity and increased Seebeck coefficient as a result of reduced Co$^{4+}$ concentration.\textsuperscript{17} The Ga\textsuperscript{3+} substitution has been found to improve the TE properties (ZT ≈ 0.26 at 700 °C) of SPS-fabricated Ca$_3$Co$_4$O$_9$.\textsuperscript{18} The Ga atoms were found to be preferentially located on the Co-sites in the NaCl-type [Ca$_3$Co$_4$O$_9$] layer increasing effective phonon scattering and thereby the reduced thermal conductivity. The main reason for the lower ZT value of the polycrystalline oxide in comparison to its single crystal counterpart is its lower power factor ($\alpha^2\sigma$) resulting from lower electrical conductivity and lower Seebeck coefficient. The TE properties of polycrystalline systems can be modified by controlling microstructural factors such as grain size, grain orientation, grain boundary, and density.

The Ca$_3$Co$_4$O$_9$ system becomes unstable on heating above 926 °C, as it starts to decompose into various phases including Ca$_3$Co$_4$O$_6$ and CoO solid solution with CaO.\textsuperscript{19} The synthesis of Ca$_3$Co$_4$O$_9$ is performed using a conventional solid--state reaction from CaCO$_3$ and Co$_3$O$_4$. The samples prepared from calcined powders are sintered at 850 °C or above. For the Ca$_3$Co$_4$O$_9$ ceramics, the thermal conductivity is found to be in the range of 0.4–1.1 W/m-K depending on structure and morphology.\textsuperscript{20} To improve the TE properties of the Ca$_3$Co$_4$O$_9$ ceramics through microstructure control, many processing techniques have been examined including texturing process and dual-doping.\textsuperscript{21–25}

To date, nanostructured materials have been employed for improving TE efficiency of TE generators. Nanosized powders and pores introduce defects and increase the density of grain boundaries giving rise to strong scattering of long wavelength phonons, which results in reduced thermal conductivity.\textsuperscript{7} The Ag doping/alloying in Ca$_3$Co$_4$O$_9$ has been considered as one of the promising nanostructuring methods because of its significant dual role, acting both as electrical connectors between grains and phonon scattering center.\textsuperscript{26,27} The Ag inclusions with new interfaces lead to an increased effective phonon scattering to suppress the lattice thermal conductivity. Because Ag has high atomic mass and comparable ionic radius (1.15 Å) with Ca (1.00 Å), the carriers and phonon scattering centers can be tuned simultaneously for modulating the electrical and thermal transport.\textsuperscript{28} The addition of Ag nanoparticles has also been found to facilitate a preferential orientation of the grains (texturing) in Ca$_3$Co$_4$O$_9$.\textsuperscript{29}

In prior literature, the nature of anisotropic properties modified through ion doping has not been investigated in detail. Here, we demonstrate the effect of codoping at Ca and Co sites on the TE response of Ca$_3$Co$_4$O$_9$ and investigate the anisotropic behavior. The schematic view of the crystalline structure of Ca$_4$Co$_4$O$_9$ and the partial substitution of Lu/Ga on Ca/Co sites in the Ca$_3$Co$_4$O$_9$ insulating layer is provided in Figure S1. Building upon the systematic experimental results, we provide a fundamental understanding of the mechanism responsible for the enhanced TE properties of SPS-fabricated p-type Ca$_3$Co$_4$O$_9$ with Lu$^{3+}$/Ga$^{3+}$ codoping. Figure 1 shows the conceptual illustration of the randomly oriented Ca$_3$Co$_4$O$_9$ and nanoscale-textured Ca$_3$Co$_4$O$_9$ with Ag inclusions.

![Randomly oriented Ca$_3$Co$_4$O$_9$](image1.png) ![Nanoscale textured Ca$_3$Co$_4$O$_9$ with Ag](image2.png)

Figure 1. Conceptual illustration of the randomly oriented Ca$_3$Co$_4$O$_9$ and nanoscale-textured Ca$_3$Co$_4$O$_9$ with Ag inclusions.

2. RESULTS AND DISCUSSION

2.1. Phase Composition and Microstructure of Lu and Ga Codoped Ca$_3$Co$_4$O$_9$. Figure S2a shows X-ray diffraction (XRD) patterns of Ca$_{3-x}$Lu$_x$Co$_4$O$_9$ ceramics ($x = 0, x = 0.05, x = 0.1S$, and $x = 0.1S, y = 0.05$). All the XRD peaks were indexed to the Ca$_3$Co$_4$O$_9$ phase, indicating that there is no secondary phase. Ca$_3$Co$_4$O$_9$ has a layered structure which consists of two monoclinic subsystems with identical $a$, $c$, and $\beta$ parameters but has a different b-axis length.\textsuperscript{35,30} All the diffraction peaks agree well with the reported monoclinic

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structure. Moreover, the big peak-shifts in Ca$_3$Co$_4$O$_9$ samples from cold isostatic pressing (CIP) to SPS were found at $2\theta \approx 16.5^\circ$ and $33.4^\circ$, as shown in Figure S2a. Because Lu$^{3+}$ (0.861 Å) and Ga$^{3+}$ (0.62 Å) ions have smaller ionic radii than Ca$^{2+}$ (1.00 Å),$^{31}$ the (002) and (004) diffraction peaks of codoped samples shifted to higher $2\theta$ angles as compared to the pristine Ca$_3$Co$_4$O$_9$ sample (Figure S2a, inset). Here, for the CIP sample, we utilized a postcalcination method to synthesize a single-phase Ca$_3$Co$_4$O$_9$ ceramics from the calcined powder at $900^\circ$C. Previously, Kang et al. reported the single phase XRD results for the Ca$_3$Co$_4$O$_9$ ceramics sintered at $1200^\circ$C with the postcalcination (with heating at $900^\circ$C for 12 h after cooling below $700^\circ$C).$^{15}$ In the present work, the XRD results indicated single-phase (without secondary phases) Ca$_3$Co$_4$O$_9$ ceramics, as shown in Figure S2a. The Rietveld method was carried out to refine XRD data, as shown in Figure S3. The refined diffraction patterns show that all the samples have monoclinic symmetry and the lattice parameters were calculated to confirm the codoping effect on the crystallographic structure. Table S1 presents the chemical compositions and lattice parameters of the pure and codoped samples. It is very clear that the lattice parameters were changed after doping. Thus, the variation in the lattice parameters indicate that Lu$^{3+}$ (0.861 Å) and Ga$^{3+}$ (0.62 Å) ions have been substituted at the Ca-site (Ca$^{2+}$: 1.00 Å) and Co-site (low spin Co$^{3+}$/high spin Co$^{3+}$/Co$^{4+}$ = 0.545 Å/0.61 Å/0.53 Å), respectively.

The microstructures of the Ca$_{3-x}$Lu$_x$Co$_{4-x}$Ga$_x$O$_9$ ceramics (x, y = 0, x = 0.05, y = 0.15, and x = 0.15, y = 0.05) were analyzed using scanning electron microscopy (SEM) as shown in Figure S2b–d. Cross-sectional images indicate a highly anisotropic lamella-like structure. The Ca$_3$Co$_4$O$_9$ samples prepared using the CIP method had a relative density of 82%. However, the Ca$_3$Co$_4$O$_9$ sample synthesized by SPS had a high relative density of 96%. Additionally, SPS-processed Lu and Ga codoped Ca$_{3-x}$Lu$_x$Co$_{4-x}$Ga$_x$O$_9$ samples (x = 0.05, y = 0.15 and x = 0.15, y = 0.05) show a higher relative density of 96% with a closed pore structure. All the samples consisted of the platelet-type grains stacked with same orientation. The average grain size and the thickness of platelets for the pure Ca$_3$Co$_4$O$_9$ was in the range of 1.8–2.1 μm and 113–123 nm, respectively, as shown in Figure 2 and Table S2. However, Lu and Ga codoped Ca$_3$Co$_4$O$_9$ exhibited a smaller average grain size (0.8–1.0 μm) and thinner platelets (34–78 nm). The thickness of platelets was found to vary with different Lu/Ga concentrations. This phenomenon was attributed to Lu/Ga ionic radius and substitution site. Because the difference in the ionic radius between Lu$^{3+}$ (0.861 Å) and Ca$^{2+}$ (1.00 Å) is higher than that between Ga$^{3+}$ (0.62 Å) and low spin Co$^{3+}$/high spin Co$^{3+}$/Co$^{4+}$ (0.545 Å/0.61 Å/0.53 Å),$^{31}$ the sample containing high concentration of Lu$^{3+}$ ion exhibited thinner platelets. Consequently, smaller grains reduced the phonon mean free path, resulting in the lower lattice thermal conductivity. Furthermore, thinner platelets created more interfaces compared to thicker platelets, which increased electron scattering, resulting in lowering electrical conductivity.

Bright field transmission electron microscopy (BF-TEM) images of the SPS sample for Ca$_3$Co$_4$O$_9$ showed typical polygonal grains with several micrometers dimension and polycrystalline layered structure, as shown in Figure S4a,b. Selected area electron diffraction of the different grains also indicated randomly oriented grains. High-resolution TEM (HR-TEM) images of grain boundaries between three adjacent grains are displayed in Figure S4c,d. The randomly oriented grains with the high-angle grain boundaries were found to exist in the samples, and thus, the boundary is expected to participate in scattering of phonons effectively. Figure S4ef shows high resolution images of grain boundaries and from these images grain boundary width is calculated to be 2 nm.

2.2. Phase Analysis and Microstructure of Textured Ca$_3$Co$_4$O$_9$ with Ag Inclusions. The XRD plot for the Ca$_{3-x}$Ag$_x$Lu$_{x}$Co$_{4-x}$Ga$_x$O$_9$ (x = 0–0.05, y = 0–0.05, z = 0–0.05) samples is shown in Figure 3. It is clearly seen that most of the diffraction peaks can be indexed to the Ca$_3$Co$_4$O$_9$ structure. An additional peak at $2\theta$ = 38.5$^\circ$ was indexed to Ag (JCPDS card # 01-1167), which can also be observed for the heavy-ion-doped Ca$_3$Co$_4$O$_9$ with low Ag content (x = 0.05). The Ag dopants are prone to agglomerate at the grain boundaries as a secondary phase, while Lu/Ga substitution will occur on Ca/Co sites. Figure 3a shows randomly oriented Ca$_3$Co$_4$O$_9$ phase in CS sample, whereas the XRD patterns for the SPS samples exhibit strong diffraction peaks along the c-axis direction, indicating evolution of texturing as shown in Figure 3b. Although Ag was used as an inclusion, Ag$^+$ entered into the Ca$_3$Co$_4$O$_9$ lattice at Ca$^{2+}$ sites, as can be seen in terms of the variation in lattice parameters (Table S3). The inevitable Ca-site defects were originated from the inserted Ag inclusions, which acted as phonon scattering centers to lower the thermal conductivity.

In order to estimate the effect of nanoscale texturing and engineered interfaces on the microstructure of Ca$_3$Co$_4$O$_9$ samples, the Lotgering factors method was employed to quantify the grain orientation degree of the SPS samples. The Lotgering factors $F$ can be described as $^{33}$

$$F = (P - P_0)/(1 - P_0)$$
where \( P = \sum I_{\{00l\}} / \sum I_{\{hkl\}} \), \( I \) is the intensity of the diffraction peak and \( P \) is calculated from XRD patterns of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) samples in Figure 3. \( P_0 \) is calculated from XRD plot for randomly oriented \( \text{Ca}_3\text{Co}_4\text{O}_9 \) sample shown in Figure 3a.

The calculated Lotgering factor increased from 0.63 to 0.82, as summarized in Table 1. The platelets within the matrix of the doped \( \text{Ca}_3\text{Co}_4\text{O}_9 \) samples were highly oriented, which led to the favorable effect on the electrical transport of \( \text{Ca}_3\text{Co}_4\text{O}_9 \).

The result indicated that the doping of Ag is favorable to promote the grain orientation. Ag is a key factor in textured \( \text{Ca}_3\text{Co}_4\text{O}_9 \) materials to create nanoscale-thin platelike grains with more interfaces and facilitate the preferred grain orientation. Because Ag is soft and plastic (Mohs hardness: 2.5), a small amount of Ag in the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) matrix can be deformed during the pressing process. Thus, it is very easy for the platelike grains to be more oriented under pressure than in the absence of Ag. It has been found that oriented grains can increase the electrical conductivity because of the reduced scattering of charge carriers at the grain boundaries and because of their shorter diffusion path. Figure S5 shows the field emission SEM (FESEM) images of the fractured surface of \( \text{Ca}_{3-x-y}\text{Ag}_x\text{Lu}_y\text{Co}_4\text{Ga}_y\text{O}_9 \) (\( x = 0–0.05, y = 0–0.05, z = 0–0.05 \)) samples. The porous microstructure existed in the CS samples, whereas SPS samples had the dense microstructure. The pure and doped \( \text{Ca}_3\text{Co}_4\text{O}_9 \) CS samples were found to be randomly oriented; however, the lamellar texture containing highly oriented grains was observed in the Ag-doped SPS samples, exhibiting enhanced Lotgering factors (0.73–0.82). The SEM micrographs of textured samples show preferred grain orientations in \( \text{Ca}_3\text{Co}_4\text{O}_9 \) samples, which was consistent with XRD results. The back-scattered electron (BSE) images of the doped \( \text{Ca}_3\text{Co}_4\text{O}_9 \) SPS samples and the energy dispersive X-ray spectroscopy (EDS) elemental mapping images of Ag in the respective samples are shown in Figure 4.

The EDS images display the distribution of Ag in the doped \( \text{Ca}_3\text{Co}_4\text{O}_9 \) samples indicating Ag as a metallic inclusion in the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) matrix. Ag was found to exist preferentially at the.

Table 1. Lotgering Factors of \( \text{Ca}_{3-x-y}\text{Ag}_x\text{Lu}_y\text{Co}_4\text{Ga}_y\text{O}_9 \) (\( x = 0.05, y = 0.15, \) and \( x = 0.15, y = 0.05 \)) and \( \text{Ca}_{3-x-y}\text{Ag}_x\text{Lu}_y\text{Co}_4\text{Ga}_y\text{O}_9 \) (\( x = 0–0.05, y = 0–0.05, z = 0–0.05 \)) Polycrystalline Samples Processed by SPS

| SPS samples | Lotgering factor F of SPS samples | Lotgering factor F of CS samples |
|-------------|---------------------------------|---------------------------------|
| \( \text{Ca}_3\text{Co}_4\text{O}_9 \) | 0.63 | 0.61 |
| \( \text{Ca}_3\text{Ag}_0\text{Co}_3\text{O}_9 \) | 0.82 | 0.65 |
| \( \text{Ca}_3\text{Ag}_0\text{Lu}_0\text{Co}_3\text{O}_9 \) | 0.73 | 0.55 |
| \( \text{Ca}_3\text{Ag}_0\text{Lu}_0\text{Co}_3\text{O}_9 \) | 0.80 | 0.61 |
boundaries between platelets, which gave rise to a mixture of nanosized and microsized inclusions, as shown in Figure 5a–d. In our material system (doped Ca$_3$Co$_4$O$_9$ SPS samples), Ag inclusions were randomly distributed mainly along the grain boundaries in sizes ranging from hundreds of nanometers to micrometers, which is important for scattering wide range of phonon spectrum.

It can be noted that the Ag inclusions had various morphology such as spherical shape, angular shape, and plate shape with the size ranging from several hundreds of nanometers to micrometers, which is important for scattering wide range of phonon spectrum. X-ray photoelectron spectroscopy (XPS) studies were performed to identify the Co valence states of the pure and doped Ca$_3$Co$_4$O$_9$ samples because the electrical transport occurs by the hopping of a hole from Co$^{4+}$ to Co$^{3+}$. Figure 6 shows the 2p XPS spectra of Co ions analyzed from Ca$_{3-x-y}$Ag$_x$Lu$_y$Co$_{4-z}$Ga$_z$O$_9$ ($x = 0−0.05$, $y = 0−0.05$, $z = 0−0.05$) polycrystalline samples. According to the literature, for the Co$^{4+}$ state, the 2p$_{1/2}$ and 2p$_{3/2}$ peaks take place at 796.8 and 781.4 eV, respectively, while for the Co$^{3+}$ state, the 2p$_{1/2}$ and 2p$_{3/2}$ peaks exist at 794.8 and 779.6 eV, respectively. The binding energies of all the samples were observed between the values expected for Co$^{4+}$ and Co$^{3+}$, indicating that Co$^{4+}$ and Co$^{3+}$ valence states coexist in the samples. The Co 2p XPS spectrum had two main peaks with a spin-orbital splitting of ∼15.0 eV, 2p$_{3/2}$ at 780.0 eV and 2p$_{1/2}$ at 795.0 eV, as shown in Figure 6. The Co 2p$_{1/2}$ and 2p$_{3/2}$ peaks for the pure Ca$_3$Co$_4$O$_9$ sample occurred at 796.1 and 780.5 eV, respectively. However, two weak satellite peaks occurred at 789.5 and 804.5 eV in the doped Ca$_3$Co$_4$O$_9$ samples, which indicated the existence of Co$^{3+}$. By curve fitting, the concentration change of Co$^{3+}$ and Co$^{4+}$ was determined in the doped Ca$_3$Co$_4$O$_9$ samples, and was compared with the pure Ca$_3$Co$_4$O$_9$ sample. The areas under the fitted curves for Co$^{3+}$ and Co$^{4+}$ were calculated to determine the

Figure 5. (a–d) Fractured cross-sectional BSE images with EDS elemental maps of Ag. (e,f) HR-TEM images of a sample cut from Ca$_{2.95}$Ag$_{0.05}$Co$_4$O$_9$ processed by SPS. (g,h) BF-TEM images of a sample cut from Ca$_{2.95}$Ag$_{0.05}$Co$_3$O$_9$ processed by SPS.

Figure 6. High resolution Co 2p$_{1/2}$ and 2p$_{3/2}$ XPS spectra analyzed from (a) Ca$_3$Co$_4$O$_9$, (b) Ca$_{2.95}$Ag$_{0.05}$Co$_4$O$_9$, (c) Ca$_{2.9}$Ag$_{0.05}$Lu$_{0.05}$Co$_4$O$_9$, and (d) Ca$_{2.95}$Ag$_{0.05}$Co$_{3.95}$Ga$_{0.05}$O$_9$ samples processed by SPS.
concentration of Co$^{3+}$ and Co$^{4+}$, respectively. Table 2 shows the calculated relative atomic concentration of Co$^{3+}$ and Co$^{4+}$. It was clearly observed that a small amount of Ag-doping is not effective in changing the concentration of Co$^{3+}$ and Co$^{4+}$ ions; however, additional Lu or Ga doping suppressed the Co$^{4+}$ concentration significantly. The lower concentration of Co$^{4+}$ was found in both Ca$_{2.9}$Ag$_{0.05}$Lu$_{0.05}$Co$_{4}$O$_{9}$ and Ca$_{2.95}$Ag$_{0.05}$Co$_{3.95}$Ga$_{0.05}$O$_{9}$ samples.

**2.3. TE Properties of Lu and Ga Codoped Ca$_3$Co$_4$O$_9$.**

The TE properties were evaluated through conventional measurement configuration (evaluation of in-plane electrical properties and out-of-plane thermal properties) to compare material characteristics with that of reported in prior literature.

Table 2. Concentration of Co$^{3+}$ and Co$^{4+}$ Calculated from Each Co 2p XPS Spectra for the Pure and Doped Ca$_3$Co$_4$O$_9$ Samples

| Sample Description | Co$^{3+}$ (concentration) (%) | Co$^{4+}$ (concentration) (%) |
|--------------------|-------------------------------|-------------------------------|
| Ca$_3$Co$_4$O$_9$   | 45.86                        | 54.14                        |
| Ca$_{2.95}$Ag$_{0.05}$Co$_4$O$_9$ | 45.66                        | 54.34                        |
| Ca$_{2.9}$Ag$_{0.05}$Lu$_{0.05}$Co$_4$O$_9$ | 57.14                        | 42.86                        |
| Ca$_{2.95}$Ag$_{0.05}$Co$_{3.95}$Ga$_{0.05}$O$_9$ | 57.93                        | 42.07                        |

Figure 7. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal conductivity, and (e) ZT for Ca$_{3-x}$Lu$_x$Co$_{4-y}$Ga$_y$O$_9$ ceramics ($x = 0$, $y = 0.05$, $x = 0.15$, and $y = 0.05$) from the conventional TE measurement.

The lower electrical conductivity of the CIP sample was related to the randomly oriented platelets and low density. At high temperatures ($>400$ °C), the decrease in carrier concentration in CIP sample originated from the loss of oxygen during measurements in the helium atmosphere. Low-density CIP sample had large interconnected pores, and thus, both the kinetics and the thermodynamics were favorable for oxygen-loss above $400$ °C. According to the literature, Ca$_3$Co$_4$O$_9$ tends to lose oxygen around $447-457$ °C in air and $347-357$ °C under a nitrogen atmosphere. However, the porosity of the SPS samples was low, which helped in reducing the loss of oxygen.

Figure 7b displays the in-plane Seebeck coefficient as a function of temperature for the Ca$_{3-x}$Lu$_x$Co$_{4-y}$Ga$_y$O$_9$ samples ($x = 0$, $y = 0.05$, $x = 0.15$, and $y = 0.05$). All the samples exhibited a positive Seebeck coefficient, indicating p-type behavior. The Seebeck coefficient of the CIP sample was significantly smaller than that for all of the SPS samples across the measured temperature range because the grain alignment noticing the decrease in carrier concentration that also resulted in increase in the Seebeck coefficient. The lower electrical conductivity of the CIP sample was related to the randomly oriented platelets and low density. At high temperatures ($>400$ °C), the decrease in carrier concentration in CIP sample originated from the loss of oxygen during measurements in the helium atmosphere. Low-density CIP sample had large interconnected pores, and thus, both the kinetics and the thermodynamics were favorable for oxygen-loss above $400$ °C. According to the literature, Ca$_3$Co$_4$O$_9$ tends to lose oxygen around $447-457$ °C in air and $347-357$ °C under a nitrogen atmosphere. However, the porosity of the SPS samples was low, which helped in reducing the loss of oxygen.

Figure 7b displays the in-plane Seebeck coefficient as a function of temperature for the Ca$_{3-x}$Lu$_x$Co$_{4-y}$Ga$_y$O$_9$ samples ($x = 0$, $y = 0.05$, $x = 0.15$, and $y = 0.05$). All the samples exhibited a positive Seebeck coefficient, indicating p-type behavior. The Seebeck coefficient of the CIP sample was significantly smaller than that for all of the SPS samples across the measured temperature range because the grain alignment
was less pronounced in the CIP sample. Among the SPS samples, the Ca$_{2.95}$Lu$_{0.05}$Co$_{3.85}$Ga$_{0.15}$O$_9$ composition was found to have lower Seebeck coefficient. According to the room temperature Hall effect measurements, as shown in Table 3, the degraded Seebeck coefficient resulted from the high carrier concentration ($1.09 \times 10^{19}$ cm$^{-3}$) and low hall mobility (50 cm$^2$/V·s). The relationship between the Seebeck coefficient and the carrier concentration can be described as

$$\alpha = \frac{8\pi^2 k_B^2}{3\hbar^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3}$$

where $k_B$ is Boltzmann’s constant, $h$ is Planck’s constant, $e$ is the charge of an electron, $n$ is the carrier concentration, and $m^*$ is the effective mass of the carrier.

When the Lutetium fraction increases from 0.05 to 0.15 with decreased Gallium fraction from 0.15 to 0.05, the carrier concentration decreases from $1.09 \times 10^{19}$ to $1.91 \times 10^{18}$ cm$^{-3}$. All samples show different hall mobility ($\mu_H$) values at a measured $n$, as shown in Table 3. These values were around 2430, 50, and 230 cm$^2$/V·s for the Ca$_3$Co$_4$O$_9$, Ca$_{2.95}$Lu$_{0.05}$Co$_{3.85}$Ga$_{0.15}$O$_9$ and Ca$_{2.85}$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ systems, respectively. The increased in-plane electrical conductivity for the Ca$_{2.95}$Lu$_{0.05}$Co$_{3.85}$Ga$_{0.15}$O$_9$ sample at room temperature was associated with the change in charge carrier concentration. Thus, high-concentration Ga doping introduced more hole carriers, which was consistent with room-temperature Hall measurements. However, the decreased carrier concentration for the Ca$_{2.85}$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ sample resulted in lower in-plane electrical conductivity at room temperature. The purpose of room temperature measurement of carrier concentration is to evaluate the effect of Lu and Ga codoping on the TE performance improvement. The power factor is evaluated by Seebeck coefficient and electrical conductivity. According to the literature, the maximum power factor is in the carrier concentration range between $10^{18}$ and $10^{20}$ cm$^{-3}$, as shown in Figure S6. Thus, we controlled the carrier concentration of the Ca$_3$Co$_4$O$_9$ sample and carrier concentrations of the Lu and Ga

| carrier concentration n (cm$^{-3}$) | Hall coefficient $R_H$ (m$^2$/C) | electrical conductivity $\sigma$ (S/m) | Hall mobility $\mu_H$ (cm$^2$/V·s) |
|-----------------------------------|---------------------------------|--------------------------------------|---------------------------------|
| Ca$_3$Co$_4$O$_9$                 | $1.84 \times 10^{17}$          | $3.40 \times 10^{-5}$               | $7.15 \times 10^{1}$           |
| Ca$_{2.95}$Lu$_{0.05}$Co$_{3.85}$Ga$_{0.15}$O$_9$ | $1.09 \times 10^{19}$          | $5.72 \times 10^{-7}$               | $8.04 \times 10^{1}$           |
| Ca$_{2.85}$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ | $1.91 \times 10^{18}$          | $3.27 \times 10^{-6}$               | $6.96 \times 10^{1}$           |

Figure 8. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal conductivity, and (e) $ZT$ for Ca$_{3-x}$Lu$_x$Co$_{4-y}$Ga$_y$O$_9$ ceramics ($x, y = 0$, $x = 0.05, y = 0.15$, and $x = 0.15, y = 0.05$) measured along the perpendicular and parallel directions to the SPS pressure axis.
codoped samples were found to be in the range between $10^{18}$ and $10^{20}$ cm$^{-3}$ at room temperature, as shown in Table 3. Interestingly, the enhanced TE performance originated mainly from the significant reduction in thermal conductivity because of the phonon scattering through the point defects.

The results indicate that the carrier concentration decreases with Lu$^{3+}$ doping, which can be attributed to the substitution of trivalent Lu$^{3+}$ for divalent Ca$^{2+}$. In terms of valence equilibrium, it can introduce Co$^{3+}$ ions and decrease the hole carrier concentration. The Hall mobility value of each sample was in good agreement with the carrier concentration value of the same composition.

The calculated power factors of all the samples are shown in Figure 7c. Because the undoped Ca$_3$Co$_4$O$_9$ sample produced by SPS exhibited the highest electrical conductivity above 300 °C with a large Seebeck coefficient, it had the largest power factor of 5.3 μW/cm·K$^2$ at 630 °C. The power factor of the Ca$_3$Co$_4$O$_9$ sample produced by SPS was significantly improved in comparison to the CIP sample (2.2 μW/cm·K$^2$ at 630 °C).

The out-of-plane thermal conductivity of the Ca$_3$Co$_4$O$_9$ samples is shown in Figure 7d. The relative density of CIP sample was found to be 82%, while the relative density of CS sample was found to be 57%. In the relatively high-density CIP sample, the porosity was low and the oxygen out-diffusion kinetics was less favorable than the CS sample. Thus, the thermal conductivity of the CIP sample (Figure 7d) is higher than the value of the CS sample (the value will be shown in Figure 9d). The samples containing Lu and Ga exhibited lower thermal conductivity because of nanoscale interfaces, which could create additional phonon scattering. Thus, these results demonstrate that Lu and Ga codoping was an effective method to reduce the thermal conductivity of Ca$_3$Co$_4$O$_9$ produced by SPS. As shown

Figure 9. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d–f) thermal conductivity, and (g) $ZT$ for Ca$_{3-x-y-z}$Ag$_x$Lu$_y$Co$_{3+z}$Ga$_y$O$_9$ ($x=0−0.05$, $y=0−0.05$, $z=0−0.05$) polycrystalline samples from the conventional TE measurement.
in Figure S2d,e, the grains with random orientations in these samples also effectively scatter phonons with various mean free path lengths to reduce the thermal conductivity. The doping of two smaller and heavier Lutetium and Gallium ions in the Ca$_2$Co$_4$O$_9$ led to an increase in nanoscale boundary scattering and a subsequent decrease in the lattice thermal conductivity. The point defect scattering results from mass fluctuations and lattice distortion. Considering the difference in mass between the dopant Lu/Ga ions and the host Ca/Co ions, the partial substitution of Lu/Ga for Ca/Co resulted in local vibrational changes. Furthermore, this doping led to lattice distortion because of the difference in ionic radius between the dopant and host ions. Therefore, the phonon mean free path is diminished by these substitutions and this effect causes a reduction in the lattice thermal conductivity of Ca$_3$Co$_4$O$_9$. Among all of the SPS samples, the Ca$_{2.85}$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ sample had a lowest thermal conductivity of 1.9 W/m-K above 300 °C.

The ZT of the Ca$_{2.85}$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ samples ($x, y = 0, x = 0.05; y = 0.15, y = 0.05$) is shown as a function of temperature in Figure 7e. The Ca$_3$Co$_4$O$_9$ sample produced by SPS reached the maximum ZT value of 0.24 at 630 °C during the conventional TE measurement. Overall, Lu and Ga codoping successfully reduced the thermal conductivity because of the nanoscale boundary scattering while only slightly reducing the electrical conductivity. This had a positive effect on the dimensionless figure of merit ZT. However, these layered nanostructure materials had a very high directional dependence. For this reason, the TE properties of Ca$_3$Co$_4$O$_9$ samples were measured along both perpendicular and parallel directions.

The temperature dependence of the electrical conductivity, Seebeck coefficient, and power factor along perpendicular and parallel directions can be seen in Figure 8. The electrical conductivities were found to increase with temperature for both directions, and all of the samples measured along the parallel direction exhibited a significant decrease in the electrical conductivities because of the layered nanostructure. Furthermore, it is obvious that the Seebeck coefficient is sensitive to the measurement direction in high temperature ranges, as shown in Figure 8b. The maximum Seebeck coefficient value of 227 μV/K was measured at 630 °C along the perpendicular direction, which was higher than that of the result of Wu et al. reporting the values of samples fabricated by autocombustion synthesis and SPS. The electrical conductivities and Seebeck coefficient values measured along the perpendicular direction exceeded the values measured along the parallel direction at high temperature ranges, the power factor difference in between perpendicular and parallel directions was pronounced with increasing temperature. However, the thermal conductivities measured along both directions (Figure 8d) were higher than the reported values from Ca$_3$Co$_4$O$_9$ polycrystalline samples. All of the codoped samples show lower thermal conductivity than the values of nondoped samples for each direction, which was still effective in terms of nanoscale boundary scattering. Also, all of the samples measured along the parallel direction exhibited reduced thermal conductivities as compared to the perpendicular direction because of the different grain alignment and orientation. The results of the present study show similarity to those found in the earlier experimental studies on bismuth telluride. In n-type Bi$_2$Te$_3$-Se$_p$, the electrical and thermal conductivities along the in-plane (perpendicular direction to the pressure) were almost 4 and 2 times larger than those along the applied pressure direction, respectively, because of the lamellar structure and the weak van der Waals bonding between Te—Te.

The ZT values calculated for both directions are shown as a function of temperature in Figure 8e. The highest ZT value along the perpendicular direction was found to be 0.16 at 630 °C, whereas the maximum ZT value along the parallel direction was found to be 0.04 at 580 °C. When considering the ratio of the ZT values, the value along the perpendicular direction is 3 to 4 times higher than the value along the parallel direction. Such measurement results suggest that perpendicular direction to the SPS pressure axis should be the preferred direction for practical TE applications.

### 2.4. TE Properties of Textured Ca$_3$Co$_4$O$_9$ with Ag Inclusions

Even after Lu/Ga doping, the electrical conductivity of the Ca$_3$Co$_4$O$_9$ is still relatively low. Thus, Ag inclusions were incorporated into the Ca$_3$Co$_4$O$_9$ matrix in order to facilitate the preferred grain orientation and further improve the electrical conductivity of the Ca$_3$Co$_4$O$_9$. The TE properties were evaluated using in-plane electrical properties and out-of-plane thermal properties in order to compare material characteristics with published literature. Figure 9a shows the temperature-dependent electrical conductivity, indicating a semiconductor-like behavior as the electrical conductivity increases with temperature. The Ag-doped Ca$_3$Co$_4$O$_9$ SPS samples exhibited a higher electrical conductivity than that of the pure Ca$_3$Co$_4$O$_9$. The values were enhanced when only small amounts of Ag were doped in the pure Ca$_3$Co$_4$O$_9$; which agreed well with the increasing degree of orientation. However, all CS samples exhibited a poor electrical conductivity because of porous microstructure.

According to the prior report, the misfit-layered Ca$_3$Co$_4$O$_9$ has anisotropic transport properties. The grain orientation along the (00l) direction dominates the electrical conductivity in the ab-plane. The (00l) grain-oriented Ca$_3$Co$_4$O$_9$ samples exhibited higher electrical conductivity because of higher carrier mobility along the (00l) direction. Here, Ag was found to be beneficial in nanoscale texturing of Ca$_3$Co$_4$O$_9$ along the c-axis orientation, thus enhancing the electrical conductivity along the ab-plane. Furthermore, Ag inclusions were expected to increase the carrier concentration because of the formation of an impurity level narrow band gap. The Seebeck coefficient for all CS and SPS samples was positive, as shown in Figure 9b, indicating that holes were the dominant charge carriers in the electrical transport. The value of the Seebeck coefficient of the pure Ca$_3$Co$_4$O$_9$ CS sample at 100 °C was 129 μV/K. Moreover, with the SPS process, the above value exhibited a steady rise till 670 °C. Compared to the SPS samples, the CS samples represented a sudden increase in the Seebeck coefficient above 400 °C. The Seebeck coefficient is inversely proportional to the carrier concentration. Therefore, the higher electrical conductivity resulting from higher carrier concentration indicates a lower Seebeck coefficient of SPS samples in the high temperature range, which is consistent with the previous results.

The calculated power factors for all the samples are shown in Figure 9c. The power factor of SPS samples exhibited a monotonous increase with the increasing temperature, and its maximum value was recorded at 670 °C. However, the CS samples exhibited poor power factor values <1.0 μW/cm-K$^2$ because of the lower electrical conductivity over the entire temperature range. The power factor values of the CS samples (0.2–0.8 μW/cm-K$^2$) were reduced in comparison to the SPS samples (1.2–4.2 μW/cm-K$^2$). The value for the SPS sample
was 5–6 times higher than that of the corresponding value for the CS sample.

The out-of-plane thermal conductivity of the Ca$_3$Co$_4$O$_9$ samples is shown in Figure 9d. Among SPS samples, the ones containing Ag inclusions exhibited lower thermal conductivity because of the effective phonon scattering. The thermal conductivity values were reduced for the Ag-doped Ca$_3$Co$_4$O$_9$ ceramics with magnitude of 2.0–1.5 W/m·K over the temperature range of 100–670 °C. These results clearly demonstrated that the Ag inclusions were effective in reducing the thermal conductivity of Ca$_3$Co$_4$O$_9$. However, the CS samples exhibited much lower thermal conductivity (0.4–0.8 W/m·K) because of porous microstructure, which hindered phonon transport. The total thermal conductivity ($\kappa$) is the sum of electronic thermal conductivity ($\kappa_e$) and lattice thermal conductivity ($\kappa_l$), $\kappa = \kappa_e + \kappa_l$. Because the electrical conductivity is tied to electronic thermal conductivity through the Wiedemann–Franz law ($\kappa_e = L\sigma T$), where $L$ is the Lorentz number and $T$ is the absolute temperature), the electrical conductivity and the thermal conductivity are interrelated. The doped Ca$_3$Co$_4$O$_9$ SPS samples exhibited a higher $\kappa_e$ than that of the pure Ca$_3$Co$_4$O$_9$ due to the increasing $\sigma$. Therefore, the higher $\kappa_e$ value of the Ca$_{2.95}$Ag$_{0.05}$Co$_{4.05}$O$_9$ sample was attributed to the higher $\sigma$ value among all the samples, as shown in Figure 9a,e. However, all the CS samples showed poor $\kappa_e$ values because of lower electrical conductivity values. The slight reduction in total thermal conductivity of the doped Ca$_3$Co$_4$O$_9$ SPS samples, as compared to the pure Ca$_3$Co$_4$O$_9$ SPS sample, was found to be associated with the strong phonon scattering caused by the increased boundaries, nanoplatelets, and nanodefects resulting from the nanoscale texturing with Ag inclusions. Figure 9d,f shows that the lowest $\kappa$ and $\kappa_l$ value was achieved for the Ca$_{2.95}$Ag$_{0.05}$Co$_{4.05}$O$_9$ SPS sample because of the higher texturing degree, which agrees well with its higher Lotgering factor.

To further analyze the contributing factors in the thermal conductivity reduction, we need to understand the source of scattering centers. Phonons are termed as acoustic or optical phonons based on their polarization. Out of these, acoustic phonons are associated with the lattice thermal conductivity. The total thermal conductivity is mainly determined by various scattering processes, such as phonon–phonon scattering, charge carriers, lattice disorder (vacancies, interstitials, and dopants), boundaries, interfaces, and inclusions, all of which limit the phonon mean free path. Short wavelength phonons are mostly scattered by impurity atoms, whereas long wavelength phonons are scattered by larger structure such as boundaries and interfaces. Considering phonon scattering, the lattice thermal conductivity can be described as

$$\kappa_l = \frac{1}{3} C v_l$$

where $C$ is the specific heat at constant volume, $v$ is the average velocity of sound in a material, and $l$ is phonon mean free path. The mean free path $l$ indicates the distance between collisions through random phonon scattering. Nanostructure in materials can lead to a spatial confinement of phonons and affect phonon
dispersion. Thus, the acoustic phonons can be scattered when the structure is similar or smaller than the mean free path of phonons. Long wavelength acoustic phonons that have low frequency and long mean free path would be hindered from transport. The acoustic impedance mismatch also plays an important role in phonon reflection at the interface. In nanostructured bulk materials, strong phonon scattering would occur to suppress the lattice thermal conductivity because of a high density of nanostructures. In other words, nanostructures in bulk materials can lead to lattice misfit and large strain (acoustic impedance mismatch). Therefore, the inclusions in the Ca$_3$Co$_4$O$_9$ system block the propagation of mid-to-long-wavelength phonons, resulting in reduction of the lattice thermal conductivity.

The $ZT$ of the Ca$_{3−x}$Ag$_x$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ (x = 0−0.05, y = 0−0.05, z = 0−0.05) samples is shown as a function of temperature in Figure 9g. The maximum $ZT$ value of 0.25 at 670 °C was obtained for the Ca$_{3.95}$Ag$_{0.05}$Co$_4$O$_9$ SPS sample from the conventional TE measurement, indicating about 100% enhancement as compared to all the CS samples and 50% enhancement compared to the pure Ca$_3$Co$_4$O$_9$ SPS sample. Overall, the nanoscale texturing in conjunction with Ag inclusions successfully increased the electrical conductivity and reduced the thermal conductivity simultaneously because of the preferred grain orientation and nanoscale-defect-induced phonon scattering. This improved the dimensionless figure of merit $ZT$. This study demonstrates that the nanoscale texturing along with the inclusions could be a promising route toward improving the TE performance of a material. This study can be extended to other anisotropic material systems for improving their TE performance. Furthermore, the nanoscale texturing refinement and inclusions of various other metals could be utilized and implemented to achieve even higher improvement in $ZT$.

2.5. Modeling Module Performance. In order to evaluate the effect of nanoscale texturing and engineered interfaces on TE performance of Ca$_3$Co$_4$O$_9$, a TE module including both n and p-type was designed and simulated with nanostructured ZnO$^{52}$ and textured Ca$_3$Co$_4$O$_9$ particles as shown in the inset of Figure 10a. A pair of n-type ZnO and p-type Ca$_3$Co$_4$O$_9$-based materials was selected for the 7.5 × 3.75 × 5.52 mm$^3$ module. The model with the ZnO and Ca$_3$Co$_4$O$_9$ was made with given boundary conditions, which were at fixed temperatures on both hot and cold side, as indicated in the inset of Figure 10a. The size for the TE generator legs was 2.4 × 2.4 × 4 mm$^3$. The detailed modeling conditions of the TE generator can be found in a paper by Lee et al.$^{53}$ The newly developed Ca$_{3.95}$Ag$_{0.05}$Co$_{3.95}$Ga$_{0.05}$O$_9$ shows a $ZT$ value of 0.15 at 430 °C, and the performance of this module is shown in Figure 10b−d. The module with reference materials produced the open circuit voltage of 0.097 V and the maximum output power of 0.028 W when the temperature difference is 300 K ($T_{hot} = 400$ °C, $T_{cold} = 100$ °C). For the module with textured Ca$_{3.95}$Ag$_{0.05}$Co$_{3.95}$Ga$_{0.05}$O$_9$ the same temperature difference condition resulted in the open circuit voltage of 0.1 V and the maximum output power of 0.044 W. The estimated TE conversion efficiency of the new Ca$_3$Co$_4$O$_9$-based device was 1.38% (~65% higher than the efficiency (0.84%) of the normal Ca$_3$Co$_4$O$_9$-based device). Furthermore, the calculations indicate that output power of 2.15 W can be obtained for the full size model (50 couples) when the hot side temperature is 400 °C (Figure 10e).

3. CONCLUSIONS

We have demonstrated the enhancement of TE performance of Ca$_3$Co$_4$O$_9$ via nanoscale texturing and engineered interfaces with Ag inclusions. This strategy modified the crystal structure of Ca$_3$Co$_4$O$_9$ and induced phonon scattering by point defects, leading to lower thermal conductivity. Codoping and SPS-based synthesis processes were found to be effective toward improving power factor and $ZT$ values of polycrystalline Ca$_3$Co$_4$O$_9$. Nanoscale texturing along c-axis provided advantage of higher electrical conductivity and reduced thermal conductivity in SPS samples. Both nanoscale texturing along c-axis and inclusions were found to be beneficial for effective phonon scattering. The lattice thermal conductivity of doped SPS samples at high temperatures was almost 50% reduced as compared to undoped SPS material, which led to the improvement in $ZT$ by 50%. The Ag inclusions also acted as electrical connectors in the matrix increasing electrical conductivity. Overall, the synergic effect of the crystallographic-textured Ca$_3$Co$_4$O$_9$ and nanoscale inclusions resulted in higher electrical conductivity and lower thermal conductivity, enhancing the TE response (enhanced $ZT$). The anisotropy in the transport properties was found to be critical for the TE performance in commercial applications. We believe that these results will be helpful in fabrication of high-performance oxide TE materials for high-temperature applications.

4. EXPERIMENTAL SECTION

4.1. Sample Preparation. Ca$_{3−x}$Lu$_x$Co$_{3.95}$Ga$_{0.05}$O$_9$ (x = 0, y = 0.05, z = 0.15, and x = 0.15, y = 0.05) and Ca$_{3−x}$Ag$_x$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ (x = 0−0.05, y = 0−0.05, z = 0−0.05) ceramic powders were synthesized through a solid-state reaction method. These powders were sintered through either CS or SPS. A stoichiometric amount of CaCO$_3$ (99.0%, Sigma-Aldrich), Co$_3$O$_4$ (99.9%, Sigma-Aldrich), AgNO$_3$ (99.9+%, Alfa Aesar), Lu$_2$O$_3$ (99.9%, Sigma-Aldrich), and Ga$_2$O$_3$ (99.99%, Sigma-Aldrich) powders were mixed through ball-milling in ethanol medium for 24 h. The mixture was dried and calcined in air at 800 °C for 24 h. The calcined powder was further ball-milled and in order to synthesize single-phase Ca$_3$Co$_4$O$_9$ and the resulting powder was calcined again in air at 850 °C for 24 h. The calcined Ca$_3$Co$_4$O$_9$ powder was ball-milled again and mixed with a polyvinyl alcohol binder solution. Next, the mixture was uniaxially pressed at 1 kpsi followed by CIP at 20 kpsi for 1 min. A binder burn-out process was performed at 600 °C for 2 h, and Ca$_3$Co$_4$O$_9$ was sintered at 1200 °C for 24 h, then cooled down to 700 °C before being sintered at 900 °C for 12 h in ambient air. Ca$_{3−x}$Ag$_x$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ samples (x = 0−0.05, y = 0−0.05, z = 0−0.05) were conventionally sintered at 900 °C for 12 h in an ambient air. During the processing, heating and cooling rates were set at a rate of 1 °C/min.

To improve the TE performance of Ca$_3$Co$_4$O$_9$, SPS processing was carried out for Ca$_{3−x}$Lu$_x$Co$_{3.95}$Ga$_{0.05}$O$_9$ (x = 0, y = 0.05, x = 0.05, y = 0.15, and x = 0.15, y = 0.05) and Ca$_{3−x}$Ag$_x$Lu$_{0.15}$Co$_{3.95}$Ga$_{0.05}$O$_9$ (x = 0−0.05, y = 0−0.05, z = 0−0.05) ceramics. The samples were heated at 850 °C under a uniaxial pressure of 50 MPa for 5 min. All samples were cut in perpendicular and parallel directions by the low-speed diamond saw to obtain bar-shaped and disk-shaped samples for TE measurements. Extreme care was taken to ensure that all the thermal and electrical measurements are conducted in the same material direction.
4.2. Material Characterization Techniques. XRD (Bruker D8 diffractometer) was used to identify the phases of the CS and SPS pellets. Microstructures of the samples were analyzed by FESEM (LEO (Zeiss) 1550 field-emission). The BSE mode in environmental SEM (FEI Quanta 600 FEG) and EDS (Bruker EDX with a silicon drifted detector) were used for elemental mapping. Transmission electron microscopy (TEM; FEI Titan 300) was employed to examine the morphology and microstructure of the sample. XPS (PHI Quantera XSM) was performed using a scanning monochromatic X-ray source with a highly focused beam (<9 µm) to identify the chemical states of the samples. The densities of the samples were measured by Archimedes’ method. The Seebeck coefficient and the electrical conductivity were measured simultaneously from 100 to 670 °C using a commercial TE measurement system (ULVAC-RIKO ZEM-3). A bar-shaped sample with dimensions 2.5 mm × 2.5 mm × 12 mm was used for the measurement in a low-pressure (0.01 MPa) helium atmosphere. The thermal diffusivity was measured using a laser flash system (ULVAC-RIKO TC-1200RH). Specific heat was measured with a differential scanning calorimeter (Netzsch DSC 404C). A disk-shaped sample of 10 mm diameter and 1 mm thickness was used for evaluating thermal conductivity. The thermal conductivity, κ, was calculated from relation, $\kappa = \alpha \rho C_p$, where $\alpha$ is thermal diffusivity, $\rho$ is density, and $C_p$ is the specific heat. Hall effect measurements were performed with the van der Pauw geometry and carrier concentration was calculated from the relation $H = \frac{V_{th}}{R_{th} \mu}$, where $V_{th}$ is the Hall voltage, $R_{th}$ is the Hall resistance, $\mu$ is the Hall mobility, and $\sigma$ is the electrical conductivity.

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**ASSOCIATED CONTENT**

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01552.

Crystalline structure of Ca3Co4O9g; XRD patterns, XRD refinement results, and SEM images of Lu and Ga-doped Ca3Co4O9g; HR-TEM images of Ca3Co4O9g; FESEM images of Ag-doped Ca3Co4O9g; the carrier concentration–TE properties plot; lattice parameters; average grain size and thickness of platelets; and chemical compositions and crystallographic data of doped samples (PDF)

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