# Synthesis and Thermoelectric Properties of Barium Doped Calcium Cobalt Oxide (Ca<sub>3-x</sub>Ba<sub>x</sub>Co<sub>4</sub>O<sub>9</sub>)

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#### Abstract

Energy dissipation in the form of heat from sources such as automobiles, aircraft turbines, power plants, and factories is largely unrecovered, accounting for approximately 70% of the primary energy produced. To address this challenge, thermoelectric energy converters can partially recover this wasted heat and improve system efficiency. Thermoelectric generators (TEGs), made from semiconducting materials, are ideal for such applications. Conventional thermoelectric generators utilize intermetallic compounds, such as lead and bismuth tellurides or silicon-germanium alloys. However, these materials face limitations such as decomposition at relatively low temperatures, low precursor availability, high toxicity, and high cost. As a result, thermoelectric oxides have emerged as a more favourable alternative, as they avoid many of the drawbacks associated with intermetallic compounds. This study synthesized barium-doped calcium cobalt oxide (Ca3xBaxCo4O9, x = 0.0, 0.02, 0.04, 0.08%) thermoelectric samples using the Sol-gel method. The thermoelectric properties, including the Seebeck coefficient, electrical conductivity, and thermal conductivity, were systematically investigated. Xray diffraction (XRD) and scanning electron microscopy (SEM) analyzed phase purity and surface morphology. XRD confirmed that all samples exhibited a single-phase structure. The doping of barium resulted in enhanced thermoelectric properties, as evidenced by significant improvements in the dimensionless Figure of merit, which reached  $1.35 \times 10^{-12}$  at room temperature, compared to the undoped sample with a zT of  $1.16 \times 10^{-12}$ . These findings demonstrate the potential of the sol-gel method to synthesize barium-doped thermoelectric materials with improved thermoelectric performance, offering promising prospects for more efficient energy conversion in various applications.

**Keywords:** Thermoelectric generators, Sol-gel method, Barium-doped materials, thermal conductivity, Figure of merit (zT).

#### **1.0 INTRODUCTION**

In recent years, there has been growing interest in thermoelectric materials due to their remarkable ability to convert waste heat directly into electricity, creating new opportunities for energy harvesting and cooling applications. This phenomenon, known as the thermoelectric effect, offers a sustainable and renewable method for thermal engineering and energy generation by converting a temperature gradient into electrical power. High-temperature waste heat plays a vital role in providing a large temperature difference, thereby improving conversion efficiency, as it can deliver a heat source temperature higher than the heat sink temperature. Most industrial applications, which require energy conversion or generate heat, lose a significant amount of energy through waste heat. These thermal losses are primarily caused by process inefficiencies and the inability of current technologies to recover and utilize the excess energy.

Furthermore, due to the need for heat-stable power sources, oxides have emerged as a promising candidate for large-scale thermoelectric applications. They are particularly suitable as p-type compounds, exhibiting excellent thermal stability in air up to 1199 K, and thermally decompose to  $Ca_3Co_2O_6$  above this temperature [2]. Thermoelectric materials can be classified according to their temperature ranges. These materials exhibit diverse thermal properties and are typically categorized into semi-metals, semiconductors, and crystalline ceramics [3]. The major classes of thermoelectric materials include Bismuth Chalcogenides, Lead Telluride, Inorganic Clathrates, Magnesium-based Group-IV Compounds, Skutterudites, Oxides, and Half-Heuslers.

Chalcogenides are compounds formed with elements from Group 16 of the periodic Table, with oxygen playing a significant role due to its position. Bismuth Chalcogenides, composed of bismuth and chalcogen elements, are highly regarded for their excellent performance at room temperature, with a figure of merit (zT) approximately equal to 1. Lead Telluride, consisting of lead and tellurium, occurs naturally in solid form and has a crystal structure similar to sodium chloride. It demonstrates good electrical conductivity due to its narrow band gap. Inorganic Clathrates, which are compounds formed by incorporating molecules of one kind into the cavity of a crystal lattice, exhibit outstanding thermoelectric properties. These materials can be synthesized to meet specific requirements and properties [4]. Thermoelectric properties of Magnesium combined with Group-IV compounds (such as BMg<sub>2</sub>, where B represents Si, Ge,

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Sn) are comparable to those of Inorganic Clathrates within certain temperature ranges. Skutterudites, represented by the formula ( $RT_4E_{12}$ ), where R is a rare earth metal, T is a transition metal, and E is a metalloid, show thermoelectric properties that lie between metals and non-metals. Thermoelectric oxides, which contain oxygen as a constituent, are created by combining different elements in various stoichiometric ratios. N-type oxides, such as zinc oxide, have attracted significant attention due to their high electrical conductivity and high melting point {5}. Despite their insulating nature, oxides are considered promising thermoelectric materials. Half-Heusler alloys, which are ferromagnetic in nature, lose their magnetic properties when combined with their unique structure, behaving instead as nonmagnetic materials. The thermoelectric properties of Half-Heusler materials are influenced by the number of free electrons in their unit cell [6].

This research focused on barium-doped calcium cobalt oxide's thermoelectric properties and synthesis techniques. The primary objective was to enhance the understanding of the intrinsic characteristics of the material and explore its potential for practical energy conversion applications. We aim to investigate various synthesis routes and evaluate the thermoelectric performance of barium-doped calcium cobalt oxide, emphasizing its suitability for energy harvesting. By examining the synthesis-structure-property relationships, this study aims to pave the way for integrating barium-doped calcium cobalt oxide into cutting-edge thermoelectric technologies [7-8]. With its significant thermoelectric properties, such as a large Seebeck coefficient, adjustable thermal conductivity, and high electrical conductivity, this material holds promise for efficient thermoelectric energy conversion. The ultimate goal is to advance the application of this material in real-world technologies that address pressing challenges in resource efficiency and energy sustainability. Future work will also explore alternative doping strategies and the impact of various doping concentrations beyond 8%.

### 2. MATERIALS AND METHODS

The samples were prepared using the sol-gel technique. In a calculated ratio, the sample powders were synthesized using chemical reagents (pentahydrate calcium nitrate and hexa-hydrate cobalt nitrate). The mixture was magnetically stirred at 360 K for 3 hours. The resulting sol-gel solution was then dried for 2 hours at a temperature of 395 K. The obtained powder was ground into a fine powder and further calcined for 4 hours at a temperature of 860 K. At room temperature, the final powder was converted into spherical pellets under a pressure of 5 MPa using cold pressing. Figure 1 illustrates the process of forming ceramic pellets from the powder obtained via the sol-gel technique.





The chemical reagents were mixed to synthesize  $Ca_{3-x}Ba_xCo_4O_9$  (x = 0.00, 0.02, 0.04, 0.08) powders using the sol-gel method. To synthesize barium-doped  $Ca_3Co_4O_9$ , tetrahydrate calcium nitrate, hexa-hydrate cobalt nitrate, and barium nitrate were dissolved in a citric acid solution. The solution was then magnetically stirred at 360 K for 3 hours. The obtained sol-gel solution was dried for 2 hours at 395 K. The powder was then calcined in a furnace for 4 hours at 860 K. The powder was compacted into 13 mm spherical pellets at room temperature under a pressure of 5 MPa for 20 minutes. The synthesized materials were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to study structural and compositional properties.

### **3. RESULTS AND DISCUSSION**

The X-ray diffraction (XRD) patterns of barium-doped  $Ca_3Co_4O_9$  samples displays in the Fig.(2), reflects the characteristic peaks identifying the  $Ca_3Co_4O_9$  phase possessing monoclinic symmetry (PDF: #23-110). It was observed that except for the sample with the highest doping concentration (x = 0.08), the XRD patterns show no significant shift in peak angles. This lack of deviation suggests that barium doping has a negligible effect on the lattice characteristics of  $Ca_3Co_4O_9$ . The consistent identification of the  $Ca_3Co_4O_9$  phase across all samples confirms the successful synthesis of barium-doped materials using the sol-gel method. The absence of notable shifts in peak angles indicates the stability of the monoclinic structure, demonstrating that barium ions were effectively incorporated without causing significant changes to the lattice [9].

### **3.1.** Crystal Structure

### 3.1.1. X-ray diffraction (XRD)

The investigation further includes the computation of crystallite size based on the obtained XRD data. While the highest doping concentration (x = 0.08) exhibits distinct characteristics, the other concentrations demonstrate similar crystallite sizes, indicating that most of the samples maintained a comparable crystal structure, highlighting the reliability of the synthesis method [10]. The lack of significant shifts in XRD peak angles, except for the highly doped sample, suggests that barium ions have minimal effect on the lattice characteristics of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>. This observation is vital for understanding the structural stability of the synthesized materials, supporting their suitability for thermoelectric applications [11]. The preservation of the monoclinic structure, as identified by XRD, indicates the robustness of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> lattice against barium doping. This structural stability is advantageous for the desired applications of these materials in thermoelectric devices, where maintaining a consistent crystal structure is vital for optimizing electronic and thermal transport properties [12].

Sample	a(Å)	b(Å)	c(Å)	β(θ)	Volume (Å <sup>3</sup> )	D (nm)
						D=Kλ/βcosθ
Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub>	4.909	4.525	10.514	99.54	233.53	40.76
$Ca_{2.98}Ba_{0.02}Co_4O_9$	4.907	4.521	10.527	99.56	233.72	54.14
$Ca_{2.96}Ba_{0.04}Co_4O_9$	4.905	4.522	10.549	99.57	233.98	55.56
$Ca_{2.98}Ba_{0.02}Co_4O_9$	4.904	4.523	10.658	99.63	234.20	59.21

Table 1: XRD results of pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and barium-doped Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>

The variations in the values are due to the doping of barium into calcium, which causes variation owing to size differences [13]. The highest intensity of highly doped  $Ca_3Co_4O_9$  is observed between 16- and 17-degree angles.



Figure 2: XRD pattern and analysis of crystallite size of pure and barium doped calcium cobalt oxide: (a) XRD of pure and barium doped calcium cobalt oxide; (b) Peak shift towards lower angle in XRD of pure and barium doped calcium cobalt oxide and crystallite size.

#### 3.1.1. Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) images, taken at a scale of 10  $\mu$ m (Fig. 3), reveal details regarding the morphology of the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> particles. The examination reveals a significant increase in crystal growth, particularly evident in the particles subjected to barium doping [14]. This growth is attributed to the presence of barium ions, indicating their role in promoting the enlargement of the crystal structures.



Figure 3: SEM Images & Histograms with different concentrations: (a) pure sample i.e. x=0; (b) barium doped i.e. x=0.02; barium doped i.e x=0.04; barium doped i.e x=0.08;

consolidates the quantitative analysis of particle sizes, confirming a noticeable enlargement induced by the doping of barium in  $Ca_3Co_4O_9$ . Presented in the Table (2). This observation aligns with the visual evidence from SEM images, providing a comprehensive understanding of the effect of barium doping on the particle dimensions [15]. The SEM images showcase crystal growth and highlight agglomeration, a phenomenon (Fig. 3).

Sr. No.	Sample	No. of particles	Average Area µm²
1.	Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub>	728	11.481
2.	$Ca_{2.98}Ba_{0.02}Co_4O_9$	1298	13.695
3.	$Ca_{2.96}Ba_{0.04}Co_4O_9$	1850	14.235
4.	$Ca_{2.92}Ba_{0.08}Co_4O_9$	2024	17.931

Table 2: Quantitative analysis of particle sizes for barium dope calcium cobalt oxide.

This agglomeration results from barium doping in  $Ca_3Co_4O_9$  and plays a vital role in the subsequent enhancement of electrical resistivity. Agglomeration introduces irregularities in the material, leading to increased scattering of charge carriers. The enhanced scattering impedes the smooth movement of incoming carriers, consequently contributing to an overall rise in electrical resistivity. This observation is consistent with the established understanding that agglomeration in materials often correlates with increased resistivity. Understanding the relationship between crystal growth, particle size, and grain clustering is crucial for optimizing the thermoelectric properties of the synthesized materials [16]. While crystal growth may contribute to improve thermoelectric characteristics, the agglomeration-induced increase in electrical resistivity necessitates careful fine-tuning to strike a balance between these competing influences. The SEM analysis provided valuable insights into the morphological changes induced by barium doping in  $Ca_3Co_4O_9$  [17]. The observed crystal growth, particle enlargement, and agglomeration contribute to the nuanced understanding of how these materials may perform in thermoelectric applications. The subsequent sections will delve into the implications of these morphological features on the overall thermoelectric performance of the synthesized materials.

#### 3.2. Thermoelectric Properties / Measurement

The relation of Seebeck Coefficient is given below;

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$$\frac{8\pi^2 K2B}{eh2m^* T(\pi/3n)^{0.66}}$$
 (1)

The Seebeck coefficient, shown in Equation (1), demonstrates a significant dependence on the doping concentration. As the effective mass increases, so does the Seebeck coefficient, with a noticeable enhancement in the Seebeck coefficient for the doped samples. The Seebeck coefficient of  $Ca_3Co_4O_9$  increases from 92 V/K to 110.7 V/K with increasing barium doping, signalling an improvement in thermoelectric efficiency. This result aligns with the general principle that lower carrier concentrations lead to higher Seebeck coefficients [18]. The enhancement in Seebeck coefficient signifies better thermoelectric performance and indicates that the material may be better suited for energy harvesting applications.



Figure 4: Influence of barium doping on Seebeck coefficient of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>

Figure(4) shows that increasing the barium concentration enhances the Seebeck coefficient. The Seebeck coefficient (S) values for Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and Ca<sub>2.92</sub>Co<sub>4</sub>O<sub>9</sub>Ba<sub>0.08</sub> exhibit a clear trend with increasing doping concentrations. Specifically, there is a significant enhancement in the Seebeck coefficient as the concentration of barium doping increases. This improvement is particularly evident when comparing the undoped sample (Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>) and the highly doped sample (Ca<sub>2.92</sub>Co<sub>4</sub>O<sub>9</sub>Ba<sub>0.08</sub>). At room temperature, the Seebeck coefficient rises from 92  $\mu$ V/K for Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> to 110.7  $\mu$ V/K for Ca<sub>2.92</sub>Co<sub>4</sub>O<sub>9</sub>Ba<sub>0.08</sub>. This increase in the Seebeck coefficient is a positive indicator of improved thermoelectric efficiency. The Seebeck coefficient is a crucial parameter in thermoelectric materials, reflecting their ability to convert temperature differences into electrical voltage. Doping introduces impurity levels and alters the carrier concentration decreases, indicating a more favourable thermoelectric behaviour. This correlation aligns with established principles in thermoelectric material science, where the interplay between carrier concentration and the Seebeck coefficient is essential for optimizing thermoelectric performance. The increase in the Seebeck coefficient signifies that the doped samples have a higher efficiency in converting thermal gradients into electrical voltage, enhancing their overall thermoelectric capabilities [20].

### 3.2. Implications for Thermoelectric Applications

The observed improvement in the Seebeck coefficient, coupled with the correlation to reduced carrier concentration, holds promising implications for the thermoelectric performance of barium-doped  $Ca_3Co_4O_9$ . Higher Seebeck coefficients contribute to increased thermoelectric efficiencies, making these materials more suitable for energy harvesting applications where converting waste heat into electricity is paramount [21].

The results demonstrate that barium doping in  $Ca_3Co_4O_9$  leads to a favourable enhancement in the Seebeck coefficient, indicative of improved thermoelectric properties.

The following formula gives the electrical resistivity:

$$\rho = RA/L$$
(2)

The electrical resistivity, as depicted in Fig.(5), demonstrates a clear dependence on barium concentration in  $Ca_3Co_4O_9$ . The observed changes in electrical resistivity highlight the dopant's influence on the material's structure and electrical properties. This is due to localized strain effects caused by substituting  $Ca^{2+}$  ions with  $Ba^{2+}$  ions, which disrupts the crystal structure, increasing the scattering of charge carriers. This structural distortion contributes to an increase in electrical resistance within the material [22].



Figure 5: Impact of barium doping on electrical resistivity of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>

As the doping level rises, the resistivity of barium-doped  $Ca_3Co_4O_9$  consistently increases. This observation suggests that a higher concentration of barium leads to greater material density, contributing to increased electron scattering. The rise in resistivity is a consequence of the enhanced hindrance to the flow of charge carriers, hindering the material's electrical conductivity. The inherent monoclinic structure of  $Ca_3Co_4O_9$  plays a significant role in its electrical characteristics.

The observation that a more aligned crystal structure may improve electrical characteristics aligns with the principles of crystalline materials. A well-aligned crystal structure facilitates more efficient charge carrier movement, enhancing electrical conductivity. The observed increase in electrical resistivity due to barium doping, while presenting a challenge in terms of electron scattering, also offers opportunities for optimization. Understanding the interplay between doping levels, structural changes, and electrical resistivity is essential for tailoring the material's properties for specific applications [23]. In thermoelectric applications, the delicate balance between resistivity and other parameters, such as the Seebeck coefficient and thermal conductivity, determines the overall efficiency of energy conversion.

Further investigations into optimizing the doping concentration and refining the crystal structure may yield materials with improved thermoelectric performance. Figure (6) shows a decrease in thermal conduction due to increased doping concentration of barium into  $Ca_3Co_4O_9$ . The doping of barium reduces the thermal conductivity of the material. The difference in thermal conductivity of material concerning doping produces a defect which resultantly scatters the phonons of short and long wavelengths. From the discussion, we deduced that adding barium as a dopant can decrease thermal conductivity. Moreover, the interplay between doping, crystal structure, and phonon-electron interactions highlights the complexity of engineering materials for specific applications. Future studies should focus on understanding the detailed mechanisms by which doping influences both electronic and phononic properties, as well as on exploring potential post-processing techniques such as annealing or strain engineering to further optimize the material's performance [24]. Through these efforts, it may be possible to develop barium-doped  $Ca_3Co_4O_9$ -based materials with improved thermoelectric efficiency, making them viable candidates for energy harvesting applications, such as in thermoelectric generators or waste heat recovery systems.



Figure 6: Effect of barium doping on thermal conductivity of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>

The Figure of merit (zT) of the sample varies and acts as a function of the concentration of barium at room temperature (Fig. 7).



Figure 7: Influence of barium doping on Figure of Merit (zT) of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>

The increase in Figure of merit(zT) is due to a considerable drop in thermal conductivity and increased thermoelectric efficiency. The rise in the zT value with respect to the doping of barium into Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> is expressed in Table(3).

Sr. No.	Sample	Doping	zT
1.	Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub>	Pure	$1.18 \times 10^{-12}$
2.	$Ca_{2.98}Ba_{0.02}Co_4O_9$	x=0.02	$1.22 \times 10^{-12}$
3.	Ca <sub>2.96</sub> Ba <sub>0.04</sub> Co <sub>4</sub> O <sub>9</sub>	x=0.04	$1.29 \times 10^{-12}$
4.	$Ca_{2.92}Ba_{0.08}Co_4O_9$	x=0.08	$1.34 \times 10^{-12}$

Table 3: Influence of barium doping on Figure of Merit (zT) of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>

Table (4) provides an overview of the influence of doping at room temperature on thermoelectric parameters and the percentage increase in thermoelectric efficiency.

<b>Sr.</b> #	Sample	Seebeck	Electrical	Thermal	zT	Percentage
		coefficient	resistivity	conductivity		increase in zT
1.	Ca <sub>3</sub> Co <sub>4</sub> O <sub>9</sub>	93.6x10 <sup>-6</sup>	$1.12 \times 10^{6}$	2.15	$1.18 \times 10^{-12}$	Pure sample
2.	$Ca_{2.98}Ba_{0.02}Co_4O_9$	96.3x10 <sup>-6</sup>	$1.21 \times 10^{6}$	2.02	$1.22 \times 10^{-12}$	3.3% increase
3.	$Ca_{2.96}Ba_{0.04}Co_4O_9$	99x10 <sup>-6</sup>	$1.32 \times 10^{6}$	1.91	$1.29 \times 10^{-12}$	9.3% increase
4.	$Ca_{2.92}Ba_{0.08}Co_4O_9$	110x10 <sup>-6</sup>	$2.05 \times 10^{6}$	1.47	$1.34 \times 10^{-12}$	13.5% increase

Table 4: Overview of thermoelectric parameters of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> with doping of barium

## Conclusion

The research has provided valuable insights into the thermoelectric properties of barium-doped Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> synthesized using the sol-gel method. Notably, the absence of Spark Plasma Sintering (SPS) during the study raises intriguing prospects for further exploration. SPS is known for reducing porosity in materials, leading to densification and enhanced electrical conductivity. While the current work focused on room temperature conditions, the absence of SPS treatment provides a unique avenue for investigation [25]. Future studies incorporating SPS could provide a comparative analysis, shedding light on the impact of densification on thermoelectric properties, especially at elevated temperatures.

Moreover, the findings presented in this paper open the door for potential research extensions. High-temperature studies could offer a more comprehensive understanding of the behaviour of the material under varying thermal conditions. Additionally, exploring different dopant concentrations or alternative doping strategies may further optimize the thermoelectric efficiency of the synthesized materials.

This work serves as a foundation for future investigations that could leverage SPS and explore a broader range of operating temperatures. The outcomes of such studies could contribute to the ongoing efforts to develop efficient and sustainable thermoelectric materials for energy conversion applications.

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