# Thermoelectric properties of hot-pressed pellets of AI and Ti co-doped calcium cobalt oxides ( $Ca_{(3-x)}AI_xCo_{(4-y)}Ti_yO_{9+\delta}$ )

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# Abstract

This work demonstrates the achievement of high thermopower in the pellets of calcium cobalt oxide (Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>) co-doped with aluminium (Al) and titanium (Ti). The pellets of Ca<sub>(3-x)</sub>Al<sub>x</sub>Co<sub>(4-y)</sub>Ti<sub>y</sub>O<sub>9+ $\delta$ </sub> with x, y = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5, oxide ceramics are prepared using a hot-press machine by applying an uniaxial pressure of 70 MPa at a dwell temperature of 850 °C. Microstructure imaging reveals compactness of good connectivity among grains with the estimated density using Archimedes principle suggests the formation of near perfect (99%) relative density for the new pelleted ceramics. All the co-doped samples exhibit lower electrical resistivity ( $\rho$ ) values compared to pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>. The maximum Seebeck coefficient (S) of 177  $\mu$ V/K at 750 K is achieved for the pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> sample. A significant improvement of 18% in the power factor (S<sup>2</sup>/ $\rho$ ) is realized at 750 K in the co-doped samples containing 0.2 mol% of Al and Ti co-doping. The demonstration of significant thermoelectric properties of Ca<sub>(3-x)</sub>Al<sub>x</sub>Co<sub>(4-y)</sub>Ti<sub>y</sub>O<sub>9+ $\delta$ </sub> suggest that these materials could be utilized as promising active material in thermoelectrics. Copyright © 2018 VBRI Press.

Keywords: Electrical resistivity, thermoelectric materials, power factor, seebeck coefficient.

# Introduction

Thermoelectric technology is considered as a safe and promising energy harvesting that converts waste heat energy from different industrial and energy producing systems directly into the electricity. Materials with higher Seebeck coefficient (S) values have potential for the thermoelectric power generation and fabrication of devices leading to the energy conversion [1]. Layered misfit chalcogenide structures have gained much attention in research and development for their potential applications in thermoelectrics. Recently, the layered cobaltites and oxide materials including NaCo<sub>2</sub>O<sub>4</sub> single crystal [2,3,4],  $Bi_2Sr_2Co_2O_x$ ,  $Bi_2Ba_2Co_2O_x$  [4], and Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> **[3,5]** have been gained significant attention as thermopower material and have demonstrated interesting thermoelectric properties with descent thermal and chemical stability at high temperature, low cost and easy manufacturing. Co-based oxide Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> has been largely investigated due to its thermal and chemical stabilities at high-temperature in air [6] with best thermoelectric property e.g., ZT = 0.83 at 973 K for the single crystal [7].

Recently, more attention towards the Co-based oxides is realised because of their good thermoelectric performance [3] with large thermopower, and thermal and

chemical stabilities at high-temperature in ambient conditions [2]. Our research group previously studied the enhancement of thermoelectric properties in the  $ZrO_2$  doped  $Ca_3Co_4O_9$  micro/nano-composites [5]. In the present work, Al and Ti co-doped Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> have been prepared by hot-press sintering method. The thermoelectric properties of the resulting  $Ca_{(3-x)}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  micro/nano-structures have been tested by analyzing various properties recorded using the imaging, spectral, and electrical techniques, and the percentage of co-doping materials have been optimized to achieve improved thermoelectric properties. The powder of calcium cobalt oxide were hot-pressed at 1123 K for 20 minutes using a hot-press machine supplied by Insmart Systems, Hyderabad, India. Highly compressed pellets using hot-press technique indicate a near perfect 99 % dense material contents, as estimated by the Archimedes principle. The parameters measuring the properties includes ΤE thermal stability by thermogravimatric and differential thermal analysis, Seebeck coefficient (S), and electrical resistivity  $(\rho)$ . The power factor estimated as  $S^2/\rho$ , are recorded for the hot-pressed pellets.

# **Experimental details**

### Materials/Chemicals

All chemicals used in this work are high purity AR grade and procured from the Alfa Aesar. In the present work, CaCO<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, alumina crucible are used as the precursors for the synthesis of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> hot-pressed pellets.

# Material synthesis/Reactions

The polycrystalline  $Ca_{(3-x)}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  samples are synthesized by solid state reaction from CaCO<sub>3</sub> (99.5%), Co<sub>3</sub>O<sub>4</sub> (99.7%), TiO<sub>2</sub> nanoparticle (99.5%), and Al<sub>2</sub>O<sub>3</sub> nanoparticles (99.9%) powders for x, y = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5, which are identified as S0, S1, S2, S3, S4, and S5, respectively in this study. The CaCO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> powders are mixed and milled for 1 h in methanol by planetary ball mill. The as-prepared mixture is taken out and milled with Co<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub> for another 1 h in the same solvent. The resulting powder is ball milled with methanol for 24 hrs using zirconia ball followed by drying and calcination in furnace at 1173 K for 24 hrs. The calcined powder is hot-pressed by a home-made system (made by Insmart system, Hyderabad, India) by employing means of hydraulic cylinder for pressing. The calcined powder (approxmately 7 g) is loaded into the graphite die, and held between two plungers. The die along with two plungers is loaded into the machine and held in place between the top & bottom ram (piston rod) of hydraulic cylinder with help of graphite discs. After loading the sample, the vacuum chamber is closed, vacuum of the order of 10<sup>-4</sup> bar is created, and electric current is passed from the top ram to the bottom ram to achieve heating of the sample piece held between the two rams in accordance with Joule's law. The sample is held under hydraulic load of 70 MPa and heated at 250°C/min to obtain 850°C. This temperature is maintained for 20 mins. For a die of 20 mm internal diameter it has been observed that the passage of about 750 A current will result in heating rate up to 250°C/min. Thereafter, the electric current is slowed down at a rate of cool down 200° C/min. The vacuum is broken and as the sample temperature falls to about 100 °C, the rams are separated and the sample piece is withdrawn from the chamber. All the prepared circular pellets of thickness 10 mm and 20 mm diameter are polished to clear the graphite foil and finally heated in a furnace at 500°C for 2 hrs. for other characterizations.

# Characterizations / device fabrications / response measurements

The surface morphology of the as-synthesized samples is imaged using the field emission scanning electron microscope (Tescan Mira 3 machine). Powder X-ray diffraction (XRD) patterns ( $2\theta$ , 5°–65°) of the sintered hotpressed pellets are recorded using X-ray diffractometer (XRD; Bruker D8 Discover). The density of the prepared samples are measured by Archimedes principle). Thermogravimetric analysis (TGA) are performed from room temperature to 1200 K on TA SDT 600 with heating rate of 10K/min. The electrical resistivity and Seebeck coefficient of the prepared samples were measured from room temperature to 750 K using a set-up supplied by Marine India pvt. Ltd, New Delhi and sintered the calcined powder by hot-press machine (Insmart Systems; Hyderabad, India).

# **Results and discussion**

# Microstructural analysis

Fig. 1 shows the FESEM images of the typical microstructure of the fractured surfaces for solid state prepared Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> materials pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and co-doped Ca<sub>(3-x)</sub>Al<sub>x</sub>Co<sub>(4-y)</sub>Ti<sub>v</sub>O<sub>9+δ</sub> samples S0, S1, S2, S3, S4, and S5. For all samples, closed packed compact disk like grains of various sizes are observed to be scatterd in all orientations. Al and Ti granulled particles are uniformly distributed, and located at the grain boundaries and voids of the origional Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> micro-platelets. The density of the co-doped granules increases with increasing the doping contents in the samples from S1 to S5. The average grain size is found to be approximately 3µm corresponding for the samples S0, S1, S2, S3, S4, and S5 respectively. After immersing the samples in water for 24 hrs., the platelets shows no weight loss or no deformations indicating no porosity and the hardness is intact in the newly formed materials after doping. The values obtained for the density of the samples are almost close to 100 percent to relative density for S0, S1, S2, S3, S4, and S5, which are estimated using Archimedes principle to be 4.66, 4.65, 4.67, 4.66, 4.65, and 4.66 g/cm<sup>3</sup>, respectively.



Fig. 1 FESEM image of the fractured surfaces of the sintered pure and co-doped samples (a) S0, (b) S1, (c) S2, (d) S3, (e) S4, and (f) S5.

#### X-ray diffraction analysis

Fig. 2 shows the XRD pattern of the hot-press sintered pure, and Al and Ti co-doped Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> samples,  $Ca_{(3-x)}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  pellets with x, y = 0, 0.1, 0.2, 0.3,0.4 and 0.5. All the indexed diffraction peaks agree well with the JCPDS data 023-0110 suggested for the pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> crystal. This confirms the formation of pure phase for the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> and indicates no unwanted reaction has taken place during co-doping of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>. The Reitveld fit (red lines) to the XRD patterns (blue data points) using TOPAS software for the pellets sintered with hot-press technique of the pure and co-doped samples S0, S1, S2, S3, S4, S5, with zero offsets (grey lines) indicates that the original Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> structure is intact after the doping with two monoclinic layered structure having same a and c axis with different  $b_1$ ,  $b_2$  axes. The composition of  $Ca_3Co_4O_{9+\delta}$  is better expressed as [Ca<sub>2</sub>CoO<sub>3</sub>][CoO<sub>2</sub>]b<sub>1</sub>/b<sub>2</sub> with the misfit-layered structure featuring different periodicities along the b-axis with b1 referring to the b-axis length of NaCl-type [Ca<sub>2</sub>CoO<sub>3</sub>] sublattice and b<sub>2</sub> referring to the b-axis length of [CoO<sub>2</sub>] sublattice. The crystal structure of  $Ca_3Co_4O_{9+\delta}$  can be viewed as being comprised of two monoclinic subsystems, i.e., the distorted NaCl-type [Ca<sub>2</sub>CoO<sub>3</sub>] sublattice and the CdI2-type [CoO2] sublattice stacking alternatively along the c-axis [3,6,7,10]. The CoO<sub>2</sub> layer is considered to be responsible for the electrical conduction, while Ca<sub>2</sub>CoO<sub>3</sub> layer is an insulating media and can be regarded a charge reservoir that supply charges to CoO<sub>2</sub> layer [4,5,8-10]. The original crystal parameters with two layer structures are tabulated in Table-1.

 Table. 1. The parameters of original crystal with two layer structures are shown.

| Sample  | а     | <b>b</b> <sub>1</sub> | <b>b</b> <sub>2</sub> | с      | β     |
|---|-------|-----------------------|-----------------------|--------|-------|
| S0 (Ca <sub>3</sub> Co <sub>4</sub> O <sub>9+δ</sub> )  | 4.841 | 4.56                  | 2.80                  | 10.881 | 98.92 |
| $ \begin{array}{c} S1 \\ (Ca_{2.9}Al_{0.1}Co_{3.9}Ti_{0.1}O_{9+\delta}) \end{array} $             | 4.842 | 4.56                  | 2.81                  | 10.882 | 98.90 |
| $\begin{array}{c} S2 \\ (Ca_{2.8}Al_{0.2}Co_{3.8}Ti_{0.2}O_{9+\delta}) \end{array}$               | 4.843 | 4.56                  | 2.81                  | 10.883 | 98.93 |
| $\begin{array}{c} S3 \\ (Ca_{2.7}Al_{0.3}Co_{3.7}Ti_{0.3}O_{9+\delta}) \end{array}$               | 4.843 | 4.56                  | 2.80                  | 10.885 | 98.86 |
| $\begin{array}{c} S4 \\ (Ca_{2.6}Al_{0.4}Co_{3.6}Ti_{0.4}O_{9+\delta}) \end{array}$               | 4.845 | 4.56                  | 2.80                  | 10.887 | 98.87 |
| S5<br>(Ca <sub>2.5</sub> Al <sub>0.5</sub> Co <sub>3.5</sub> Ti <sub>0.5</sub> O <sub>9+δ</sub> ) | 4.846 | 4.56                  | 2.80                  | 10.889 | 98.72 |

#### Thermogravimetric and differential thermal analysis

**Fig. 3(a)** presents the thermogravimetric analysis (TGA) for the pure and co-doped material of  $Ca_{(3-x)}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  samples, for x, y = 0, 0.1, 0.2, 0.3, 0.4, and 0.5. It is noticed that all samples have near identical TGA curves and the mass loss starts at 780 K while ramping the heat room temperature towards higher temperature. The thermal stability of S0, S1, S2, S3, S4, and S5 samples have been tested with the differential thermal analysis (DTA) and plotted in **Fig. 3(b)** for all the samples. The kinks at 980 K indicate structural instability of the materials that finally decomposes at 1230 K. This agrees well with the decomposition of CaCO<sub>3</sub> Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub>

and Ca<sub>(1-x)</sub>Co<sub>x</sub>O **[13,15]**. It is noticed from the transition starts at 800 K with 25% weight loss when approaching towards 980 K and exhibit peaks at 1230 K. This suggests that all the composites are thermally stable in wide temperature range up to 1230 K which is good enough for utilizing in thermoelectric batteries.



Fig. 2 XRD patterns of the hot-pressed sintered pure and co-doped samples.



Fig. 3 (a) TGA and (b) DTA for the pure and co-doped of raw materials of  $Ca_{(3-x)}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  samples (S0, S1, S2, S3, S4, and S5).

#### Seebeck coefficient

The temperature dependent Seebeck coefficients (S) of pure and co-doped  $Ca_{(3-x)}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  samples (S0, S1, S2, S3, S4, S5) are plotted in **Fig. 4** by varying the temperature from the room temperature to 750 K (upto the temperature of samples without degradation of the samples indicated by TGA and DTA). The values of S are measured from the thermoelectric voltage and the temperature difference between two ends of the samples of dimensions 20 mm x 10mm rectangular bars. The Seebeck coefficients of all the samples increase linearly with increasing the temperature. The positive Seebeck coefficients over the whole measured temperature range indicates that holes are the majority carriers in the conduction process and defines the electronic transport properties of the samples. Pure sample S0 exhibits higher Seebeck coefficient (177  $\mu$ V/K) in comparison to the co-doped samples over the entire temperature range and ascribed to the grain boundary potential barrier scattering [16]. The maximum value of Seebeck coefficient achieved in the present study is higher than the value reported for the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> composite [8, 10, 11, 14, 12] at ~750 K.



Fig. 4. Temperature dependence of the Seebeck coefficient of pure  $Ca_3Co_4O_9$  and co-doped samples.

#### Electrical resistivity

Fig. 5 Illustrates the variation of electrical resistivity  $(\rho)$ of the as-prepared  $Ca_{(3-x)}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  samples (S0, S1, S2, S3, S4, and S5) as a function of temperature as varying from the room temperature to 750 K. The resistivity was measured by a dc four probe method by applying current 10 mA to the rectangular samples of dimensions 20 mm x 10 mm. identical electrical resistivity behaviors have been observed for the all the samples with decrease in electrical resistivity with increasing the temperature. This indicates the characteristic semiconducting behavior of  $d\rho/dT \leq 0$ , where T is the temperature. All co-doped samples shows lower resistivity (higher conductivity) values in comparison to the pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> within the measured temperature range and the observed behavior can be explained as the increased scattering of the grains that reduces the electrical resistivity (increase in electrical conductivity) in the co-doped samples. The increase in electrical conductivity in  $Ca_{(3-x)}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  samples with increase in Al and Ti content can be attributed to the well dispersed Al and Ti particle in the Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> matrix that fills the voids of original pure crystallites. The lowest electrical resistivity achieved is  $0.9 \text{ m}\Omega\text{cm}$  for the S3sample i.e. 0.3 mol% co-doped of Al and Ti at temperature 750K.



Fig. 5. Temperature dependence of the electrical resistivity of pure  $Ca_3Co_4O_9$  and co-doped samples.

#### **Power factor**

To evaluate the thermoelectric performance of the asprepared and co-doped samples, power factor (PF) is estimated from the Seebeck coefficient and electrical resistivity values with the formula  $PF = S^2/\rho$ . Fig. 6 shows the temperature dependence of power factor for Ca(3- $_{x}Al_xCo_{(4-y)}Ti_yO_{9+\delta}$  samples (S0, S1, S2, S3, S4, and S5) as a function of temperature as varying from the room temperature to 750 K. Power factor for all the samples tend to increase with temperature. At 750 K, all co-doped samples except the S5 sample demonstrates higher values of power factor than the pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> sample. The maximum power factor obtained is 2.9 mW/K<sup>2</sup>m at 750 K for the S2 sample which is ~45% higher than the pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> sample. This suggests that the addition of Al and Ti in the matrix of Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> results in improved values for power factor and provides enhanced thermoelectric behavior.



Fig. 6. Temperature dependence of the power factor (PF) of pure  $Ca_3Co_4O_9$  and co-doped samples.

# Conclusion

The  $Ca_{(3-x)}Al_xCo_{4-y}Ti_yO_{9+\delta}$  compounds with x, y = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 have been synthesized by solid state reaction method, then sintered using hot-press and the thermoelectric properties are examined as a function of temperature. The disk like microstructures in FESEM imaging and highly pure crystal phases in XRD patterns confirm that no unwanted reaction is occurred in Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> matrix after the Al and Ti co-doping. Reitveld analysis by TOPAS software shows two layered structure of Ca<sub>2</sub>CoO<sub>3</sub> and CoO<sub>2</sub> layers. In comparison to pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>, all co-doped samples exhibit lower electrical resistivity in the entire measurement temperature range. Due to the significant reduction in the resistivity values for the S2 co-doped sample in comparison to the pure Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>, the maximum power factor achieved is 2.92 mW/K<sup>2</sup>m at 750 K. The observed improvement in the power factor is attributed to significant reduction in the electrical resistivity values. The current study demonstrates the preparation of pure and stable chemical structure for Al and Ti co-doped Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> compounds with enhanced thermoelectric properties using the solid state ball milling and hot-press technique, and could be further utilized as an efficient material for thermoelectric applications.

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#### Author's contributions

Conceived the plan: RPT, AKM, RKG; Performed the expeirments: RKG; Data analysis: RPT, AKM, RKG; Wrote the paper: RPT, AKM, RKG. Authors have no competing financial interests.

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