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Thermoelectric properties of $La_{1-x}Ca_xMO_{3-\delta}$ (x = 0.1 - 0.6, M = Co, Fe) derived by aqueous citrate precursors

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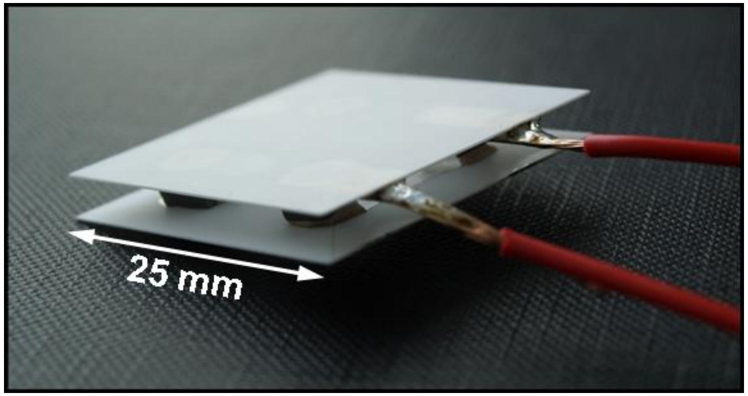
Motivation

Objective:

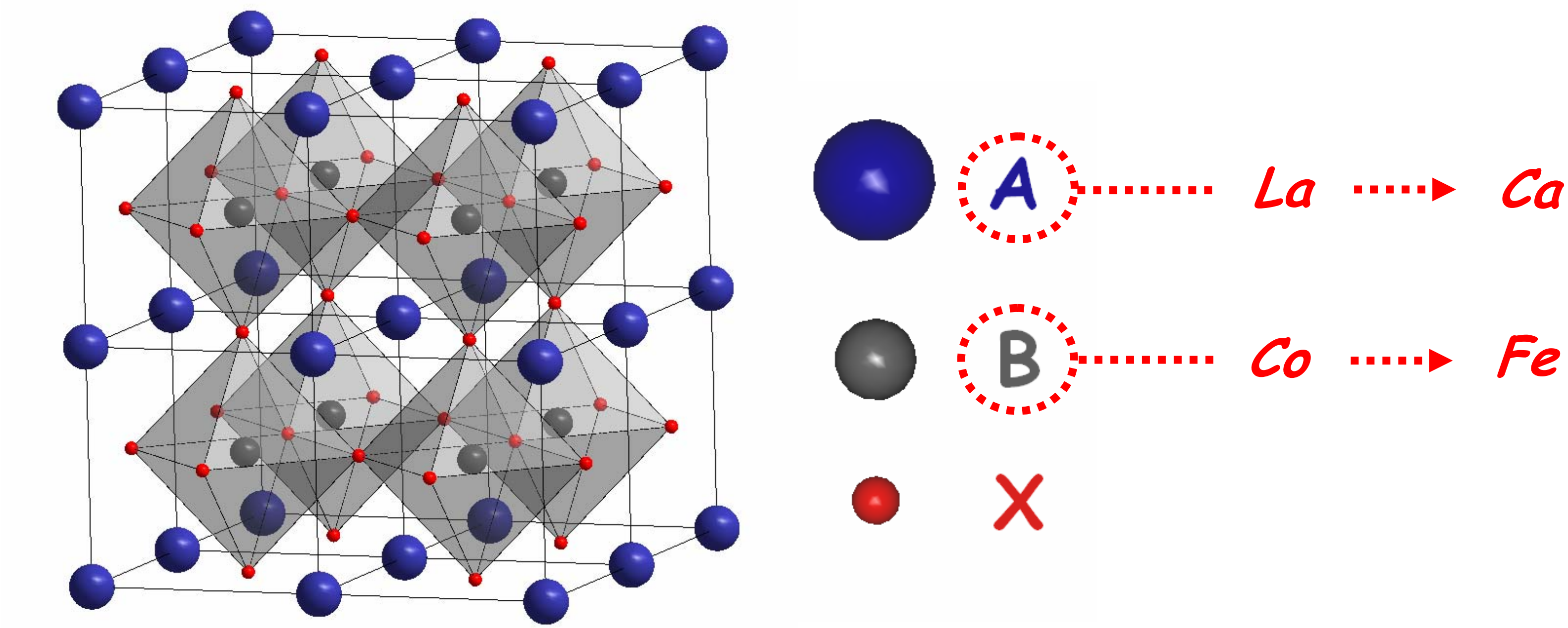
• Determine the thermoelectric properties of perovskite type compounds with a general composition: $La_{1-x}Ca_xMO_{3-\delta}$ (M=Co, Fe) (x=0.1 – 0.6) derived by Soft Chemistry

Aim of the study:

• To find better materials for high-temperature thermoelectric oxide converters



Perovskite $LaCoO_3$



The present perovskite structure is composed of La (at the A-site), Co (at the B-site) and O (at the X-site)

In following, two substitutions were studied:

On A-site : La → Ca

On B-site : Co → Fe

$La_{1-x}Ca_xCo_{1-y}Fe_yO_3$

$x = 0.1 - 0.6$

$y = 0.5 - 1$

Calculation of tolerance factor for perovskite structures

$$t = \frac{(Ra + Rx)}{\sqrt{2} \times (Rb + Rx)}$$

A-site substitution (Ca) has an effect on the tolerance factor:

Composition	$La_{0.9}Ca_{0.1}CoO_3$	$La_{0.7}Ca_{0.3}CoO_3$	$La_{0.4}Ca_{0.6}CoO_3$
Tolerance factor	0.950	0.947	0.943

Decrease

B-site substitution (Fe) has an effect on the tolerance factor:

Composition	$La_{0.9}Ca_{0.1}CoO_3$	$La_{0.9}Ca_{0.1}Co_{0.5}Fe_{0.5}O_3$	$La_{0.9}Ca_{0.1}FeO_3$
Tolerance factor	0.950	0.949	0.947

Decrease

Synthesis of the materials

Chimie douce methods were used to prepare a series of powders with a general composition $La_{1-x}Ca_xMO_{3-\delta}$ (x = 0.1 - 0.6, M = Co, Fe)

- <u>First step:</u>

Dissolution of stoichiometric amounts of metal nitrates together with citric acid in water

- <u>Second step:</u>

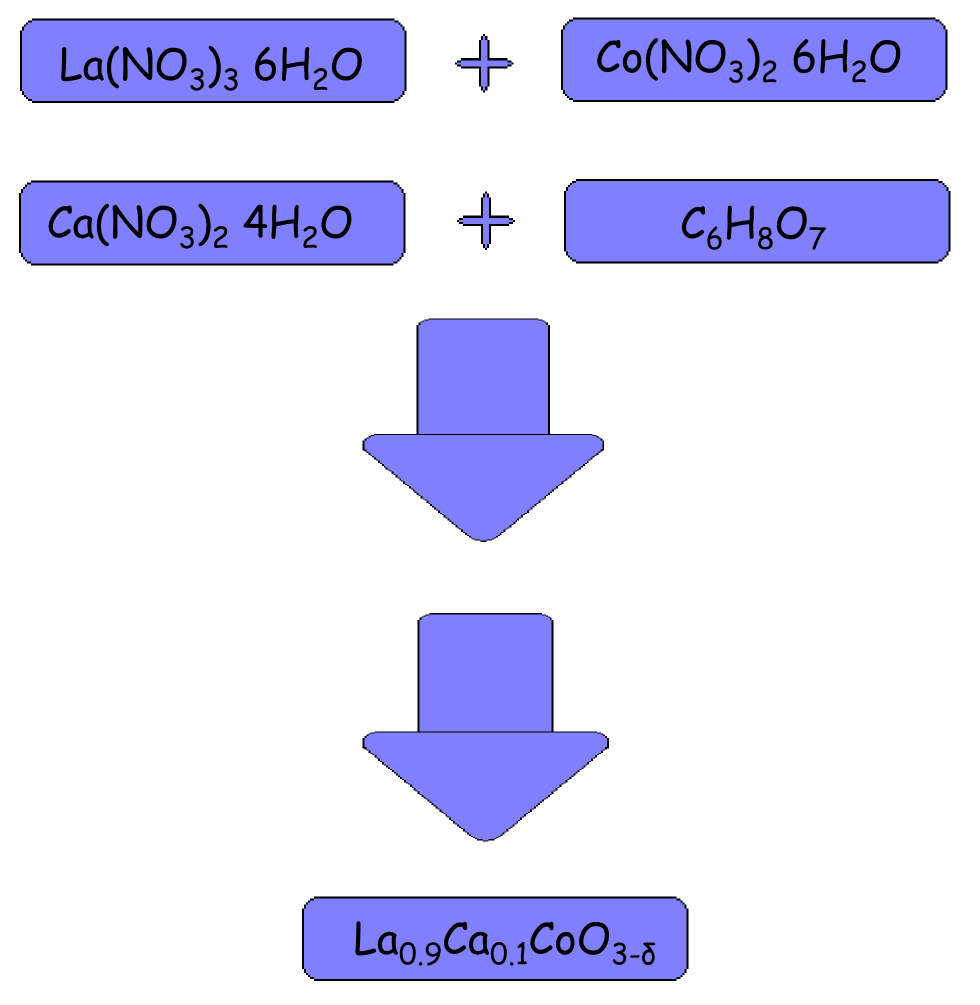
Heating and mixing of the solution to homogenize and polymerize the product

- <u>Third step:</u>

Drying in a furnace at 300°C to remove the solvent

- <u>Fourth step:</u>

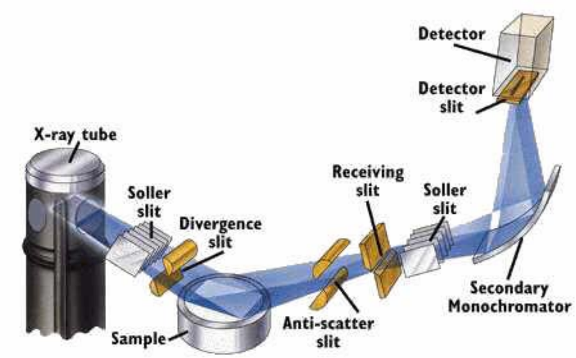
Calcinations at ambient conditions to obtain the final composition



Characterization methods I

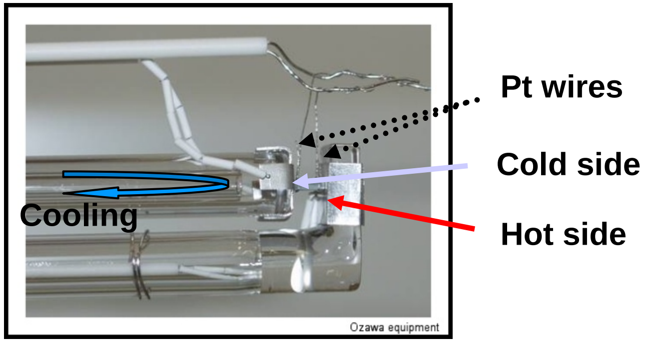
Characterization techniques for determination of crystallographic and thermoelectric properties of $La_{1-x}Ca_xMO_{3-\delta}$ (M = Co, Fe) (x = 0.1 - 0.6):

• Phase purity and crystallographic parameters were studied by X-ray Diffraction (XRD) coupled with Rietveld refinement (for $La_{0.9}Ca_{0.1}CoO_{3-\delta}$)



• Oxygen content measurement by Thermogravimetric Analysis (TGA) (for Ca substituted samples)

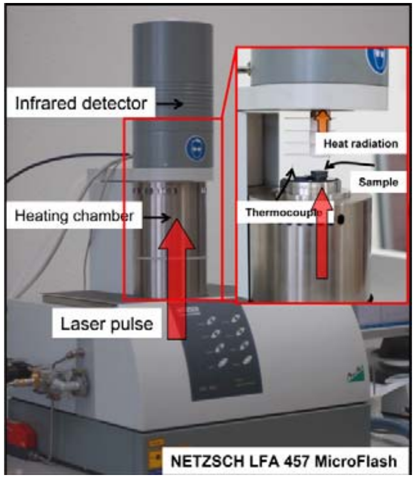
• Seebeck coefficient (S) and electrical conductivity (σ) measured by the four-contact method



Characterization methods II

- Thermal diffusivity measurements (a) by Laser Flash Analysis (LFA)

NETZSCH LFA 457 MicroFlash™



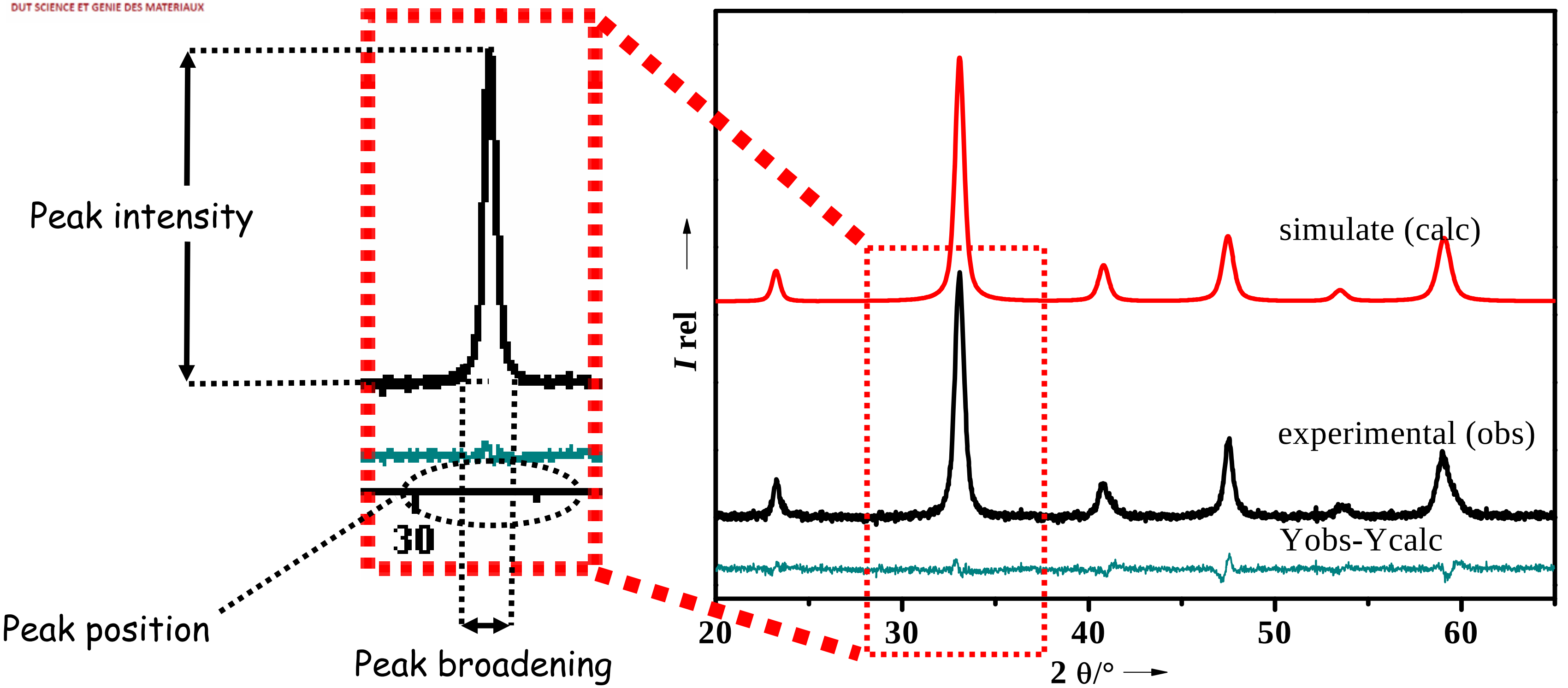
- Heat capacity measurements (Cp) by Differential Scanning Calorimetry (DSC)

NETZSCH DSC 404 C

- The combined use of LFA and DSC allowed calculations of the thermal conductivity (κ)

- Figure of Merit (ZT) was calculated from the above measurements of S, σ , κ

XRD and Rietveld method



Experimental and simulated patterns for $La_{0.9}Ca_{0.1}CoO_{3-\delta}$

Examples for information provided by the Rietveld method:

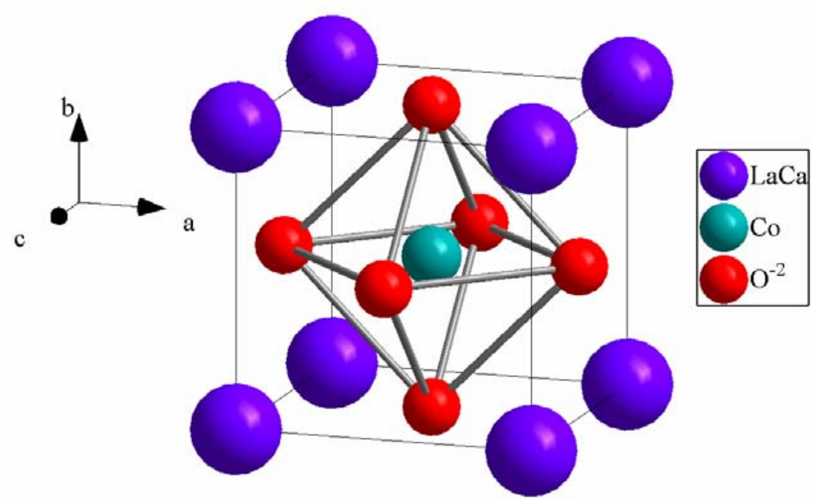
peak position ■ ■ ■ ■ ■ ■ ■ ■ ■ ■	Crystallographic parameters and dimension of the unit cell
peak intensity ■ ■ ■ ■ ■ ■ ■ ■ ■	Occupancy
peak broadening ■ ■ ■ ■ ■ ■ ■ ■	Strain/crystallite size

Results

Results of Rietveld refinement

- SG: P m -3 m
- Cell parameters (Å): a = 3.8328
- Volume (Å³): 56.25

Crystal structure of $La_{0.9}Ca_{0.1}CoO_3$

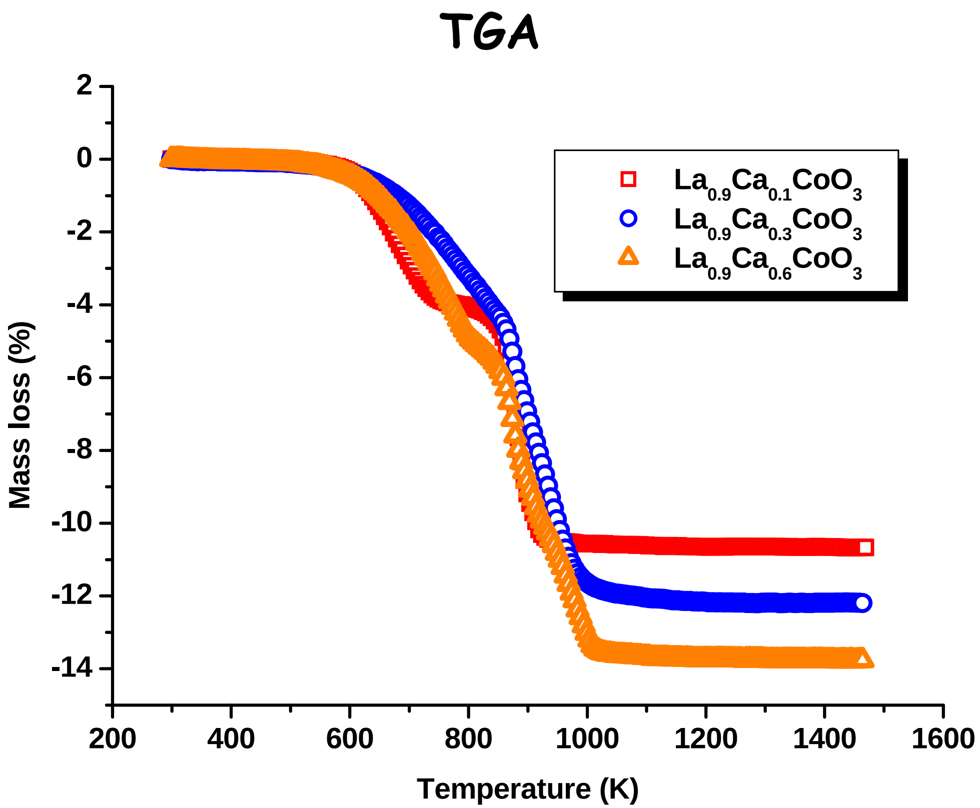


Atomic Coordinates, occupancy and equivalent isotropic displacement parameters for $La_{0.9}Ca_{0.1}CoO_3$

Name	X	y	z	Ueq (Å²)	Wyckoff position	occupancy
La	0	0	0	0.013(5)	1a	0.899
Ca	0	0	0	0.056(2)	1a	0.101
Co	0.5	0.5	0.5	0.019(1)	1b	1
O	0	0.5	0.5	0.035(1)	3c	1

TGA measurement for $La_{0.9}Ca_{0.1}CoO_{3-\delta}$

Reductions were performed between 300 K and 1470 K using 20 vol.% H_2/He



According to the TGA results, the oxygen amount was calculated to be:

$La_{0.9}Ca_{0.1}CoO_{2.99}$

$La_{0.9}Ca_{0.3}CoO_{2.89}$

$La_{0.9}Ca_{0.6}CoO_{2.64}$

Calculation of the Figure of Merit

Seebeck coefficent

Figure of Merit

$$ZT = \frac{S^2 T}{\rho \kappa}$$

Electrical Resistivity

Thermal conductivity

Heat capacity

$$\kappa(T) = a(T)\,D(T)\,Cp(T)$$

Thermal diffusivity

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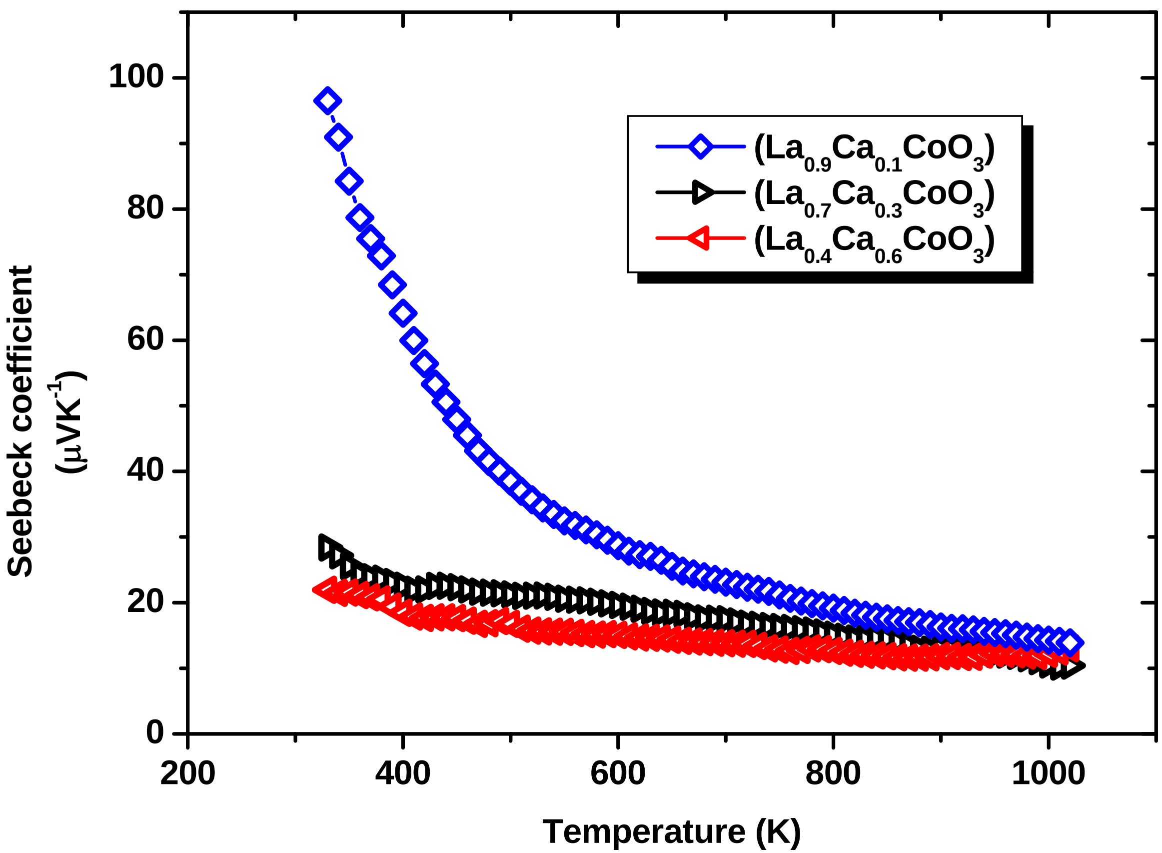
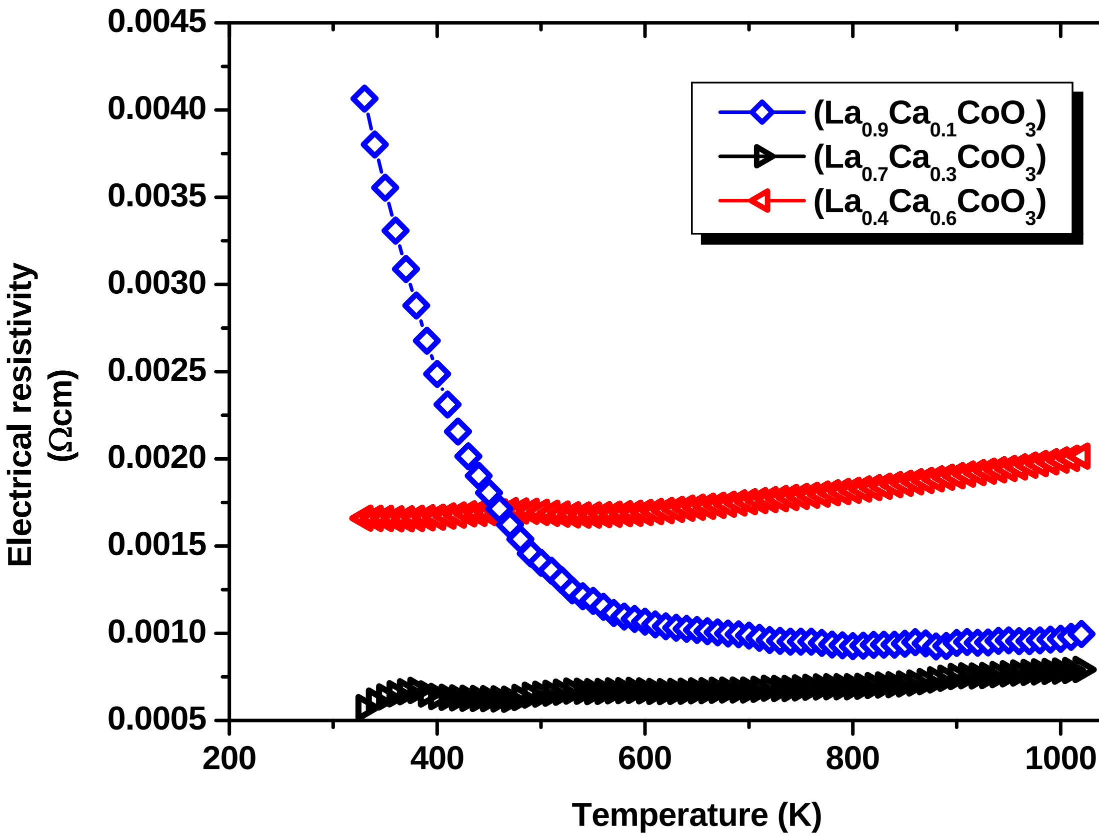
Seebeck coefficient of $La_{0.9}Ca_{0.1}CoO_{3-\delta}$, $La_{0.7}Ca_{0.3}CoO_{3-\delta}$ and $La_{0.4}Ca_{0.6}CoO_{3-\delta}$ in the temperature range 300 - 1000 K.



Electrical resistivity of $La_{0.9}Ca_{0.1}CoO_{3-\delta}$, $La_{0.7}Ca_{0.3}CoO_{3-\delta}$ and $La_{0.4}Ca_{0.6}CoO_{3-\delta}$ in the temperature range 300 - 1020 K.



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Thermal conductivities of $La_{0.9}Ca_{0.1}CoO_{3-\delta}$, $La_{0.7}Ca_{0.3}CoO_{3-\delta}$ and $La_{0.4}Ca_{0.6}CoO_{3-\delta}$ in the temperature range 300 - 1000 K.

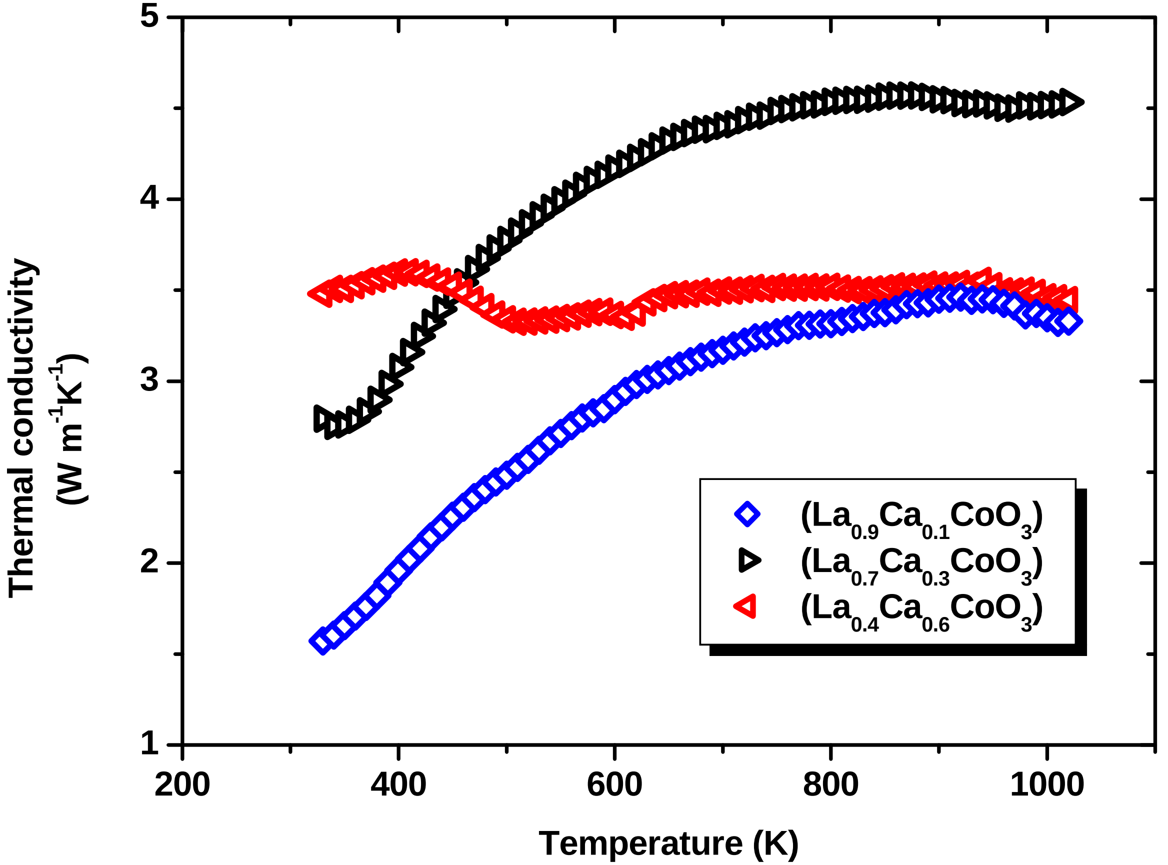

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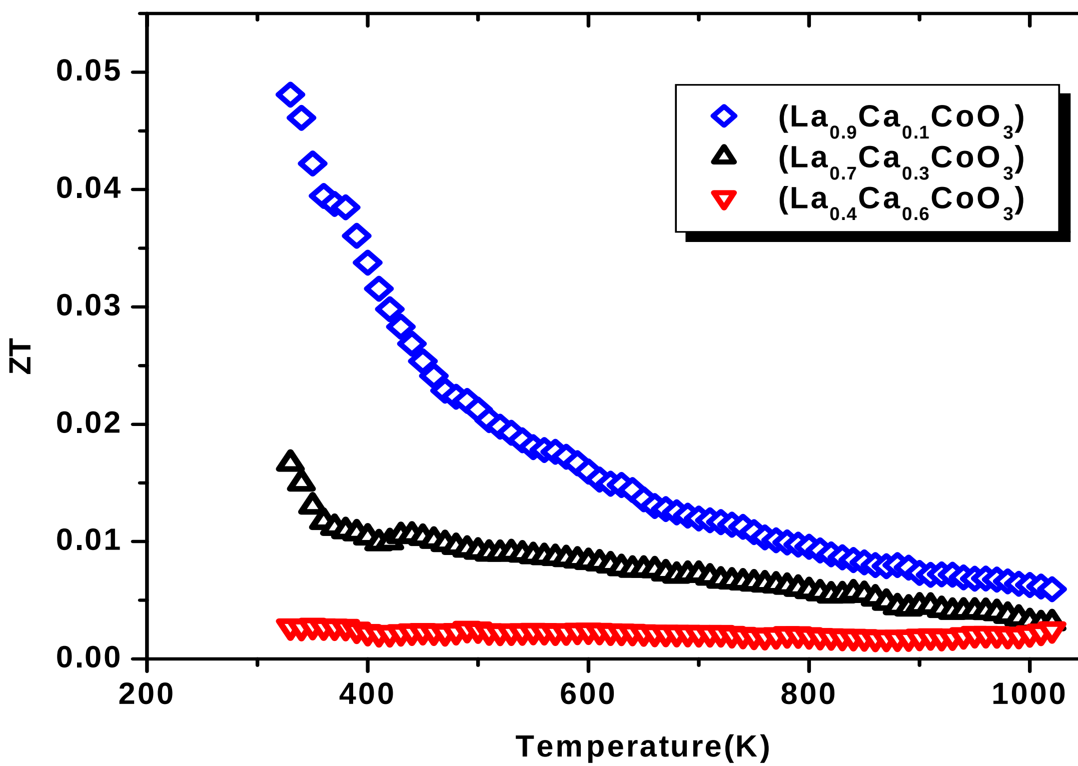
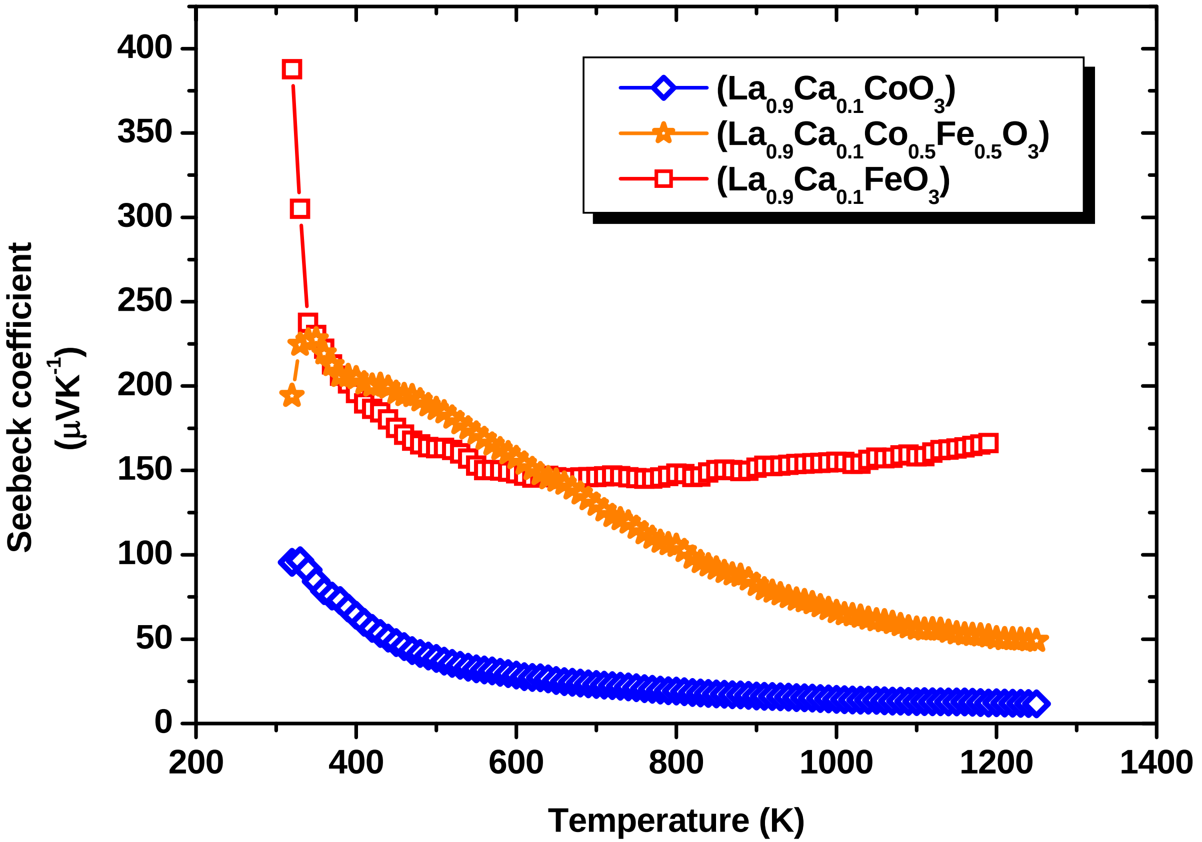
Figure of merit

Influence of the A – site (Ca) substitution on the ZT. The ZT decreases with the increasing Ca content



Seebeck coefficient of $La_{0.9}Ca_{0.1}CoO_{3-\delta}$, $La_{0.9}Ca_{0.1}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ in the temperature range 300 - 1250 K



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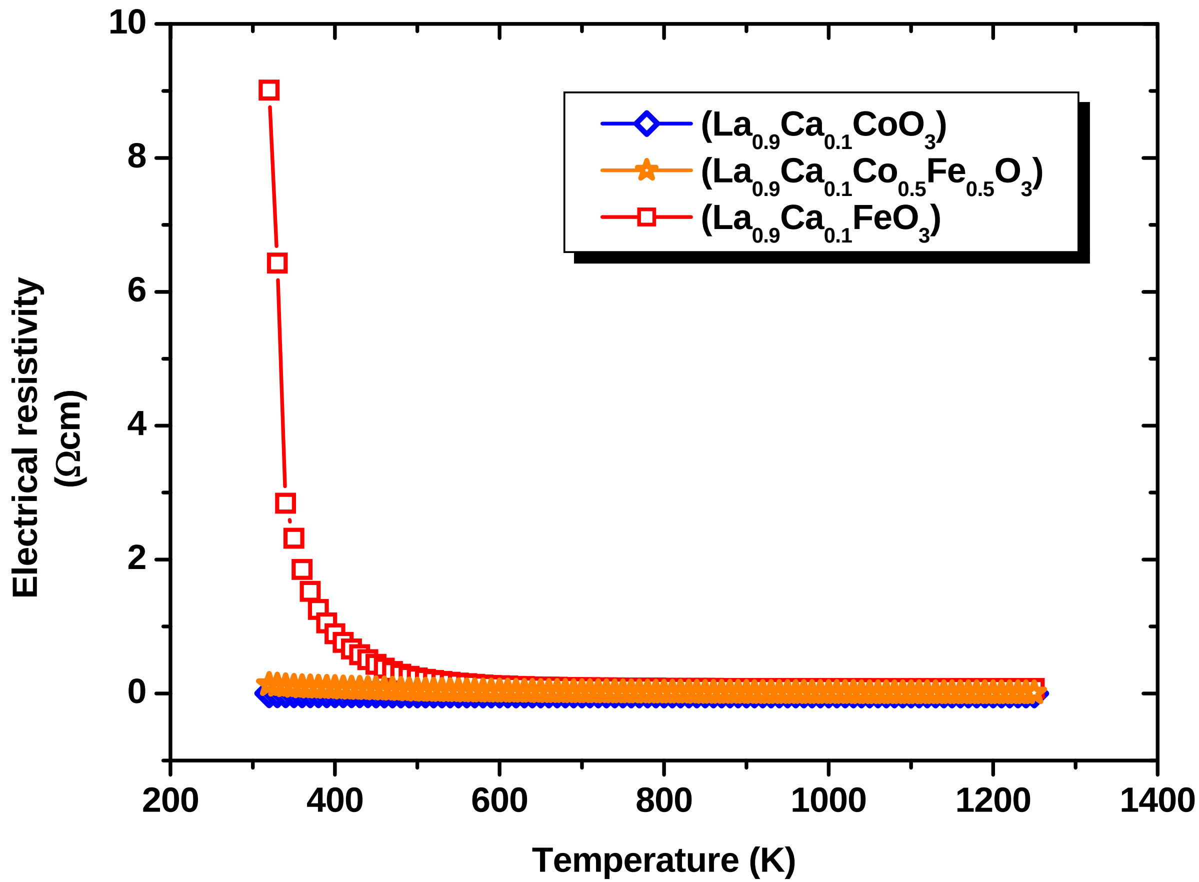
Electrical resistivity of $La_{0.9}Ca_{0.1}CoO_{3-\delta}$, $La_{0.9}Ca_{0.1}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ in the temperature range 300 - 1250 K.



Thermal conductivity of $La_{0.9}Ca_{0.1}CoO_{3-\delta}$, $La_{0.9}Ca_{0.1}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ in the temperature range 300 - 1250 K

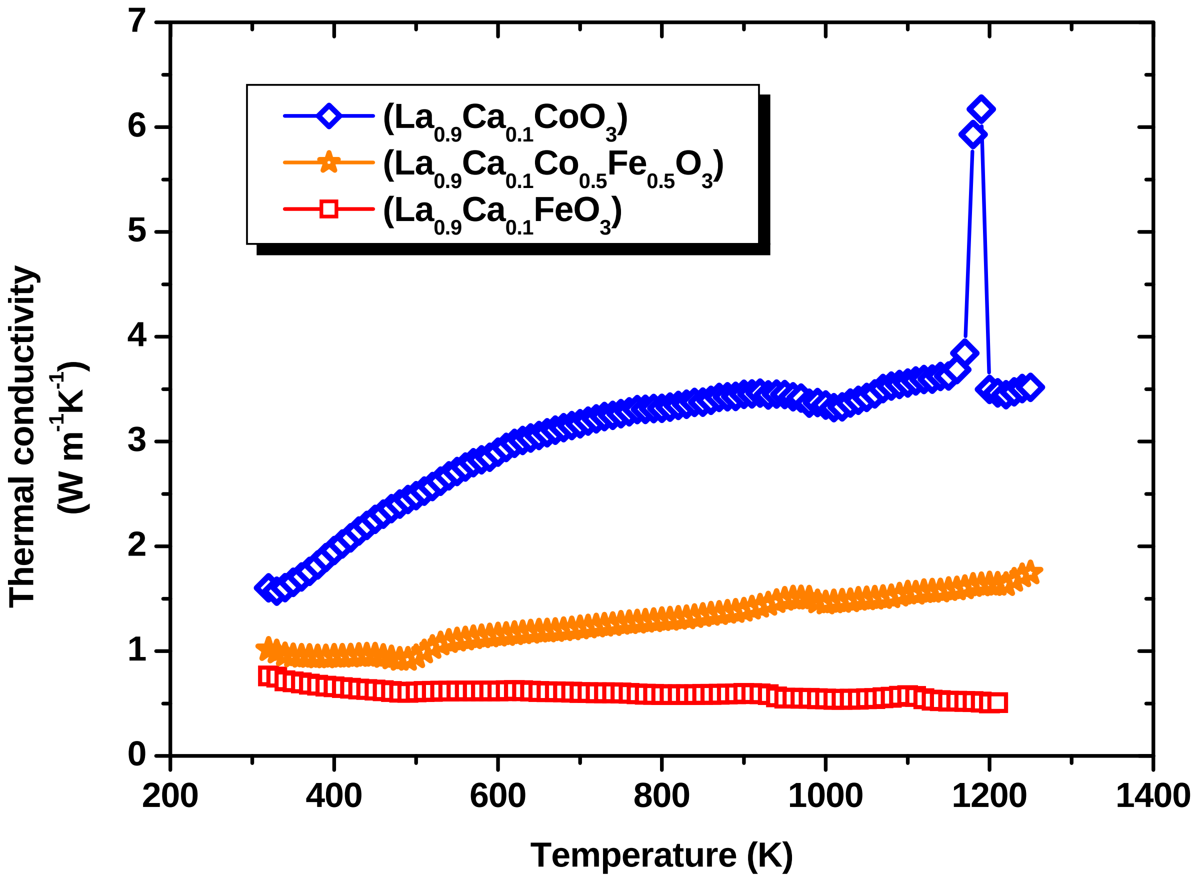
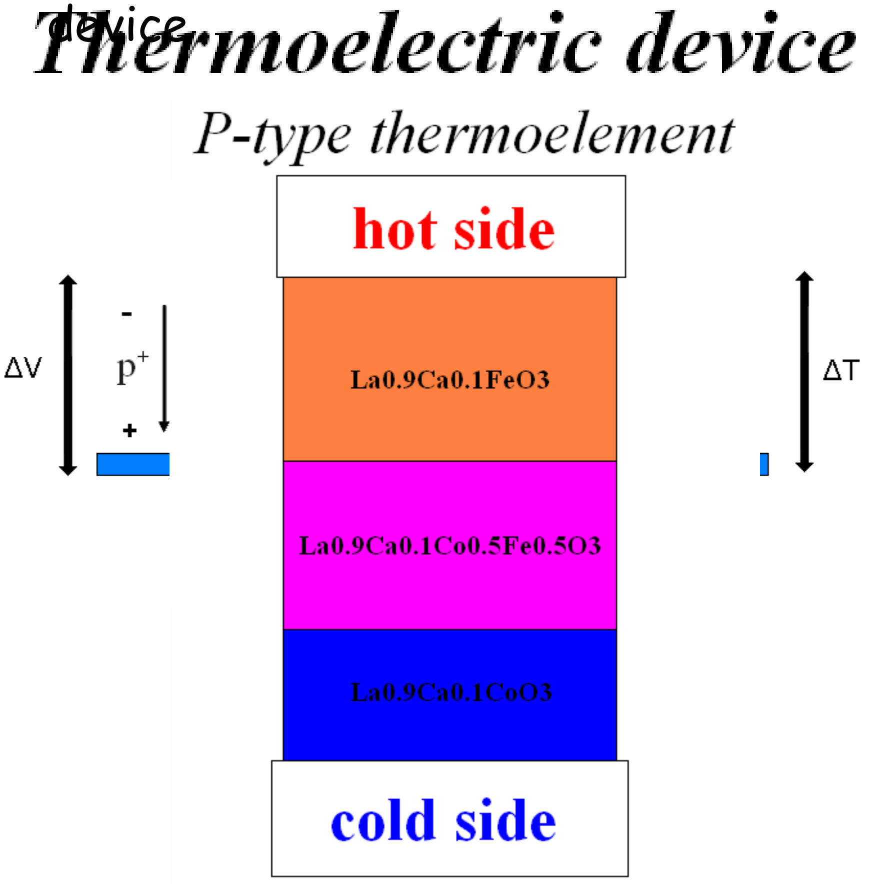
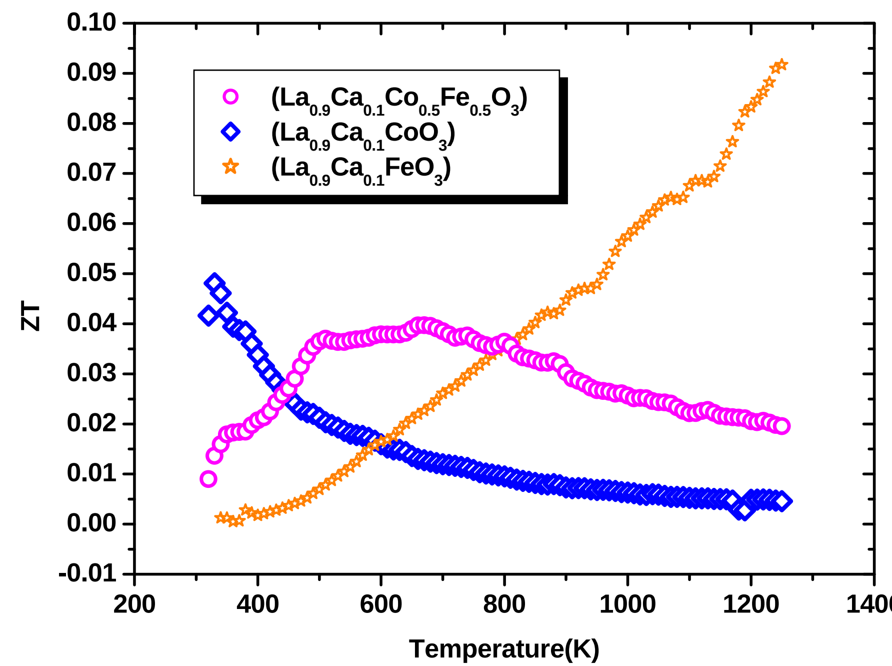


Figure of merit

By combining different materials, we could built a layered thermoelectric device



B - site (Fe) substitution effects the value of the figure of Merit



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Summary + Outlook

• A series of powders with different compositions were synthesized successfully by chimie douce methods

• Co substitution for Fe at the B site improve the thermoelectric activity (ZT) at high temperature, thus suggesting potential application in segmented TE legs

• Selective cationic substitution (La – Ca substitution) causes modification of the observed thermoelectric properties. The ZT decreases with increasing Ca content

• The study showed that the combination of the different techniques: XRD (with Rietved refinement), thermal analysis and thermoelectric measurements are necessary to describe the chemical and physical properties of $La_{1-x}Ca_xMO_{3-\delta}$ (x = 0.1 - 0.6, M = Co, Fe)

Outlook:

• Study in more detail the influence of oxygen deficiency on the crystallographic structure, charge carrier concentration, and thermoelectric properties

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Thank you for your kind attention!