Embedded High-Temperature Sensors: Enhancing Thermoelectrical Performance with Refractory Composites Gradient Layers

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Advanced Materials for Harsh Environments

Introduction

- Processes such as energy generation, metals/glass manufacturing, coal gasification and aerospace technology applications require health and process monitoring in harsh-environments.

- **Harsh-environments conditions include:**
  - High temperature (500-1800^{o}C)
  - High pressure (up to 1000 psi)
  - **Corrosive, erosive and reducing environments.**

- **Ability to monitor:**
  - Temperature
  - Structural stability of systems components.

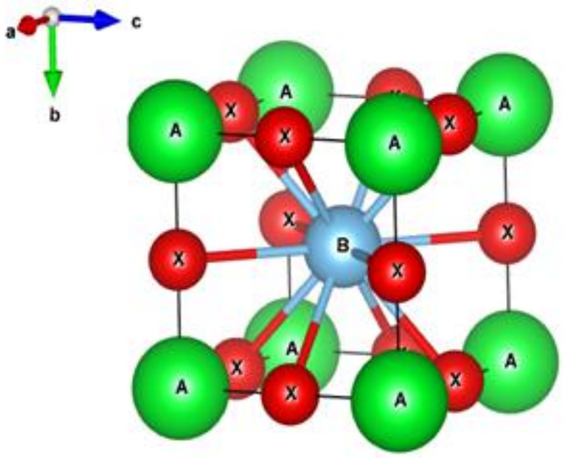
- **US DOE Overall Goal:** Develop health and temperature sensors (and sensor arrays) embedded into refractory compositions.

Objectives of This Work

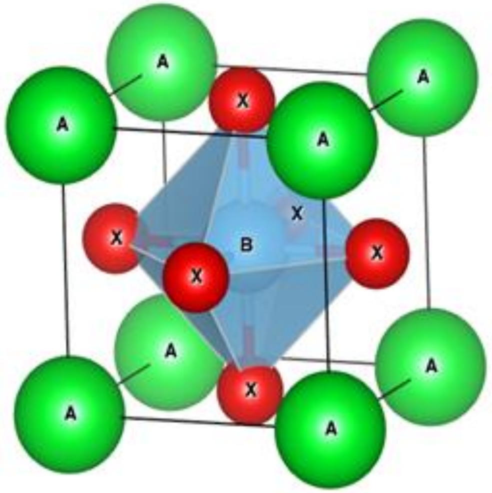
- To synthesize doped lanthanum oxides perovskites by Sol-Gel method and prepare conductive refractory composites.
- To study thermoelectrical properties: Seebeck coefficients of such compositions at temperatures up to 1500 ^{o}C.
- To study cation interdiffusion and phase development in fabricated composites at high temperatures.
- To fabricate embedded multilayer sensors utilizing these materials and to determine their thermoelectrical response.

Lanthanum Chromite: General Aspects

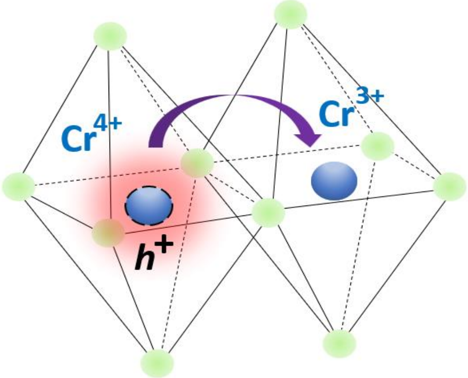
- High melting point (~2500 °C).
- Chemically stable under oxidative and reducing atmospheres.
- Pure $LaCrO_3$ shows semiconducting behavior with no to low ionic conduction.
- Calcium substitution increase conductivity from 1.0 to 40.0 S·cm at 1000°C (Mori *et al.* 1997)
- Compatibility (thermal expansion coefficients matching) near refractory materials, ~$10×10^{-6}$ $^{o}C^{-1}$.



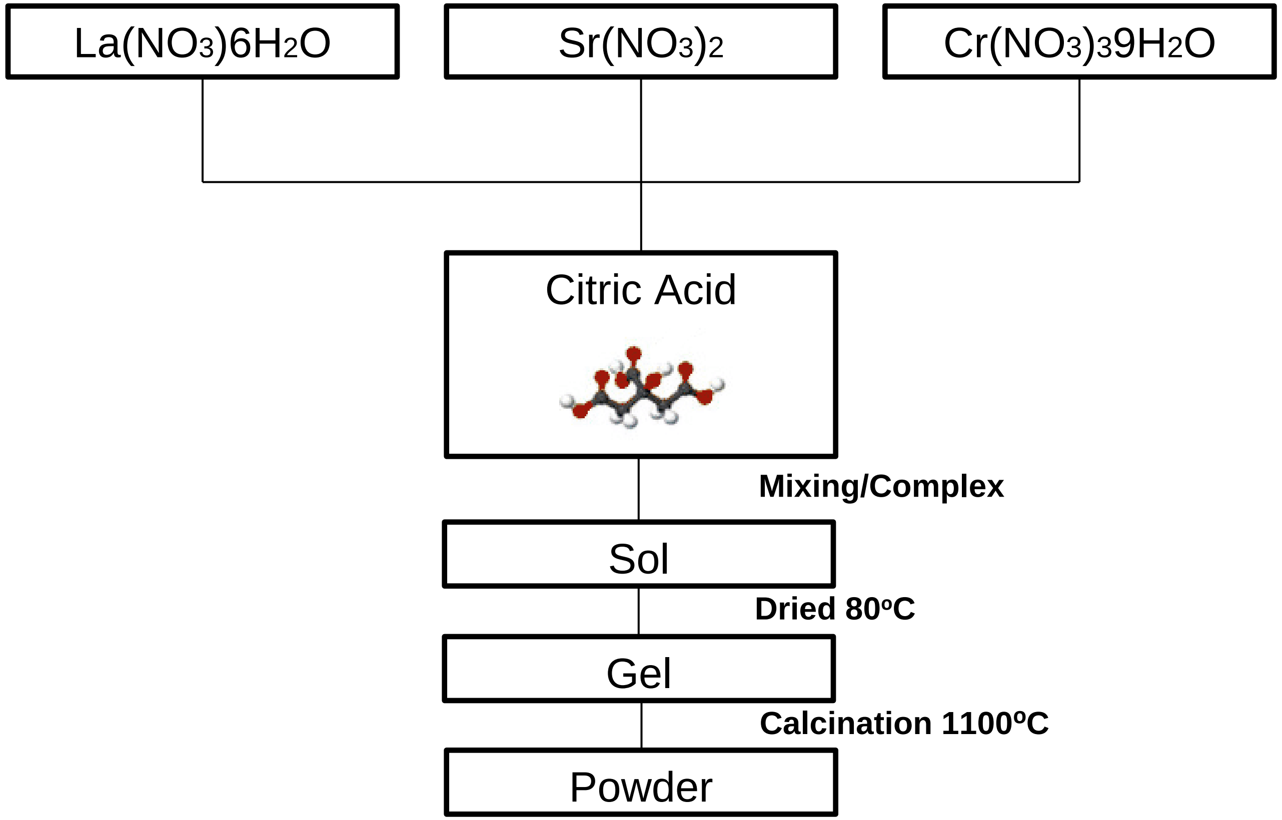
A atom cubic unit cell

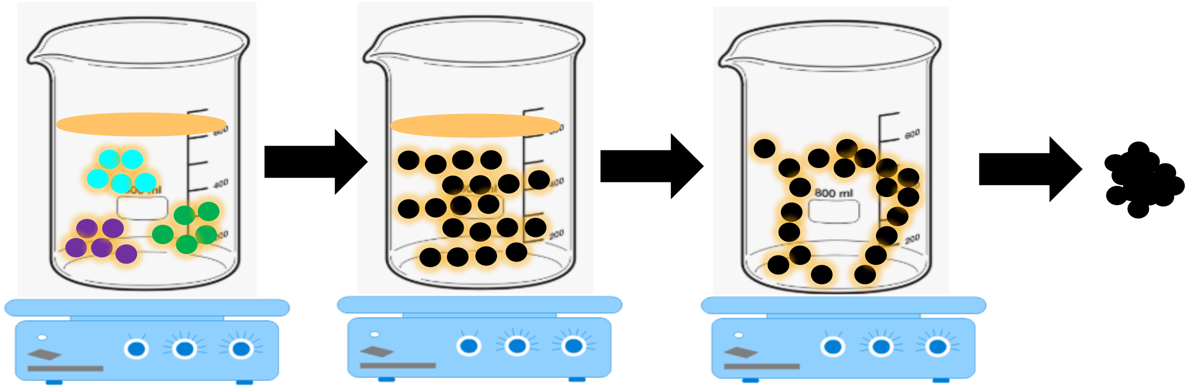


B atom cubic unit cell



Sol Gel Synthesis





- ✓ Pechini-like process used.
- ✓ High homogenous and adequate sintering.
- ✓ High density (typical in literature <93% density).

Low yields and not easy to scale-up

<u>Compositions Studied:</u>

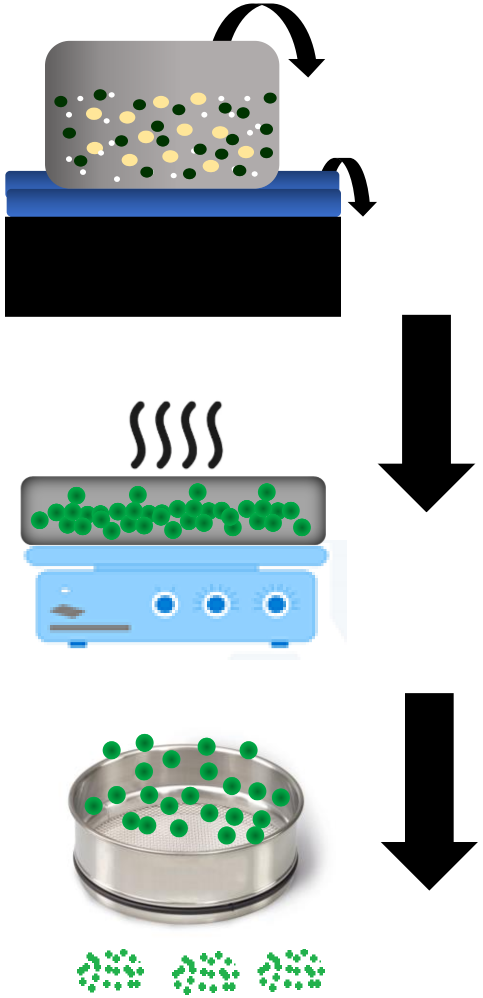
A-site: (LSC) $La_{1-x}\mathbf{Sr}_xCrO_3$, **(LCC)** $La_{1-x}\mathbf{Ca}_xCrO_3$

(x = 0.1, 0.2, 0.3, 0.4)

B-site: (LSCM) $La_{0.8}Sr_{0.2}Cr_{1-y}\mathbf{Mn}_yO_3$

(y = 0.1, 0.2, 0.3, 0.4)

Composites Fabrication



*Pure or Calcium $LaCrO_3$ Powder

Zirconia milling media + Al_2O_3/Cr_2O_3 Powder

↓

Ball milling in isopropanol for 2 h

↓

Zirconia milling media removal

↓

Isopropanol evaporation and composite powder drying at 80 °C

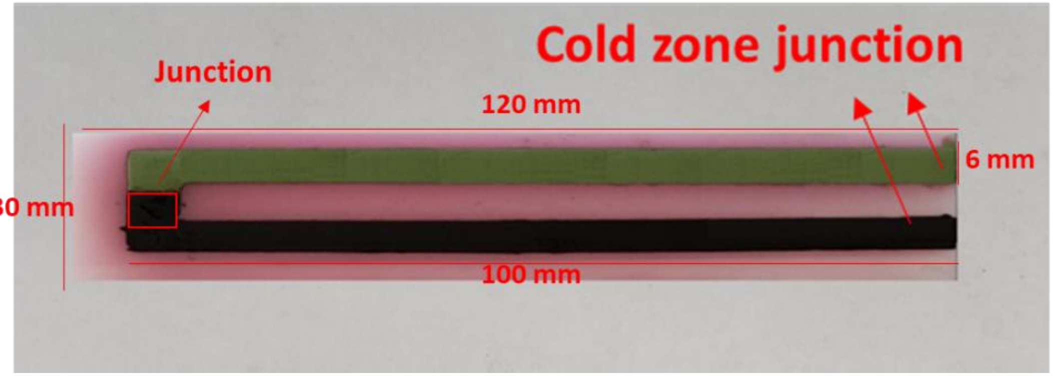
↓

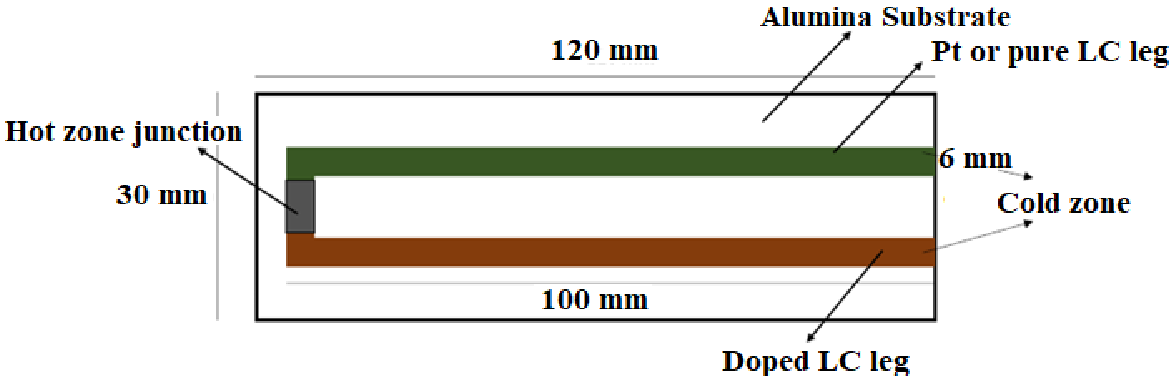
Dried pure/ doped $LaCrO_3$ -Al_2O_3 based composite powders sieving

***The composites were prepared mixing 30% Ca doped $LaCrO_3$ (LCC30) with Al_2O_3 at different (v/v)% ratios: [90-10], [80-20] and [70-30] where the first number corresponds to LCC30 volume content and the second to Al_2O_3.**

Thick Film Thermocouple Fabrication

- High-temperature thermocouples that function >1200°C (in R-type range) new exciting development.





Leg 1 (Pt or pure-$LaCrO_3$) | Leg 2 (Doped $LaCrO_3$)

↓

Ball milling in isopropanol for 8 h and drying

↓

Ink preparation by mixing with an organic vehicle and ultrasonication

↓

Stencil printing on as-prepared alumina substrates (120 x 30 mm) and drying

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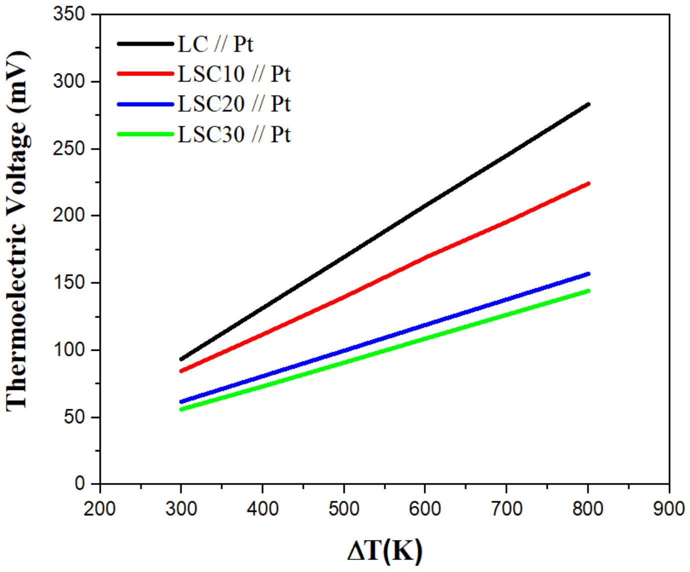
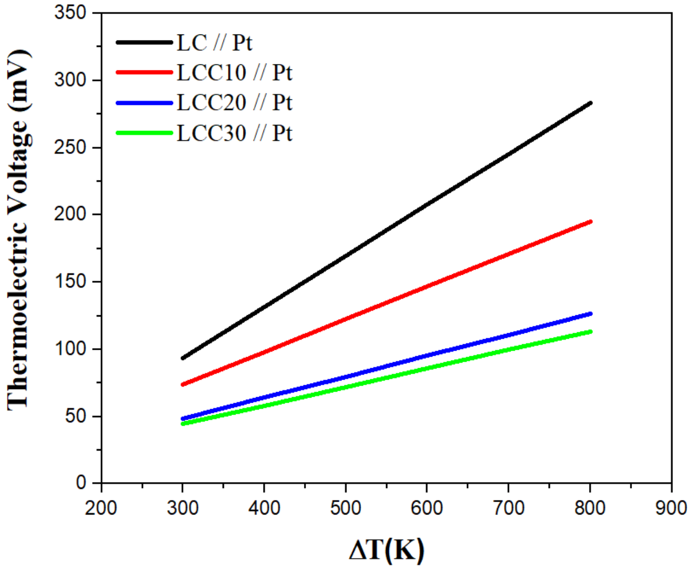
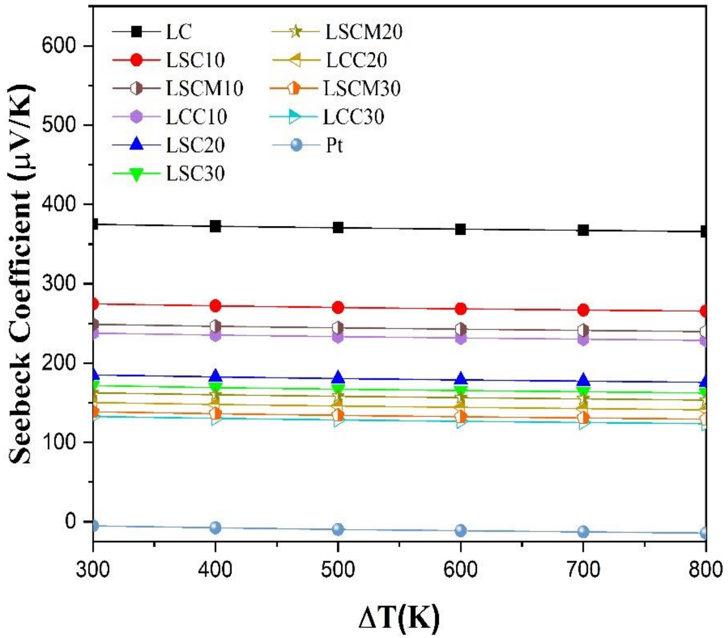
Sintering of the thermocouples (2°C/min, 1500°C, 1 h)

Thermoelectrical Characterization

Seebeck Coefficient Determination (Using Pt Standard)







$$S(c) = (k_B/e)\ln[2(1-c)/c]$$

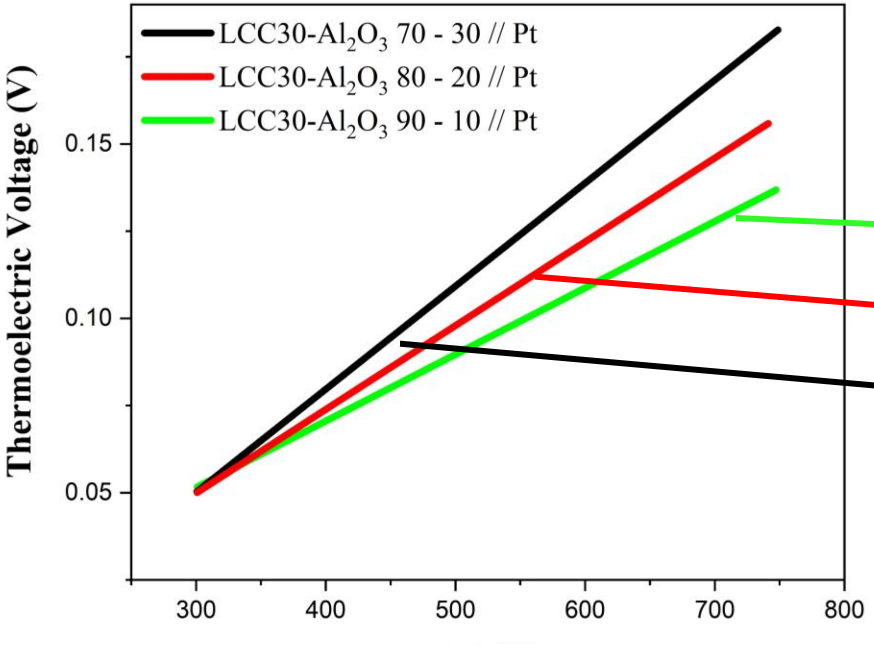
Heikes Equation

- **Linear correlation between temperature difference and thermoelectric voltage was observed for all the compositions.**
- **Doped-$LaCrO_3$/Pt couples were fabricated to estimate intrinsic Seebeck coefficient (S_{Pt}~ -18 µV/K*) up to 1000°C.**
- **Ca doping shows lowest intrinsic Seebeck coefficient with increasing Ca content.**

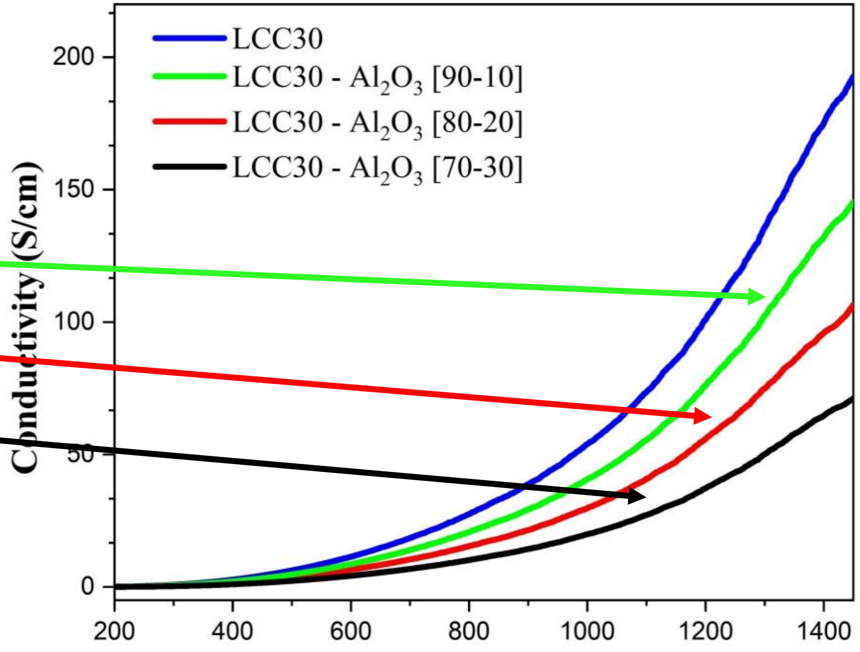
*Moore, J. P. (1973). Journal of Applied Physics. 44 (3): 1174–1178

Thermoelectric Characterization of Thermocouples

Thermoelectrical response of LCC30-Al_2O_3 composites // Pt



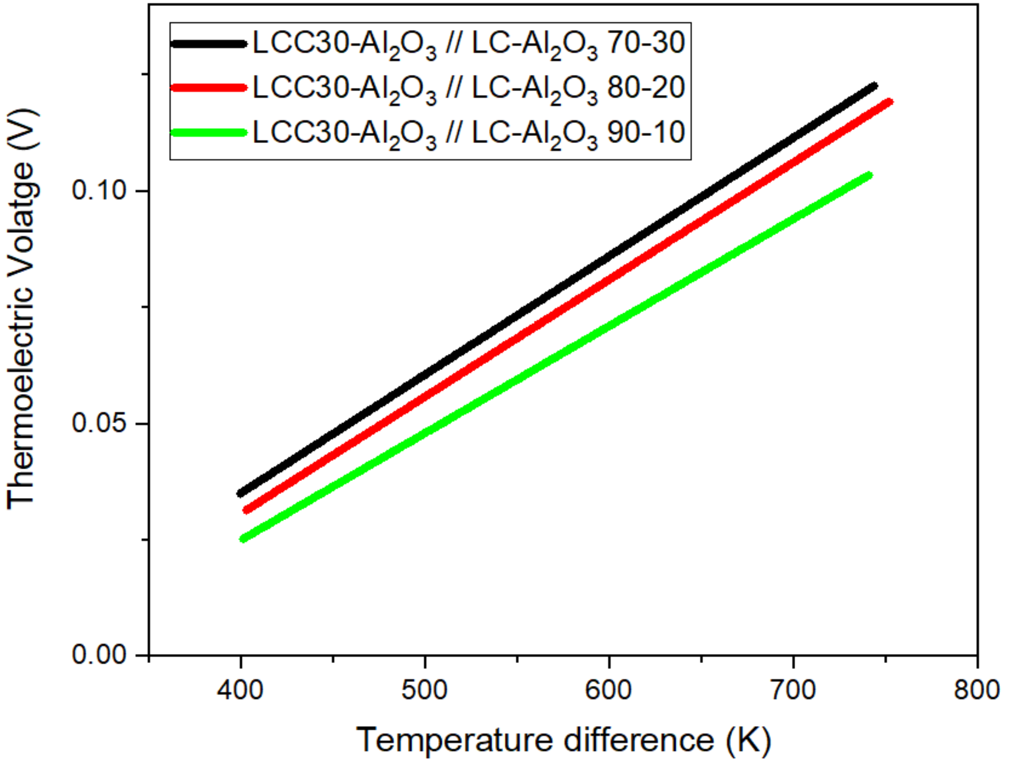
Electrical conductivity vs. temperature of LCC30-Al_2O_3 composites



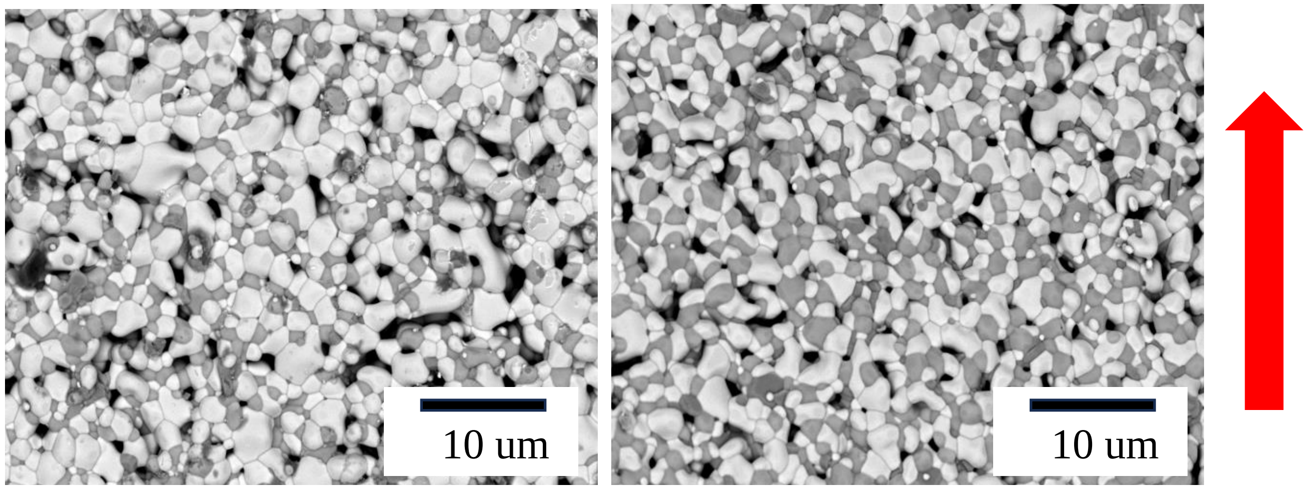
- **Electrical conductivity and Thermoelectric voltage of LCC30-Al_2O_3 composites-based thick layer thermocouples were obtained.**

- **Inverse correlation between thermoelectric voltage response and electrical conductivity trends. Al_2O_3 content the resistivity of the composites.**

Thermoelectric Characterization of Thermocouples



BSE - SEM



LCC30-Al_2O_3 [80-20] **LCC30-Al_2O_3 [70-30]**

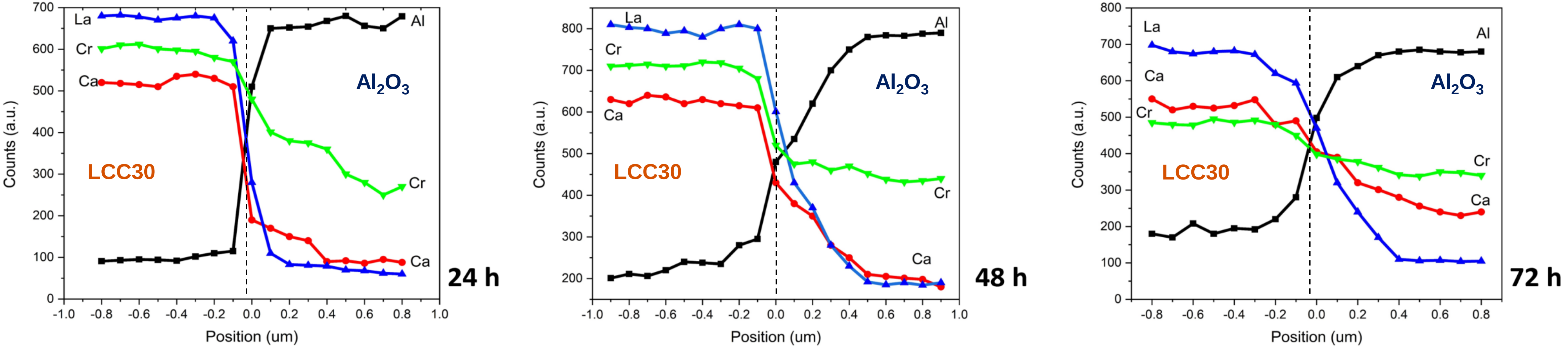
Microstructures: LCC30 (white grains) - Al_2O_3/Aluminates (grey grains)

- **LC-Al_2O_3 and LCC30-Al_2O_3 composites-based thick layer thermocouples fabricated were tested in a range between 30 to 850°C during showing linear correlation between thermoelectric voltage and temperature.**

- **Increase of Al_2O_3 content in thermocouples materials increase the driving potential by formation of aluminates secondary phases and higher concentration of Al_2O_3 grains.**

Composites Chemical Reactivity Studies

LCC30-Al_2O_3 80-20   1500 °C



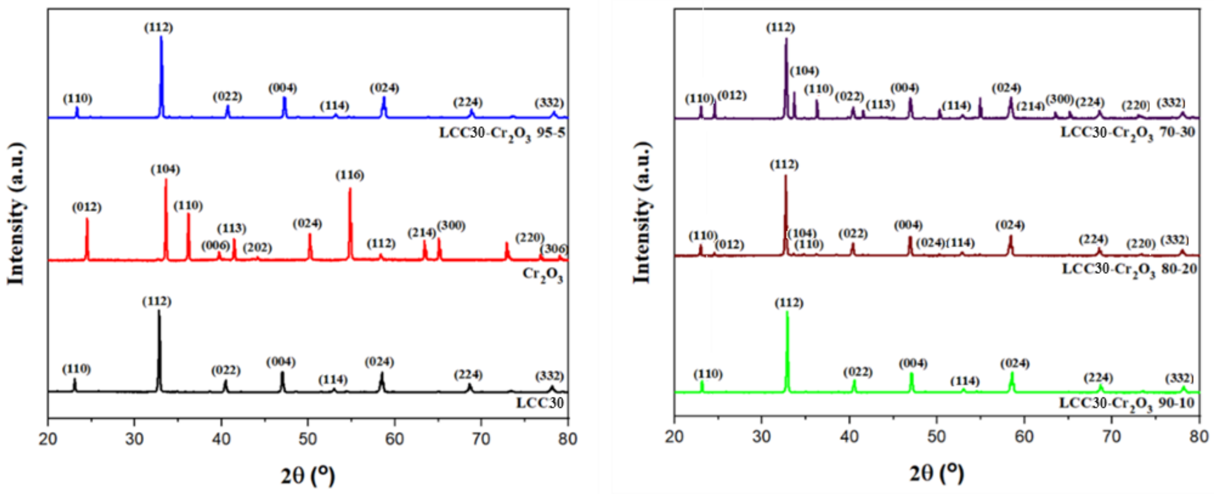
❖Cr^{+3} concentration decreases in LCC30, while Ca^{+2} diffuses into Al_2O_3, forming aluminates.

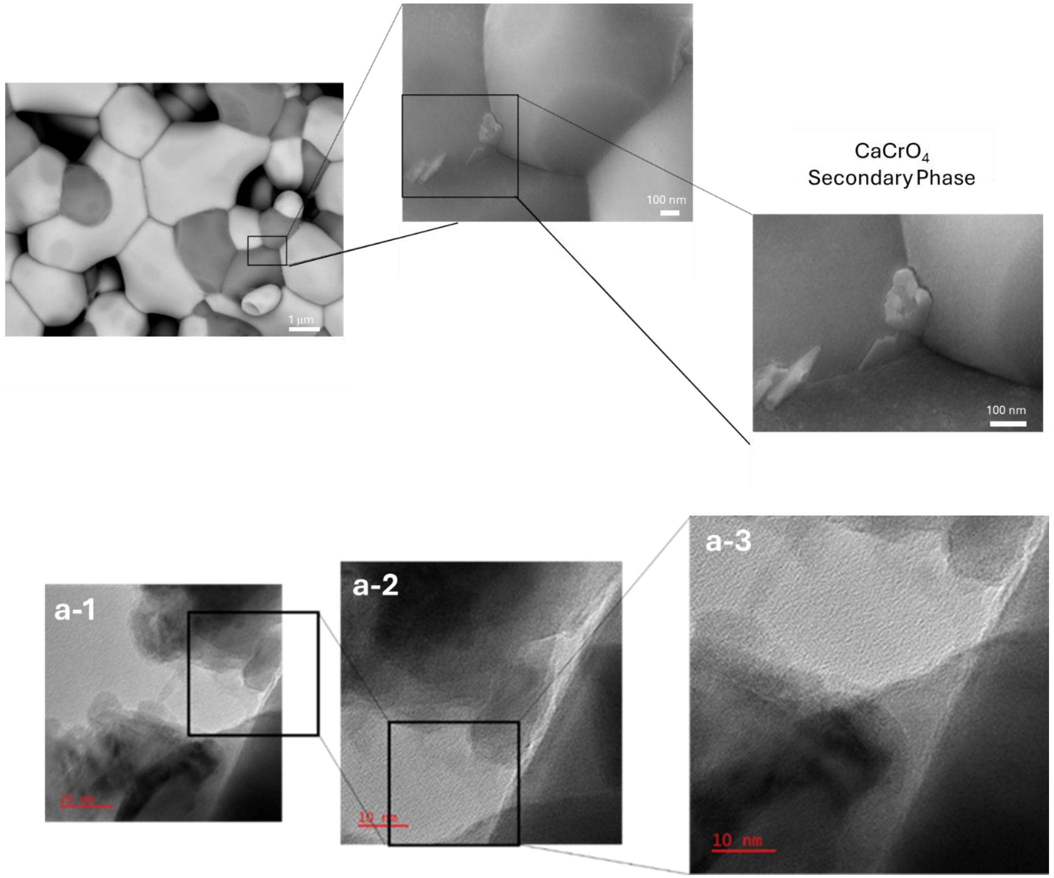
❖LCC30-Al_2O_3: After 72 hours at 1500 °C, Cr^{+3} cations distribute homogeneously.

❖Cation interdiffusion and the formation of secondary phases, could impact electrical conductivity and thermoelectrical output.

Composites Chemical Reactivity Studies

XRD characterization



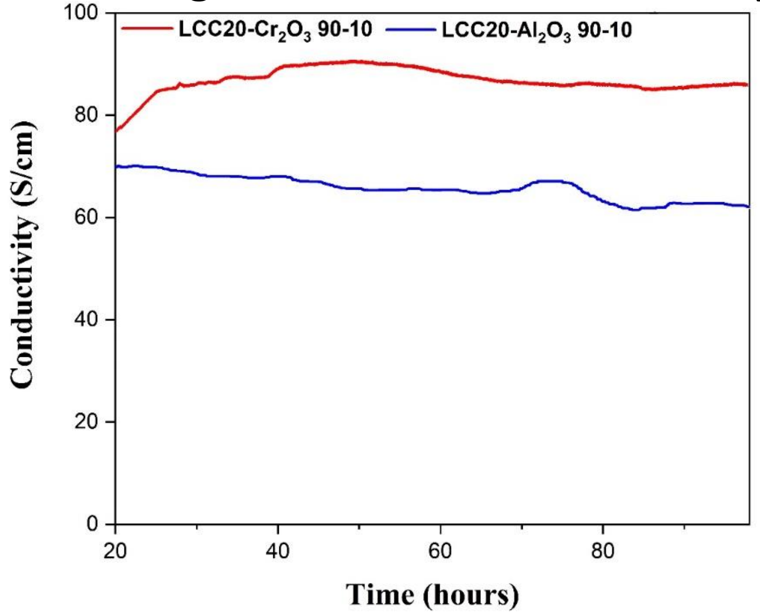


SEM and TEM characterization

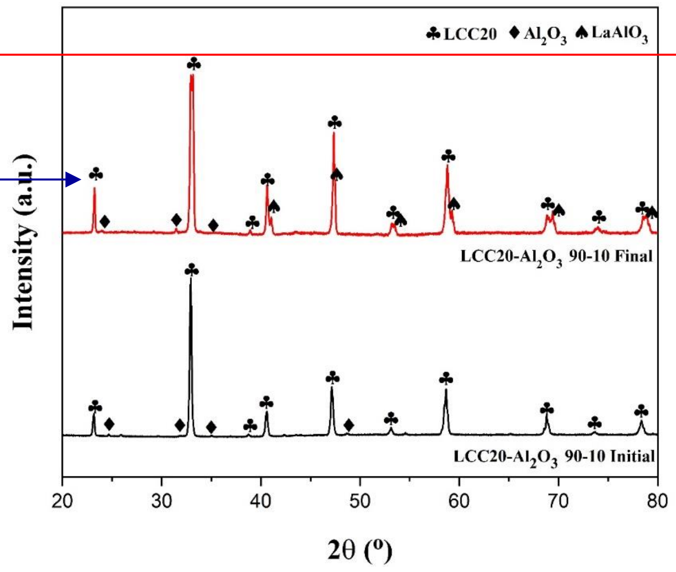
- TEM and SEM show $CaCrO_4$ grains among LCC and Al_2O_3 grains.
- Formation of $CaCrO_4$ secondary phase observed at 30% vol/vol Cr_2O_3 content.
- Despite this, a uniform mix of LCC30 and Cr_2O_3 observed in composites sintered at 1500°C.

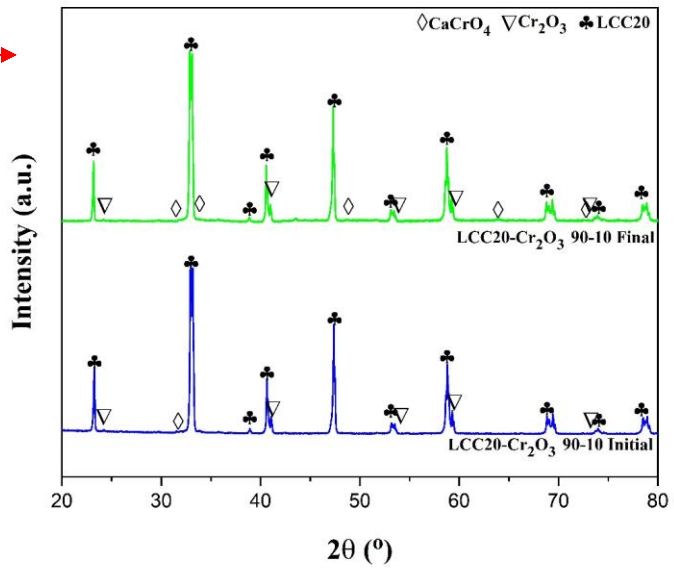
DC Conductivity Long-Term Characterization

Long-term Electrical Conductivity



XRD characterization



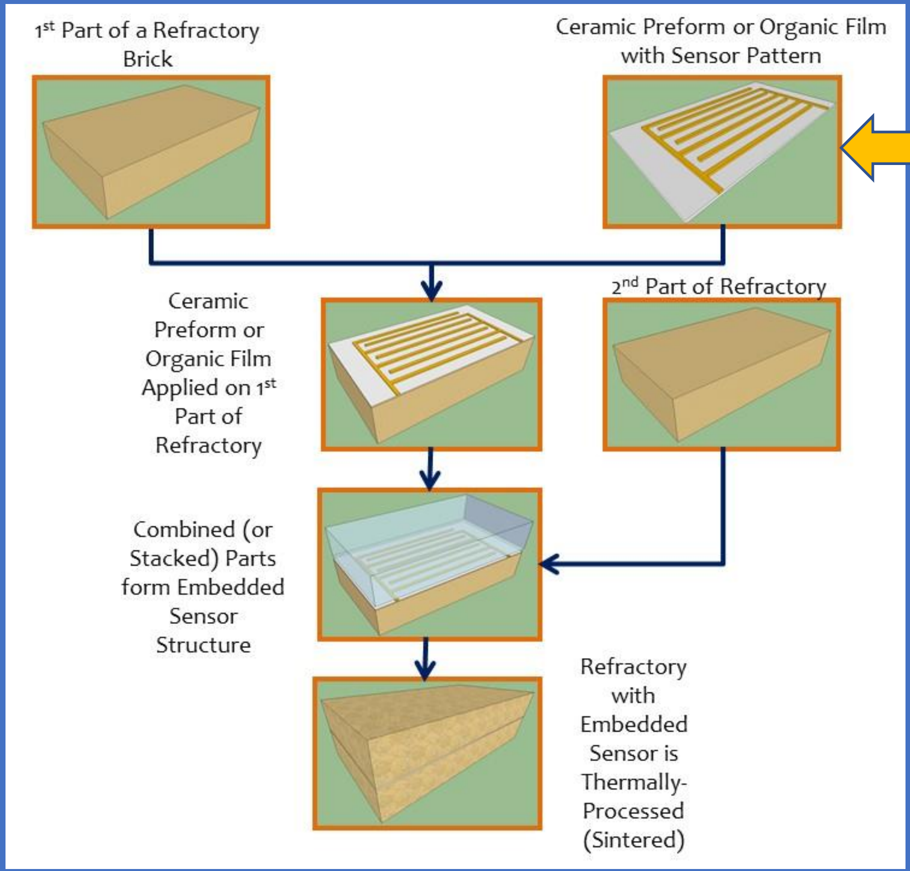


- ❖Initial conductivity ~70 S/cm, decreases slightly over time due to Al^{+3} diffusion into LCC20 and Ca^{+2} migration to Al_2O_3.
- ❖XRD shows $LaAlO_3$ and minor $Al_{1.9}Cr_{0.1}O_3$ formation after annealing. Peak conductivity ~90 S/cm, more stable than Al_2O_3-based composites.
- ❖XRD reveals LCC20, Cr_2O_3, and $CaCrO_4$ phases. LCC20-Cr_2O_3 90-10 composite shows promise for high-temp sensor layers.

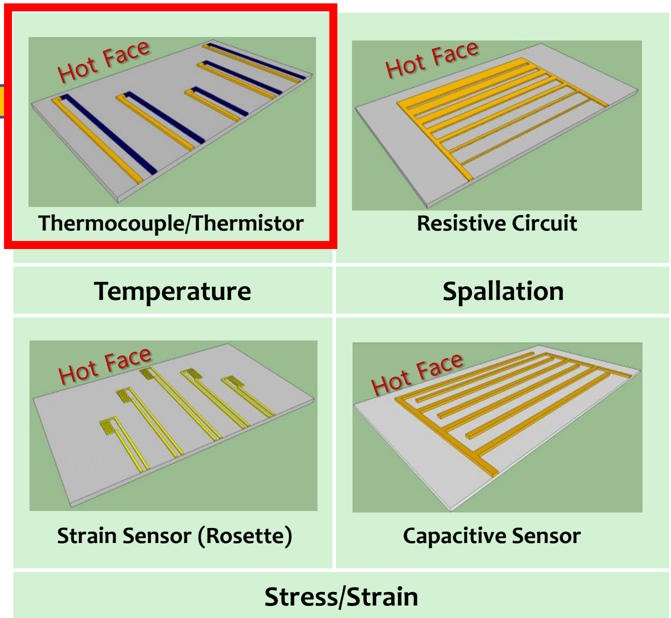
Sensors Embedded into Refractory

Embedded Sensors Fabrication

General Smart Refractory Processing Method

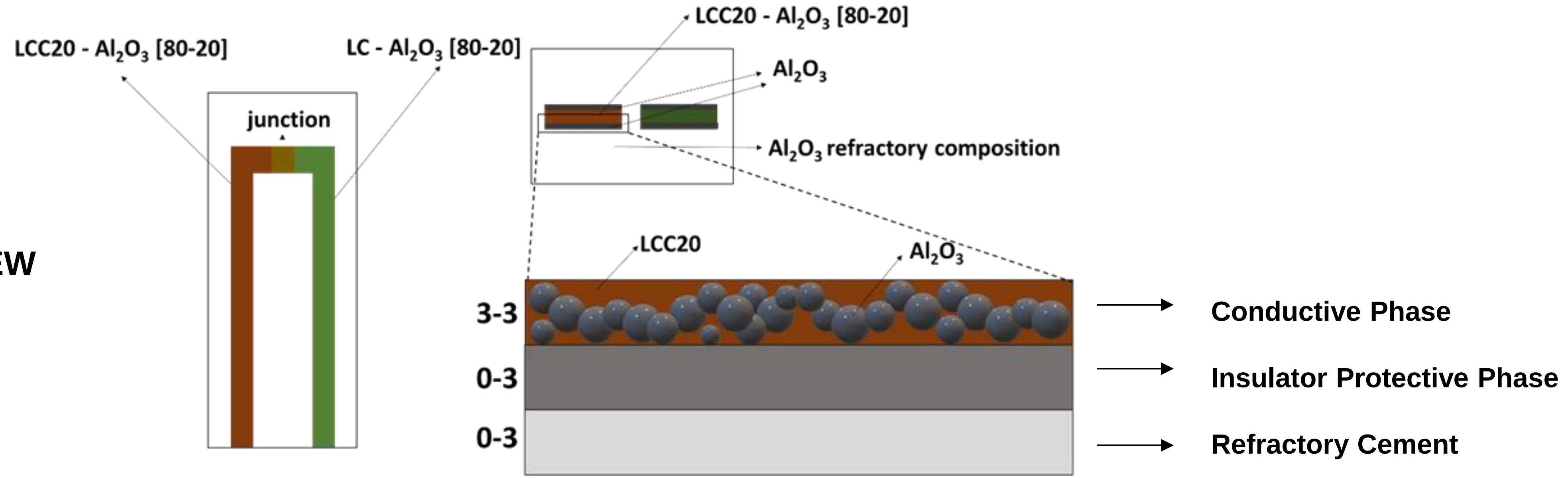


Examples of Sensor Preforms



Embedded Sensors Fabrication

TOP VIEW



Refractory Cement

Al_2O_3-Cr_2O_3 [50-50]	Al_2O_3-Cr_2O_3 [50-50]
$LaCrO_3$	Ca doped $LaCrO_3$
Al_2O_3-Cr_2O_3 [50-50]	Al_2O_3-Cr_2O_3 [50-50]

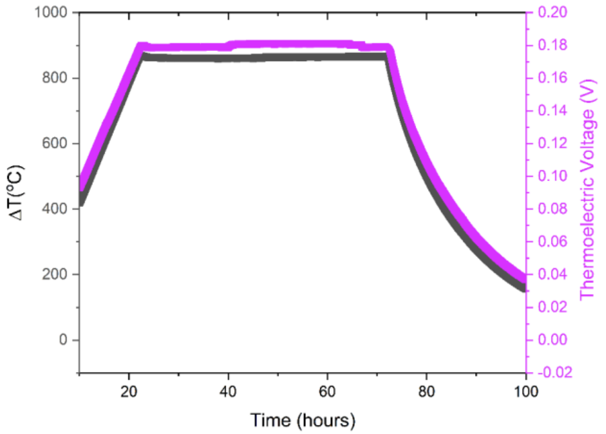
Refractory Cement

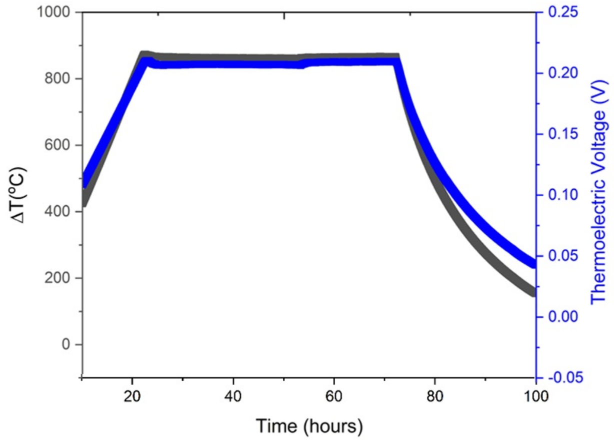
Al_2O_3-Cr_2O_3 [70-30]	Al_2O_3-Cr_2O_3 [70-30]
$LaCrO_3$-Cr_2O_3 [90-10]	Ca doped $LaCrO_3$-Cr_2O_3 [90-10]
Al_2O_3-Cr_2O_3 [70-30]	Al_2O_3-Cr_2O_3 [70-30]

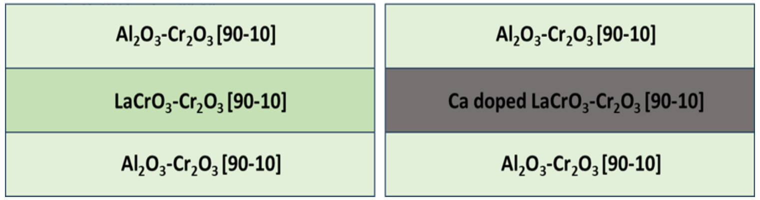
CROSS-SECTION VIEW

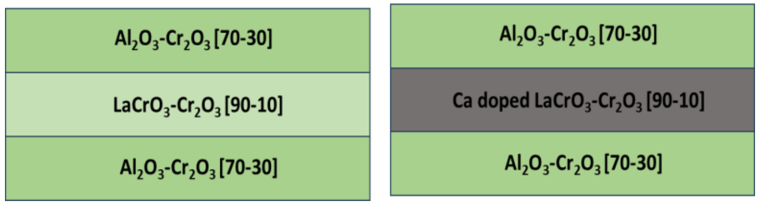
Thermoelectric Long-Term Characterization

Long-term Thermoelectrical characterization









Thermocouples Conductive Phase	Thermocouples Protective Phase	Percentual Drift Rate (%/ h)
LC/LCC20	Al_2O_3 - Cr_2O_3 [50-50]	0.017
LC- Cr_2O_3 [90-10]/ LCC20- Cr_2O_3 [90-10]	Al_2O_3 - Cr_2O_3 [50-50]	0.007
LC- Cr_2O_3 [90-10]/ LCC20- Cr_2O_3 [90-10]	Cr_2O_3 - Al_2O_3 [30-70]	0.020
LC- Cr_2O_3 [90-10]/ LCC20- Cr_2O_3 [90-10]	Cr_2O_3 - Al_2O_3 [10-90]	0.029
LC- Cr_2O_3 [80-20]/ LCC20- Cr_2O_3 [80-20]	Cr_2O_3 - Al_2O_3 [30-70]	0.008

- **Thermocouples with LC-Cr_2O_3 [90-10]/LCC20-Cr_2O_3 [90-10] legs and Al_2O_3-Cr_2O_3 [50-50] layers exhibit improved stability.**

- **Drift rates for tested thermocouples range from 0.007% to 0.029% per hour over 60 hours, indicating sensor accuracy.**

Conclusions

Conclusions

- **All the Seebeck coefficients were determined as the slope of the obtained plots, observing constant behavior as expected for polaron hopping active semiconductors such as doped $LaCrO_3$.**

- **It was observed that Seebeck coefficient reduces with the increase in dopant substituents as expected by Heikes model.**

- **Secondary phases observed on composites incl. $LaAlO_3$, $Ca_2Al_2O_5$, $CaCrO_4$, and Cr-doped Al_2O_3.**

Conclusions

- Conductivity variations were investigated, notably in LCC20-Al_2O_3 [90-10].

- LCC20-Cr_2O_3 composites show enhanced conductivity and stability.

- Promising results with Al_2O_3-Cr_2O_3 50-50 protective layers and LC-Cr_2O_3 [90-10]/LCC20-Cr_2O_3 [90-10] conductive layers, hinting at long-term industrial potential.

Acknowledgment

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- We also would like to thank HWI, for support us in developing real-life applications sensing systems/devices.

- Kindly acknowledge faculty and staff of West Virginia University for their support.

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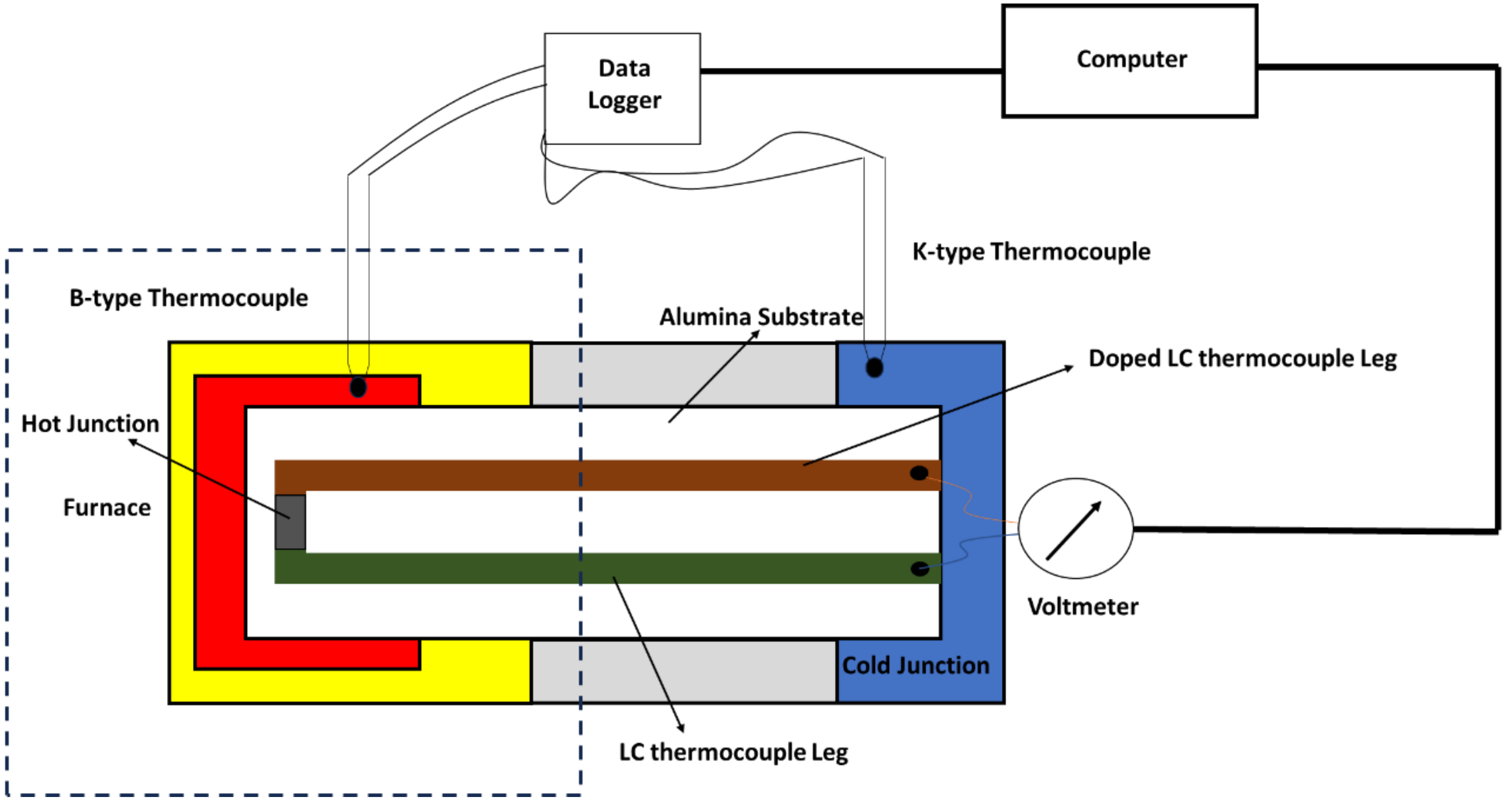
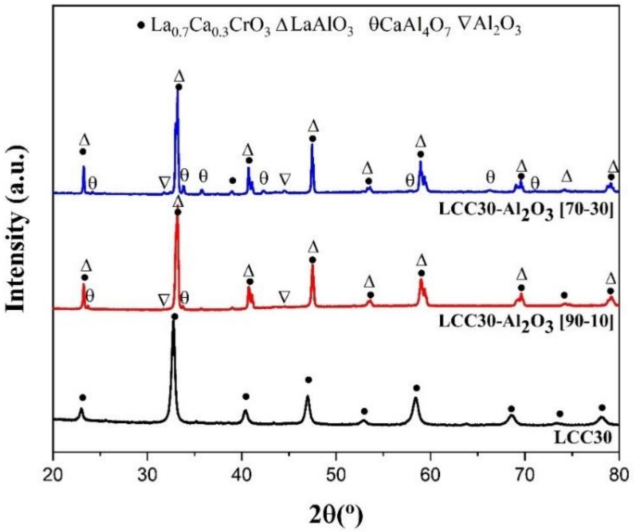
Seebeck Coefficient Determination

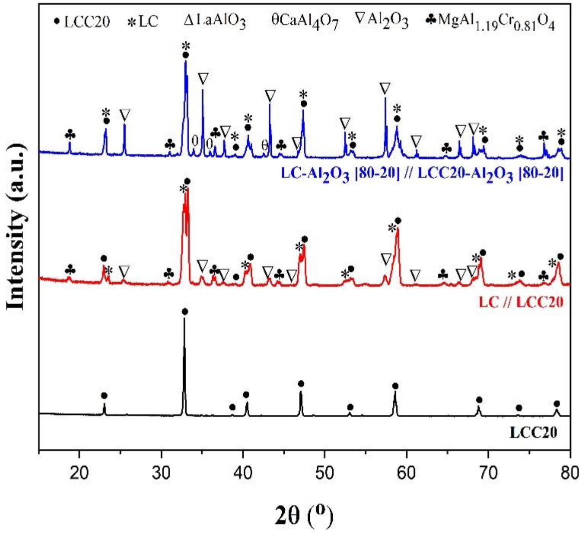


XRD - Composites characterization

LCC30-Al_2O_3 Composites



LC-LCC30// Al_2O_3 junctions



Al_2O_3 substrates before and after legs printing and sintering

- LCC30-Al_2O_3 [70-30] diffractogram shows LCC30 and lanthanum aluminate ($LaAlO_3$), calcium aluminate ($Ca_2Al_2O_5$) and pure Al_2O_3.
- X-ray diffractograms of junctions between composites show secondary phases such as $LaAlO_3$ and $Ca_2Al_2O_5$ due to cation interdiffusion.
- Evidence of chromium diffusion to the substrate phase is observed in all junctions.