Impact of oxidizing atmospheres on secondary phases, microstructure and dielectric response of nonstoichiometric $Ca_{1.1}Cu_3Ti_4O_{12}$ ceramics

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ABSTRACT

Nonstoichiometric $Ca_{1.1}Cu_3Ti_4O_{12}$ ceramics offer an effective route to tailor defect chemistry and secondary phases in CCTO-based materials, since Ca excess favors $CaTiO_3$ formation and modifies grain growth and grain-boundary properties [1,2]. The atmosphere used during calcination and sintering controls oxygen activity and the distribution of Ca-rich phases, affecting microstructure and dielectric behavior [2,3]. This work investigates the influence of atmospheric air and pure O_2 on the phase assemblage, microstructure and dielectric properties of $Ca_{1.1}Cu_3Ti_4O_{12}$ ceramics. Powders were synthesized by coprecipitation, calcined at 850, 950 and 1000 °C for 6 h in air or O_2, uniaxially pressed and sintered at 1050 or 1100 °C for 2 h in the same atmosphere. Phase fractions (CCTO, CuO, TiO_2, $CaTiO_3$) were quantified by XRD with Rietveld refinement, grain size distributions by SEM, and dielectric properties by impedance spectroscopy. Air-calcined powders retained more than 16 wt% of secondary phases, while O_2 favored CCTO formation (up to 97.1 wt% at 1000 °C). After sintering, all ceramics exceeded 95 wt% CCTO and residual TiO_2 was consumed by the Ca excess, forming $CaTiO_3$. Located at grain boundaries, $CaTiO_3$ pinned grain growth, yielding smaller and more uniform grains than in stoichiometric CCTO; sintering at 1100 °C increased D_{50} to 6.0–6.8 μm and relative density to 92–93 %. Ceramics processed in O_2 showed higher dielectric constant than in air; the sample calcined at 850 °C and sintered at 1100 °C in O_2 reached $\varepsilon'_r \approx 3.95\times10^4$ at 1 kHz, 56 % above its air analogue. Losses depended on sintering temperature: O_2 reduced tan δ at 1050 °C (0.134 vs. 0.179), whereas at 1100 °C the higher permittivity came with higher losses (0.230 vs. 0.123). These results show that combining Ca excess, an oxidizing atmosphere and a low calcination temperature is an effective route to tune the phase assemblage, grain size and permittivity–loss balance of CCTO ceramics.

EXPERIMENTAL

1 | Powder synthesis – coprecipitation route

Raw materials
- $Cu(NO_3)_2{\cdot}3H_2O$
- $CaCO_3$
- $Ti(OC_4H_9)_4$
- $Ca_{1.1}Cu_3Ti_4O_{12}$ (10 % Ca excess, no Cu/Ti compensation)

→ **Dissolution**
- $Ti(OC_4H_9)_4$ in HNO_3 [6 M]
- 70 °C, stirring
- + $CaCO_3$, + $Cu(NO_3)_2$
- Blue solution, pH ≈ 2

→ **Coprecipitation**
- NH_4OH [10 M]
- pH > 11
- Ti, Ca, Cu hydroxides precipitate

→ **Drying**
- Oven: 70 °C / 24 h
- Grinding in mortar

→ **Pre-calcination**
- 350 °C / 1 h, air
- Removal of organics
- Grinding (10 min)

→ **Calcination**
- 850, 950 or 1000 °C
- 6 h, 10 °C/min
- Air or O_2 (50 mL/min)

→ **Deagglomeration**
- Mortar: 15 min dry
- + 10 min in isopropyl alcohol

→ **Shaping**
- Uniaxial pressing, 180 MPa
- Disks: Ø 12 mm × 1.5 mm (≈ 0.45 g)

2 | Sintering and sample preparation

Sintering
- 1050 or 1100 °C / 2 h
- 10 °C/min
- Same atmosphere as calcination (air or O_2)

→ **Finishing**
- SiC papers P80 → P1200
- Parallel faces
- Ø 10 mm × 1 mm

→ **Electrodes**
- Ag paste
- Fired at 600 °C / 5 min

→ **12** $Ca_{1.1}Cu_3Ti_4O_{12}$ **ceramics**
3 calcination temperature × 2 sintering temperature × 2 atmospheres

3 | Sample matrix and characterization

Calcin.	Air		O_2	
	1050 °C	1100 °C	1050 °C	1100 °C
850 °C	NA11	NA12	NO11	**NO12**
950 °C	NA21	NA22	NO21	NO22
1000 °C	NA31	NA32	NO31	NO32

Code: N = nonstoichiometric; A/O = atmosphere; 1st digit = calcination T; 2nd digit = sintering T (1 = 1050, 2 = 1100 °C)

Highlighted: NO12 – highest ε'_r (≈ 3.9×10^4 at 1 kHz)

XRD + Rietveld
- PANalytical X'Pert PRO, CuKα
- 2θ = 10–90°, step 0.02°
- Phase fractions: CCTO, CuO, TiO_2, $CaTiO_3$

SEM / BSE
- Phenom ProX
- Powders and fracture surfaces
- Grain size distribution (ImageJ, D_{10}, D_{50}, D_{90})

Density
- Archimedes method (ASTM C20)
- Relative to weighted theoretical density

Impedance spectroscopy
- Keysight E4990A
- 20 Hz – 5 MHz, 500 mV, RT
- ε'_r and tan δ

RESULTS

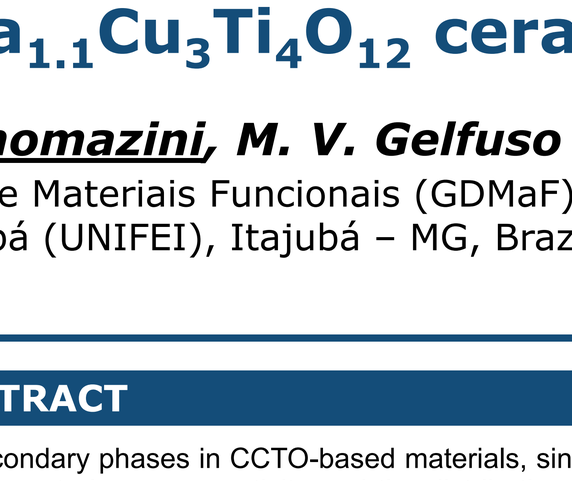


Figure 1 – Rietveld phase quantification of calcined powders: CCTO1.0 (reference) and CCTO1.1.

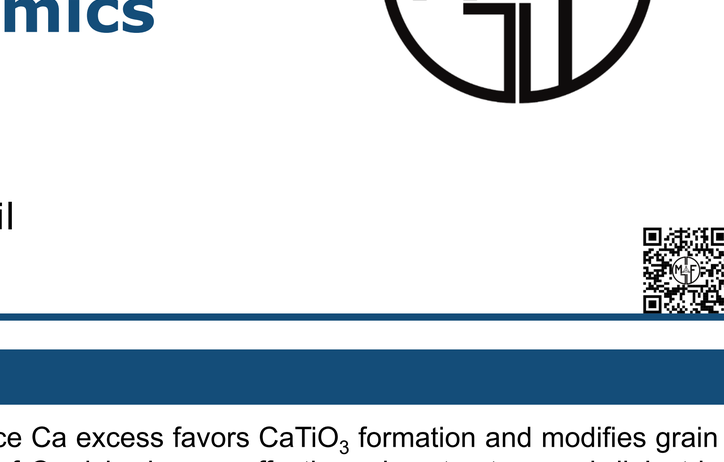


Figure 2 – Rietveld phase quantification of the $Ca_{1.1}Cu_3Ti_4O_{12}$ sintered ceramics.

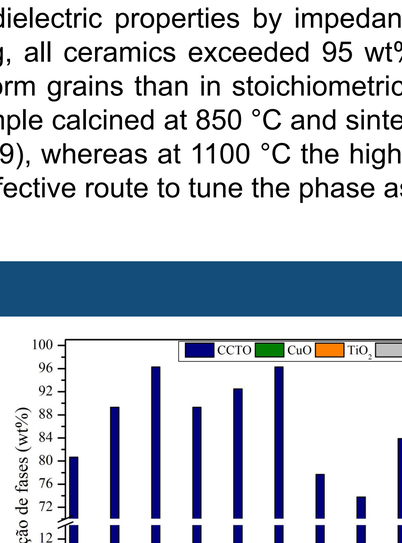


Figure 3 – Fracture surfaces of ceramics sintered in air: a) NA11, b) NA12, c) NA21, d) NA22, e) NA31, f) NA32.

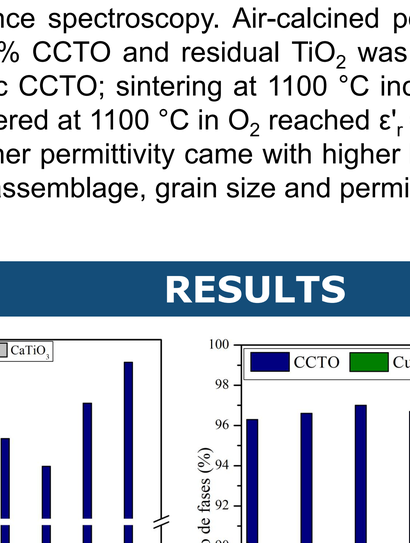


Figure 4 – Fracture surfaces of ceramics sintered in O_2: a) NO11, b) NO12, c) NO21, d) NO22, e) NO31, f) NO32.

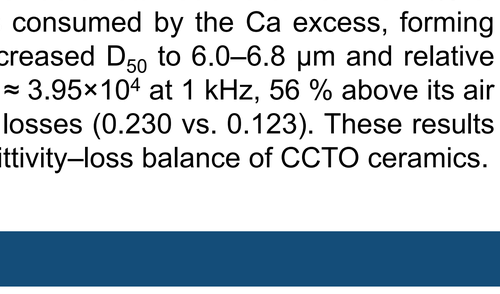


Figure 5 – Grain size distribution of the $Ca_{1.1}Cu_3Ti_4O_{12}$ ceramics.

Table 1 – ε'_r and tan δ at 1 kHz (powders calcined at 850 °C).

	NA11	NO11	NA12	NO12
ε'_r	1.88×10^4	2.12×10^4	2.53×10^4	**3.95×10^4**
tan δ	0.179	0.134	0.123	**0.230**

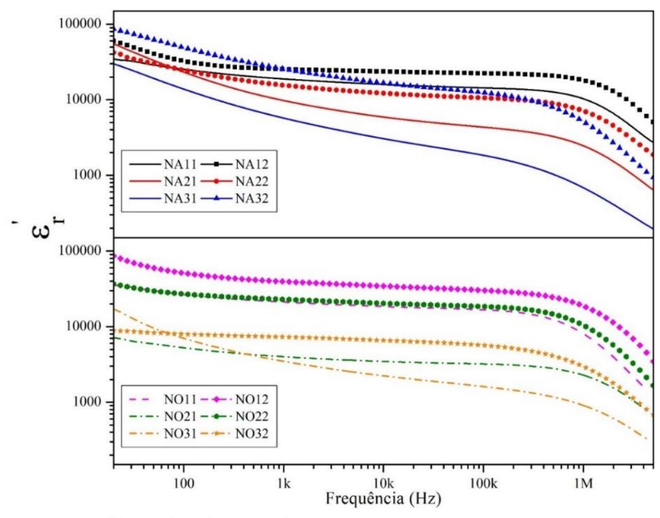


Figure 6 – ε'_r versus frequency at room temperature.

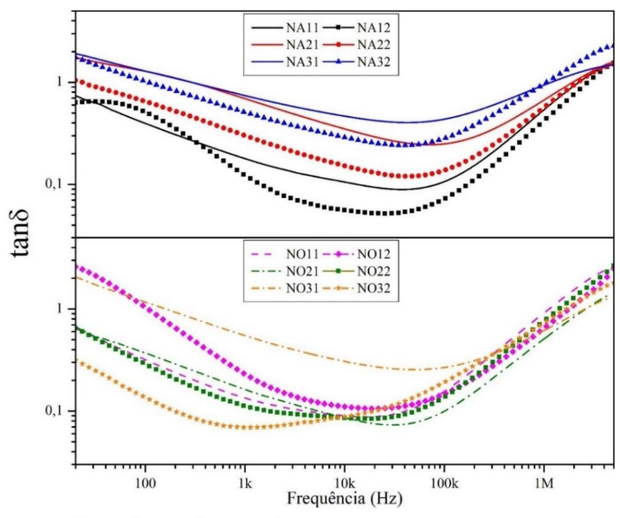


Figure 7 – tan δ versus frequency at room temperature.

CONCLUSIONS

- **Phase formation:** air-calcined $Ca_{1.1}$ powders retained > 16 wt% of secondary phases, whereas O_2 favored CCTO formation (up to 97.1 wt% at 1000 °C). After sintering, all ceramics reached ≥ 95 wt% CCTO, with no residual TiO_2: the Ca excess consumed it as $CaTiO_3$ (≈ 1–2.5 wt%).
- **Microstructure:** $CaTiO_3$ at grain boundaries pinned grain growth, giving smaller and more uniform grains than stoichiometric CCTO. Sintering at 1100 °C raised D_{50} from ≈ 2 μm to 6.0–6.8 μm (NA12/NO12) and the relative density to 92–93 %.
- **Dielectric response:** O_2-processed ceramics showed higher ε'_r than their air counterparts. NO12 (850 °C calcination, 1100 °C sintering) reached $\varepsilon'_r \approx 3.95\times10^4$ at 1 kHz, 56 % above NA12 (2.53×10^4).
- **Losses:** at 1050 °C, O_2 lowered tan δ (0.134 vs 0.179); at 1100 °C the higher ε'_r of NO12 came with higher losses (0.230 vs 0.123), likely linked to $CaTiO_3$ incorporated into the grain/subgrain barrier layers.
- Combining Ca excess with an oxidizing atmosphere and low calcination temperature is an effective route to tune phase assemblage, grain size and the permittivity–loss balance of CCTO.

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REFERENCES