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Electric field–assisted flash sintering of fine–grained and high–permittivity CaCu3Ti4O12 electroceramics

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[1] Subramanian, M. A. et al., High dielectric constant in ACu3Ti4O12 and ACu3Ti3FeO12 phases. J. Solid State Chem. 151, 323-325 (2000). [2] Cologna, M., Rashkova, B., RAJ, R., Flash sintering of nanograin zirconia in < 5 s at 850 °C. J. Am. Ceram. Soc. 93, 3556-3559 (2010). [3] Jesus, L. M. et al., Polymeric synthesis and conventional versus laser sintering of CaCu3Ti4O12 electroceramics: (micro)structures, phase development and dielectric properties. J. Alloys Compd., In press, DOI: 10.1016/j.jallcom.2015.09.027 (2015).

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Electric field-assisted flash sintering of fine-grained and high-permittivity $CaCu_3Ti_4O_{12}$ (CCTO) electroceramics

Lílian Menezes de Jesus

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Prof. Dr. Rishi Raj (University of Colorado Boulder)

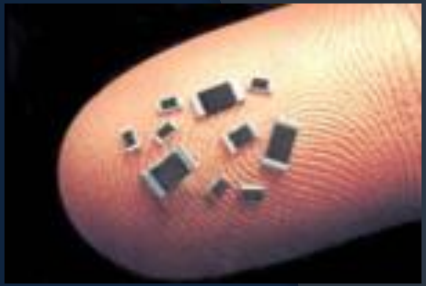
Presentation Outline

- ✓ **Introduction**
- ✓ **Experimental Procedure**
  - Synthesis using a polymeric precursor method;
  - Field-assisted flash sintering;
  - Characterization techniques.
- ✓ **Results**
  - Effects of electric field (*E*) on CCTO Sintering;
  - (Micro)structural Characteristics;
  - Correlation between AGS and dielectric constant.
- ✓ **Summary**

Introduction

Introduction

Why should we study CCTO?



- ✓ $CaCu_3Ti_4O_{12}$ (CCTO)
  - ε' ~ 10^4 (at RT and 100 kHz) [1]
  - Non-Ferroelectric (ε' is stable in a wide range of T)
  - Remarkable nonlinear current-voltage response ($\alpha = 912$ [2])
- ✓ **Potential use in electronic devices**

- ➢ Processing conditions strongly affects CCTO properties;
- ➢ Field-assisted flash sintering has been applied for the preparation of several materials [3-5];
  - However, there are no reports for CCTO ceramics;

- ➢ **How does electric field affect the CCTO sintering?**

[1] M.A. Subramanian, et al., J. Solid State Chem. 151 (2000) 323-325.
[2] S.-Y. Chung, et al., Nature Mater. 31 (2004) 774-778.
[3] M. Cologna, et al., J. Am. Ceram. Soc. 93 (2010) 3556-3559.
[4] X. Hao,et al., J. Power Sources 210 (2012) 86-91.
[5] S.K. Jha, R. Raj, J. Am. Ceram. Soc. 97 (2014) 527-534.

Experimental Procedure

Experimental Procedure

Powder synthesis: Polymeric precursor method

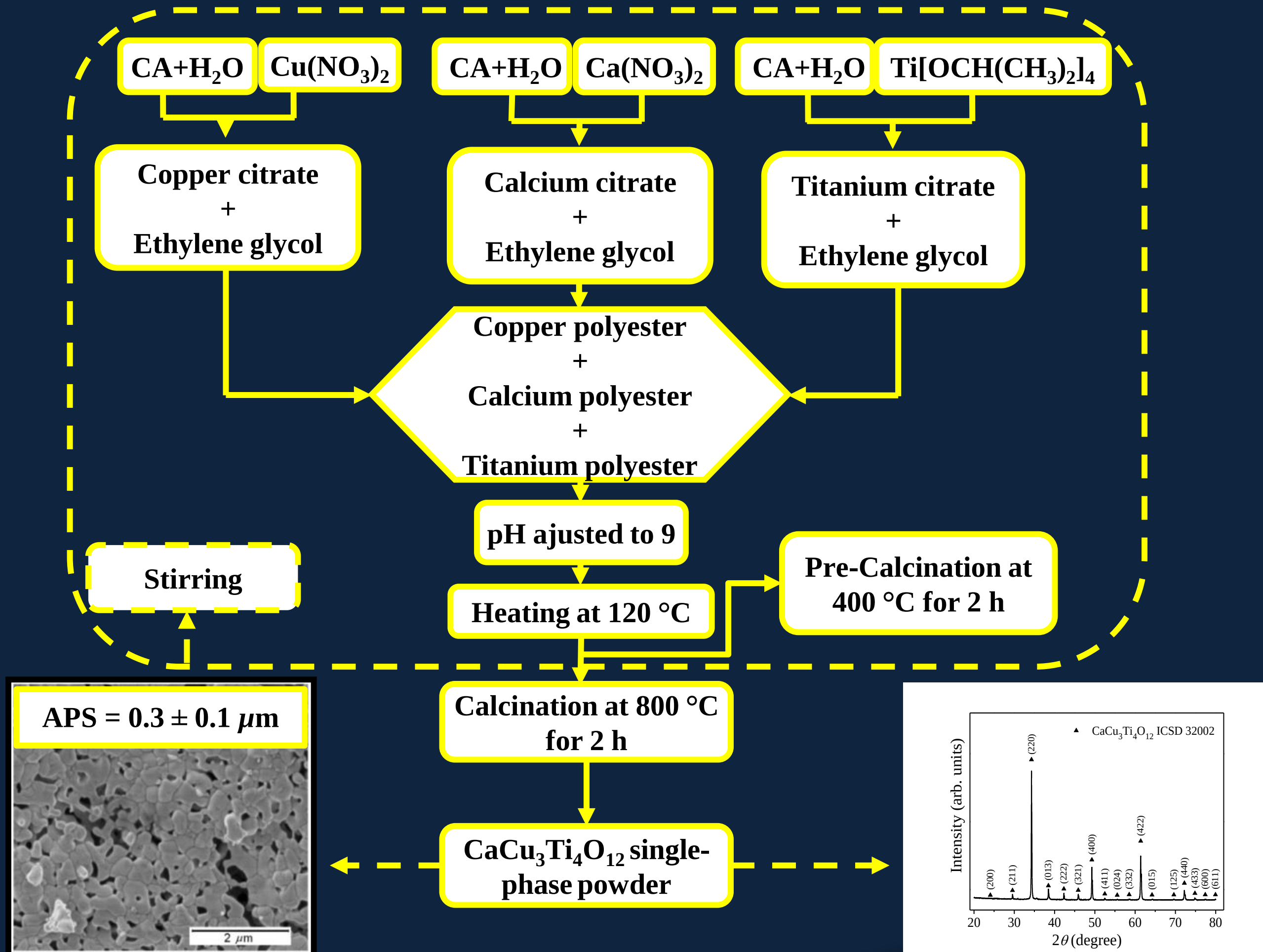


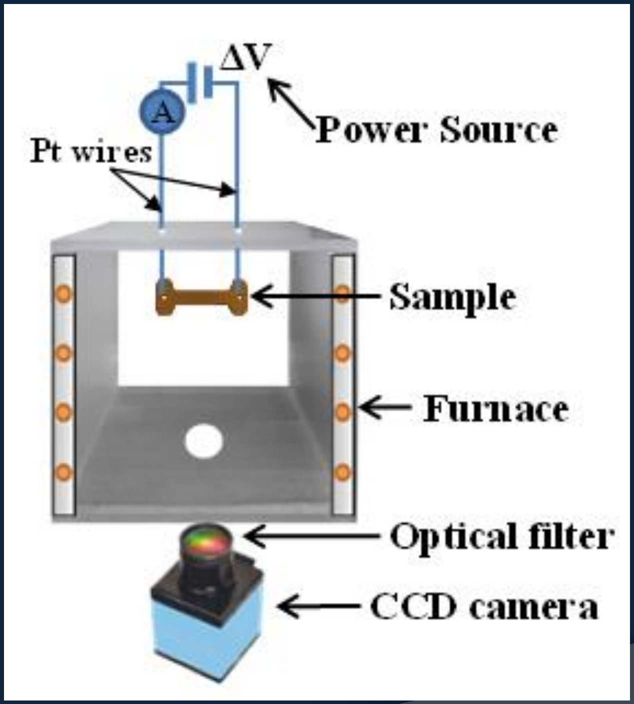
Fig. 1: Flowchart of the $CaCu_3Ti_4O_{12}$ synthesis process.

[6] Jesus, L. M. *et al*., Polymeric synthesis and conventional versus laser sintering of $CaCu_3Ti_4O_{12}$ electroceramics: (micro)structures, phase development and dielectric properties. *J. Alloys Compd*. **654**, 482-490 (2016).

Experimental Procedure

Electric field-assisted flash sintering

Powder synthesis → Consolidation (dog-bone shaped sample) → Sintering



$0 \leq E \leq 60$ V/cm
$I = 300$ m A ($J = 75$ mA/mm^2)
Holding time = 1 min
Heating rate = 10 °C/min

$$\epsilon = \ln(L/L_o)$$

Fig. 2: Flash Sintering Experimental apparatus.

Experimental Procedure

Characterization techniques

- ✓ **Temperature measurement by optical pyrometry;**
  - using a CLTM-1 Micro-Epsilon optical pyrometer.
- ✓ **Density determination by Archimedes method;**
  - using distilled water as the immersion fluid.
- ✓ **X-ray diffraction (XRD);**
  - using a Rigaku RINT 2000/PC equipment operating with CuKα radiation.
- ✓ **Scanning electron microscopy (SEM);**
  - using a FEG-SEM, FEI Inspect F50 microscope.
- ✓ **Measurement of ε' at room temperature and 1 MHz.**
  - using an impedance analyzer HP 4192A.

Results

Results

True Strain and Power Dissipation (Flash Sintering)

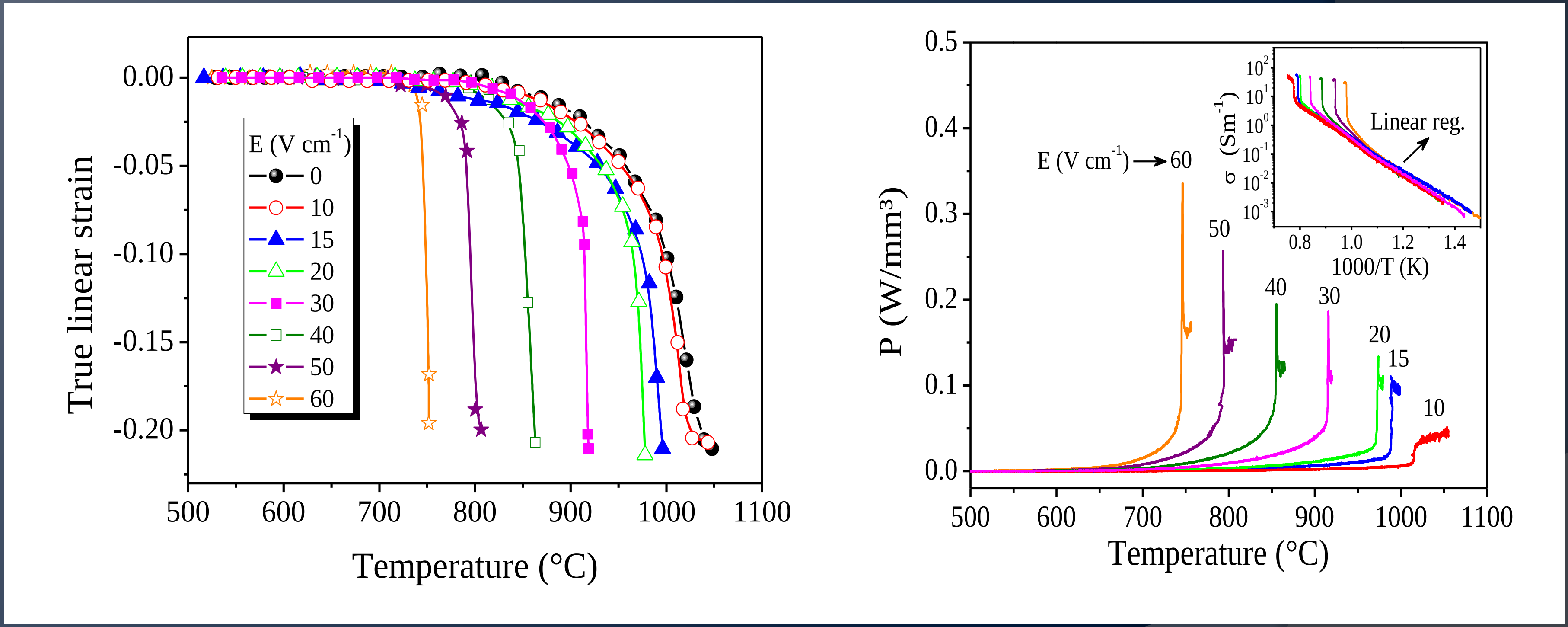


Fig. 3: Temperature dependence of true strain (ϵ) and power density during electric field-assisted sintering. J_{max} = 75 mA/mm² and dwell time of 60 s.

Results

Sample temperature during flash sintering

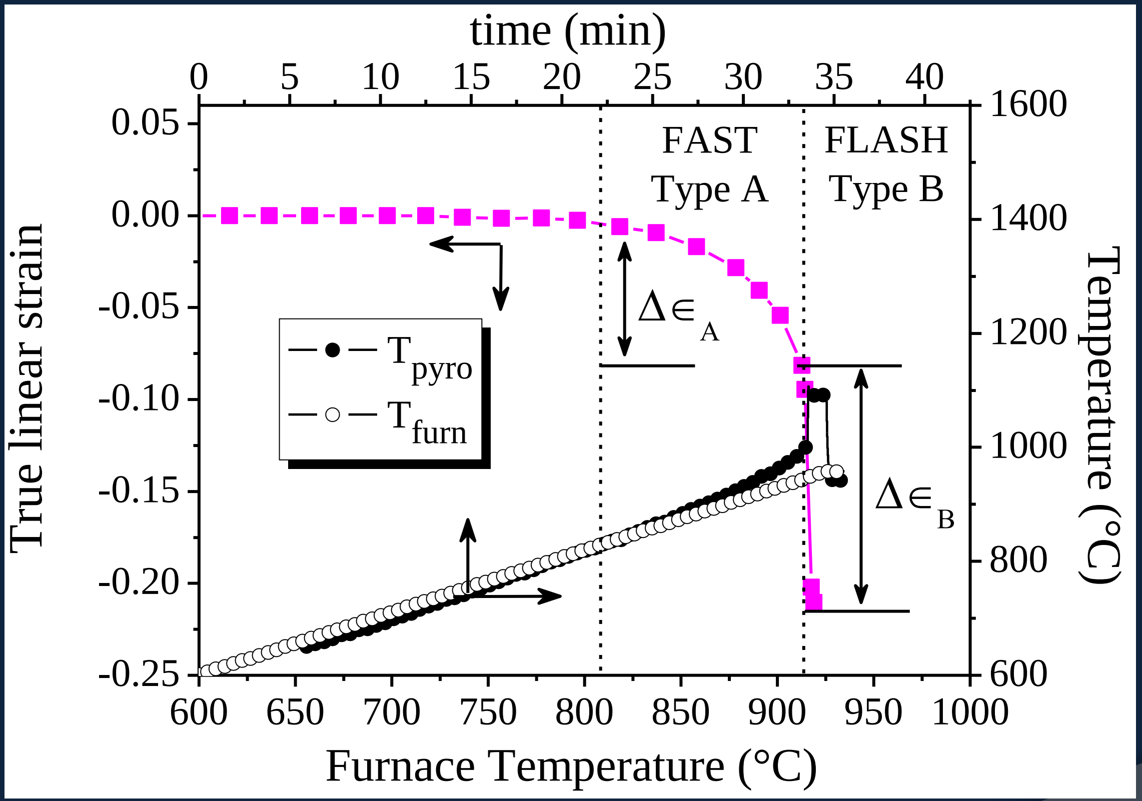
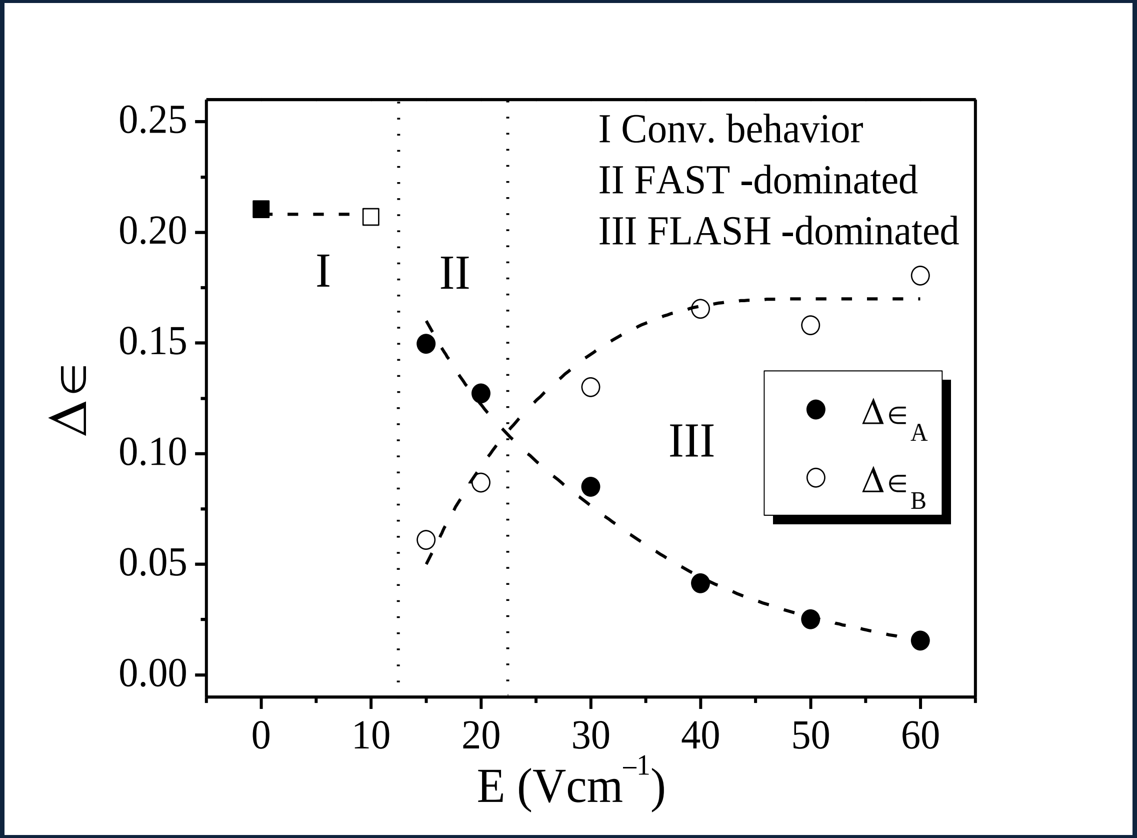


Fig. 4: Dependence of strain on furnace temperature and time evolution of furnace and pyrometer temperatures during sintering for E = 30 V/cm.

[7] R. Raj, Joule heating during flash-sintering, J. Eur. Ceram. Soc. 32 (2012) 2293-2301.

Results

Type A and Type B contribution to strain



- Y_2O_3-doped Z_rO_2 [3]
- Gd-doped CeO_2 [4]
- TiO_2 [5]

✓ They have a pure FAST region

Fig. 5: Shrinkage strain attributed to conventional-like behavior (I), FAST- (II) and FLASH-dominated regions (III).

[4] M. Cologna, B. Rashkova, R. Raj, J. Am. Ceram. Soc. 93 (2010) 3556-3559.
[5] X. Hao, Y. Liu, Z. Wang, J. Qiao, K. Sun, J. Power Sources 210 (2012) 86-91.
[6] S.K. Jha, R. Raj, J. Am. Ceram. Soc. 97 (2014) 527-534.

Results

Structural characterization of the ceramics - XRD

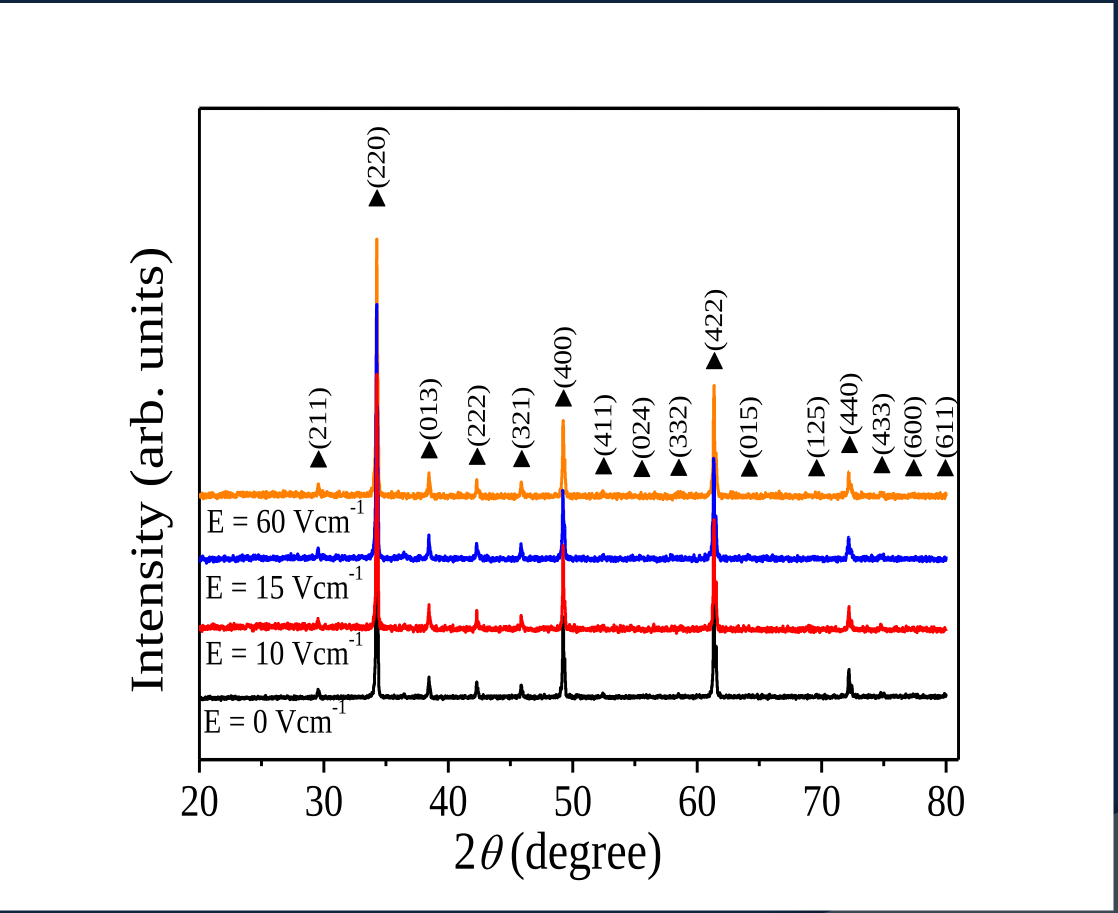


Fig. 9: XRD of CCTO ceramic sample conventionally sintered at 1050 °C for 60 s (0 V/cm) and flash-sintered samples under different electric fields.

Results

Microstructural characterization - SEM

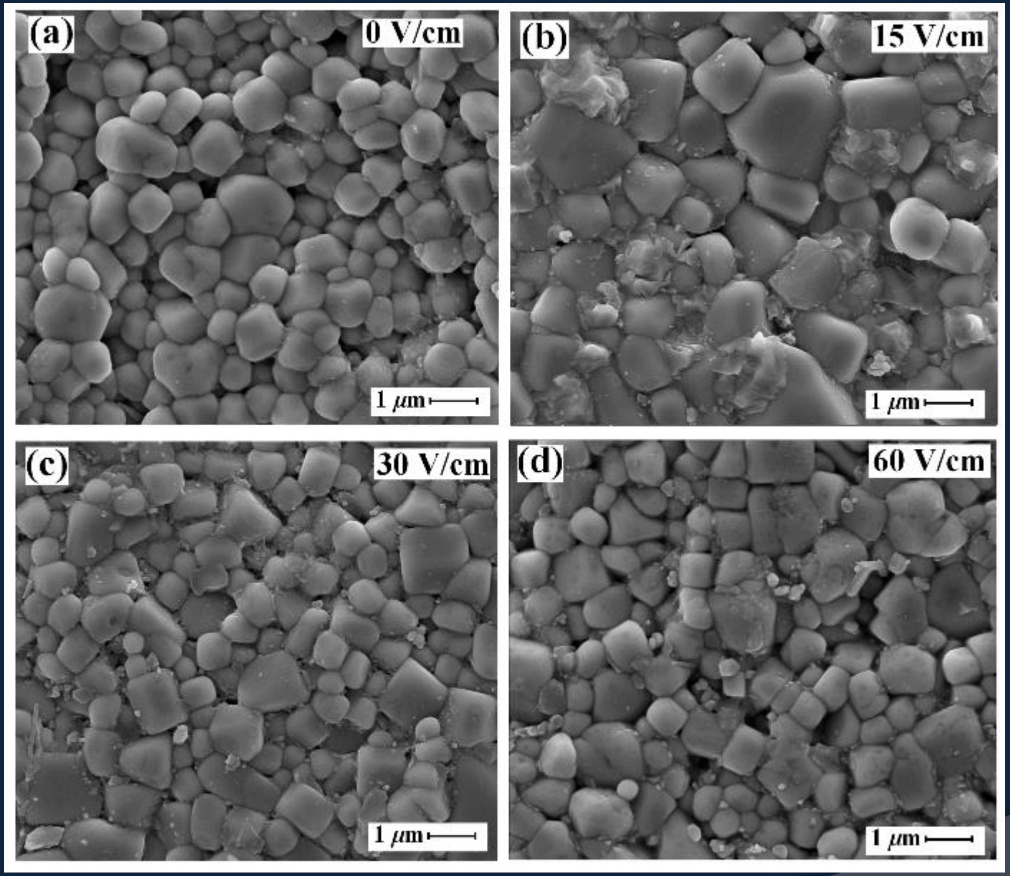


Fig. 6: SEM micrographs of the specimens after conventional (a) and electric field-assisted sintering (b-d).

Results

Table 1: Applied field (*E*), relative density (ρ_{rel}), furnace (T_{furn}^{flash}) and pyrometer (T_{pyro}^{flash}) temperatures at flash and average grain size (AGS).

E (V/cm)	ρ_{rel} (%)	T_{furn}^{flash} (ºC)	T_{pyro}^{flash} (ºC)	AGS (μm)
0	94	n/a†	1050	0.64
10	93	n/a†	1103	1.32
15	94	995	1120	1.55
20	95	975	1113	0.98
30	94	918	1090	0.85
40	93	860	1053	0.77
50	91	800	1036	0.70
60	90	750	1044	0.73

†These specimens were sintered at a furnace temperature of 1050 ˚C.

Results

Correlation between grain size and dielectric constant

- Gd-doped CeO_2 [4]
- $BaTiO_3$ [5]

✓ E ↑ → AGS ↓

$$\left.\begin{array}{c}\sigma_{Bulk} \gg \sigma_{gb} \\ \text{AGS} \gg \delta\end{array}\right\} \quad \boxed{\varepsilon_{gb}^{(mac)} \cong \varepsilon_{gb}^{(sp)}\, AGS/\delta}$$

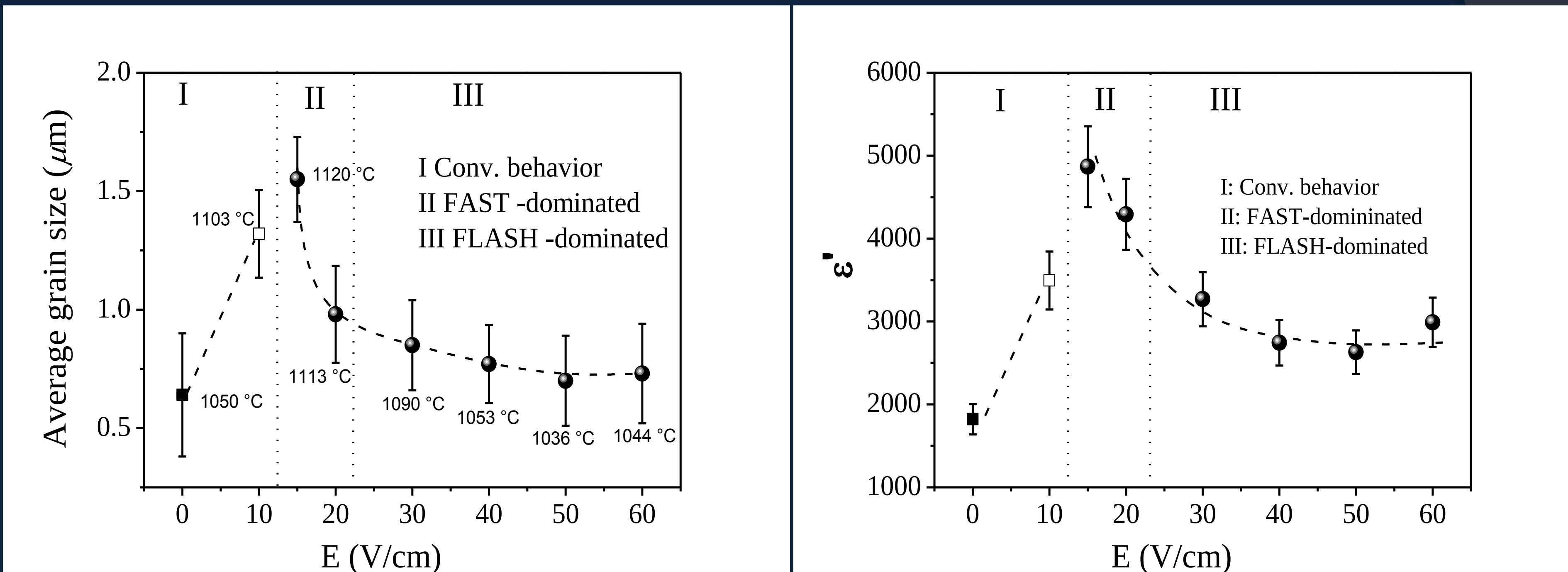


Fig. 7: (a) Variation of the average grain size and (b) dielectric constant at room temperature and 1 MHZ in the CCTO ceramics upon applied electric field.

[4] X. Hao, Y. Liu, Z. Wang, J. Qiao, K. Sun, J. Power Sources 210 (2012) 86-91.
[8] J.-C. M'Peko, J.S.C. Francis, R. Raj, J. Eur. Ceram. Soc. 34 (2014) 3655-3660.

Summary

Summary

- ✓ Sintering is accelerated (FAST effect) for $E \gtrsim 15$ V/cm, ending with a FLASH event;
- ✓ Both events implied sintering at furnace temperatures considerably lower than in conventional processing;
- ✓ for $E < 15$ V/cm, there was no improved sintering rate, and AGS increased with field (Joule heating);
- ✓ for $E \gtrsim 15$ V/cm, the AGS decreased with E;
- ✓ ε' values reproduced thoroughly the behavior of AGS with varying E, suggesting ε' to be modulated by the dielectric response from grain boundaries;

Flash sintering is shown to be a good approach for producing high-quality CCTO electroceramics.

CAPES

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Thank you!

University of Colorado **Boulder**