Electric current as a driving force for interphase growth in spark plasma sintered dielectric composites

Catherine Elissalde
CNRS

Follow this and additional works at: http://dc.engconfintl.org/efa_sintering
Part of the Engineering Commons

Recommended Citation

This Abstract and Presentation is brought to you for free and open access by the Proceedings at ECI Digital Archives. It has been accepted for inclusion in Electric Field Assisted Sintering and Related Phenomena Far From Equilibrium by an authorized administrator of ECI Digital Archives. For more information, please contact franco@bepress.com.
Electric Field Assisted Sintering and Related Phenomena Far from Equilibrium

March 6-11, 2016 - Tomar Portugal

Electric current as a driving force for interphase growth in Spark Plasma Sintered dielectric composites

Catherine Elissalde,1 Marjorie Albino1, U-Chan Chung1, G. Philippot1, R. Epherre2, G. Chevallier2, D. Bernard1, C. Aymonier1, C. Estournès2 and Mario Maglione1

1CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
2CNRS; Institut Carnot Cirimat; F-31062 Toulouse, France, Université de Toulouse
Outline

• Motivations

• Ferroelectric materials : contribution of Spark Plasma Sintering – Thermal and pressure effects

• Electrical current effects and Interface control : Multilayers and 3D composites
  - BaSrTiO$_3$ /TiO$_2$

• Conclusion
Designing ferroelectric materials for electronic applications

\[ \Rightarrow \text{Adapt the permittivity values, thermal stability, tunability (E)} \]
\[ \Rightarrow \text{Control dielectric losses - (kHz –GHz)} \]

- MLCC: Thinner Smaller:
  - Improve volumetric efficiency

- Resonators, tunable filters
  - Moderate permittivity, tunability \( \varepsilon = f(E) \)

- Supercapacitors, High-energy-density storage
  \[
  E = \frac{1}{2} CV^2 \Rightarrow C = \varepsilon_0 \varepsilon_0 \frac{S}{e} \\
  \Rightarrow \text{Energy storage}
  \]

- Performances
  - Control of Interfaces: layer/electrode
  - Grain boundaries
  - Cristallinity

- Key role of interfaces

The properties of ferroelectric based-ceramics (Tc, permittivity, losses, conductivity) are related to their crystal structure, chemical composition, defects chemistry and nano/microstructure.
Sintering: a key step

Temperature
Time
Heating/cooling rates
Atmosphere
Stoichiometry/defects
Ionic valency
Interdiffusion/interphase
Heterogeneity
Materials chemistry

Nanomaterials
Multi-materials

Grain growth

BaTiO$_3$

SPS:
Interfacial effects?
Defects chemistry?

Post Annealing in air 800 -1100°C eliminate presence of residual graphite and reduction effects (oxygen vacancies associated with Ti$^{4+}$ reduction into Ti$^{3+}$
Outline

• Motivations

• Ferroelectric materials: contribution of Spark Plasma Sintering – Thermal and pressure effects

• Electrical current effects and Interface control: Multilayers and 3D composites
  - BaSrTiO$_3$ /TiO$_2$
  - BaTiO$_3$ /ZrO$_2$

• Conclusion
**Contribution of SPS in the field of ferroelectric ceramics:**

*Thermal and Pressure effects*

**BaTiO$_3$@MgO**


**Pressure at the grain scale is high enough to compete with the surface stress arising from nanometer grain size**

Increase of the lattice distortion

**Grain size, interfaces, strain**

**750°C - 2’ - Air**

**RD: 92%**

**BaSrTiO$_3$**

500 MPa

**100 nm**

**1 μm**

**✓ broadening of the transition**

✓ η E - η losses

**✓**

**S**

**PS**

**T$_{Curie}$ (K)**

SPS Pressure (MPa)

**BT/MgO**

**BT/MgO**

**BT**

Contribution of SPS in the field of ferroelectric ceramics:

- **Thermal and Pressure effects**
- **Interfaces - Anisotropy**

Multilayers

Random 3D mixing

- MgO: $\varepsilon'$ and tan$\delta$
- Tunability: Electric field redistribution


R. Epherre et al. Scripta Materialia, 110 (2016) 82

SPS and giant permittivity ceramics: MLCC, High-energy-density storage, ...

Giant permittivity related to accumulation of charges at interfaces
→thermally activated carrier hopping associated with defect states

(Nb + In) co-doped TiO₂

Colossal permittivity: space charges at GB
↘GB resistivity: weak blocking effect

Silica coating: dielectric and re-oxidation barrier ⇒ Stable reduction Ti⁴⁺/Ti³⁺

Outline

• Motivations

• Ferroelectric materials: contribution of Spark Plasma Sintering – Thermal and pressure effects

• Electrical current effects and Interface control: Multilayers and 3D composites
  - BaSrTiO$_3$ /TiO$_2$

• Conclusion
**Electrical current effects and Interface control**

**Multilayers intermetallic systems: Current and/or temperature effects on the growth of interphases**


**Current effects in insulating oxides?**

(12:2)

(2:6)

Sintering of reactive alumina–hematite solid solutions

✓ thickness of the composite layer depends on pulse sequence


**Giant Permittivity in all-oxide composites: Control interfacial dielectric relaxation?**

TiO$_2$ vs BaSrTiO$_3$ 

Ti$^{3+}$?

1) Bi-layers

2) Multilayers

Random 3D mixing

TiO$_2$ inclusions

BST matrix high permittivity

Insulating
Bi-layer

BST

TiO$_2$ (Oxygen vacancies and associated Ti$^{3+}$ localized in TiO$_2$ layer)

Re-oxidation Step:
calcination 800°C – 10h -air

XPS

Normalized intensity (a.u.)

Binding energy (eV)

O vacancies

Interstitial X-ray microprobe analysis

Interphase

TI0$_2$

$\rightarrow$Ba$_{1.14-1.33}$Ti$_8$O$_{16-\delta}$

Oxygen deficient Barium Titanate Hollandite type interphase

Rich Ti interphase $\rightarrow$ Diffusion of Ba into TiO$_2$

Compositions obtained under highly reducing atmosphere (gradient of composition expected depending on thickness)

**Current effect on reactivity**

Changing layers sequence versus the direction of the current during SPS

I. Current effect

II. Sintering temperature

T=1300°C

T=1200°C

Linking dielectric relaxation to the thickness of interphase in BST/TiO$_2$ bilayers

$E_a \downarrow$ in thinner interphase (composition gradients - charges mobility)

Conductivity barrier in thick and stable interphase

Increasing the number of interfaces: Multilayer

Re-oxidation step (800°C -10h) impacts strongly the dielectric properties

\[ \text{Ba}_{1.14-1.33}\text{Ti}_8\text{O}_{16-\delta} \]
Increasing the number of interfaces

Random 3D mixing

1200°C

1400°C

BST-TiO$_2$ random 3D mixing after SPS sintering

1200°C

1400°C

Hard spherical TiO$_2$: isolated conductive particles in a high permittivity insulating matrix

(*) Same interphase than in bi- and multilayers: $\text{Ba}_{1.14-1.33}\text{Ti}_8\text{O}_{16-\delta}$
Dielectric properties

- Dielectric properties tuned through re-oxidation steps
calcination 800°C - Air

- Charged defects Ti$^{3+}$ stabilized within TiO$_2$ inclusions
Conclusion

Tunability of dielectric properties:

**Composite approach (Ferro/Diel) + Spark Plasma Sintering**

- Coexistence of Ferroelectricity and giant permittivity
- Low temperature dielectric relaxation
- Stabilization of charged defects in SPS ceramics (located at interface or within the matrix)

- Nature of the dielectric oxide (interdiffusion; reduction ability)
- Composite architecture (bi-layers, multilayer, inclusions)
- SPS T : impact on reduction state (Ti$^{4+}$/Ti$^{3+}$)
- T + Electric current : impact on interphase growth rate
- Re-oxidation steps

**BT@SiO$_2$**

**BST/TiO$_2$**