Heterostructured ceramic materials based on PZTN-CFO compounds

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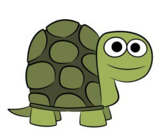
Abstract

Multiferroic composites are currently one of the hot research topics [1]. A great research effort is in progress to improve the fabrication of PZT–$CoFe_2O_4$ (PZT–CFO) composites due to the excellent piezoelectric properties showed by the PZT material class and the large magnetostrictive coefficient of the CFO. Unfortunately unwanted reactions occur during densification of PZT–CFO materials at 1100-1200 °C. They are promoted by initial PbO loss that is calculated through XRD analysis, considering the amount of ZrO_2 and variation of perovskite's tetragonality. The resulting titania reacts with CFO to form cobalt titanate [2].

The microstructure of the composites at 26-81 mol% CFO content was thoroughly investigated; the CFO grain size distribution can be mono- or bi-modal and overgrowth [3] occurs. By setting a quite-fast sintering full densification and prevention of unwanted reactions was achieved for the PZT:CFO 74:26 composites. The high coercivity (789 Oe) shown by these composites is correlated to the good dispersion of euhedral CF grains (250 nm) in the PZT matrix that is affected as well by limited grain growth (240 nm).

Experimental



• Conventional Sintering

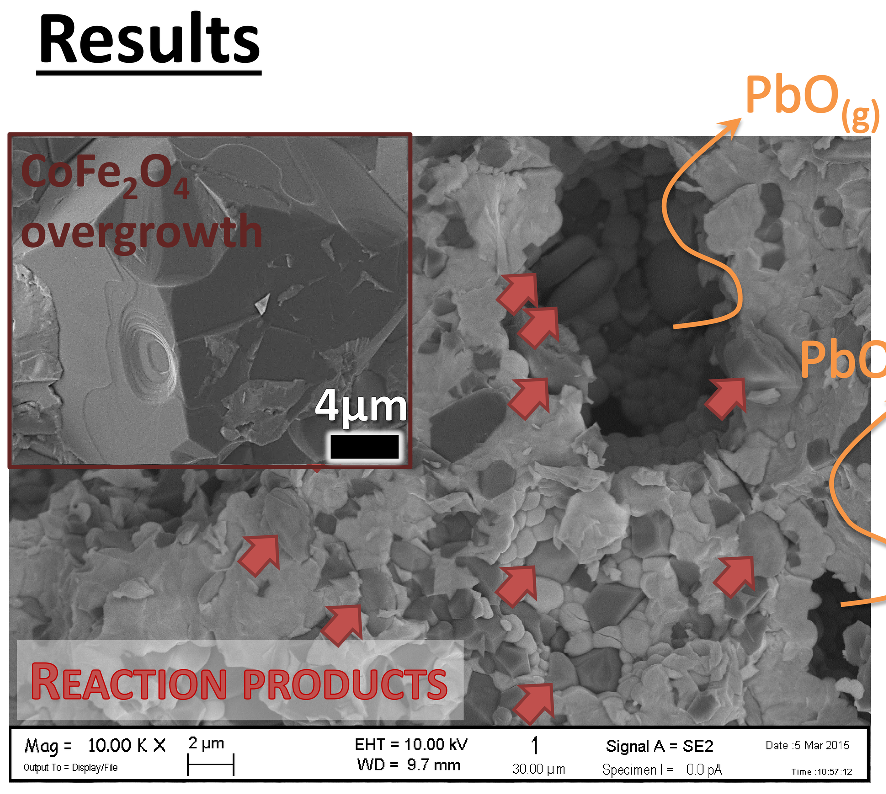
- Heating rate < 300 °C/h
- Sintering temperature ≈ 70% T_m
- Soaking time > 0.5 h
- Natural cooling

• Quite-Fast Sintering [2]

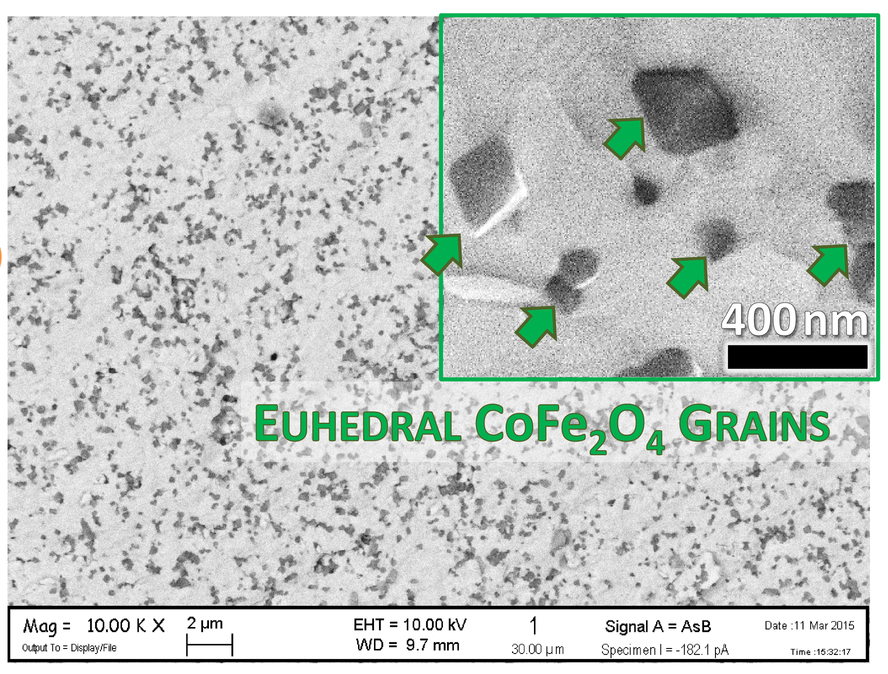
- Heating rate > 300 °C/h
- Sintering temperature < 70% T_m
- Soaking time < 0.5 h
- Cooling rate > 30 °C/min

T_m: melting point

Results



- Relative density ≈ 82%
- PbO loss: 11%
- Bi-modal $CoFe_2O_4$ grain size distribution
- $CoFe_2O_4$ overgrowth by multiple parallel twinning [3]
- Coercivity: 239 Oe
- Reduced remnant magnetisation M_r/M_s = 0.17



- Relative density ≈ 99%
- PbO loss < 0.2%
- mono-modal $CoFe_2O_4$ grain size distr.
- Euhedral $CoFe_2O_4$ grains ≈ 250 nm
- Coercivity: 789 Oe
- Reduced remnant magnetisation M_r/M_s = 0.38

Discussion

Reactions due to the PbO loss at the PZT/CFO interfaces [2]

1°) $Pb(Zr_{0.52}Ti_{0.48})O_3 \rightarrow \boldsymbol{f}PbO_{(g)} + (1-\boldsymbol{f})Pb(Zr_{0.52\text{-}\boldsymbol{y}}Ti_{0.48\text{-}\boldsymbol{z}})O_3 +$

$$+ \underbrace{0.52(1-\boldsymbol{y}+\boldsymbol{fy})ZrO_2}_{ZrO_2\text{: baddeleyite}} + 0.48(1-\boldsymbol{z}+\boldsymbol{fz})TiO_2$$

2°) Displacement reaction [2, 4]:

$$TiO_2 + CoFe_2O_4 \rightarrow CoTiO_3 + Fe_2O_3$$

Acknowledgements

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Novelty

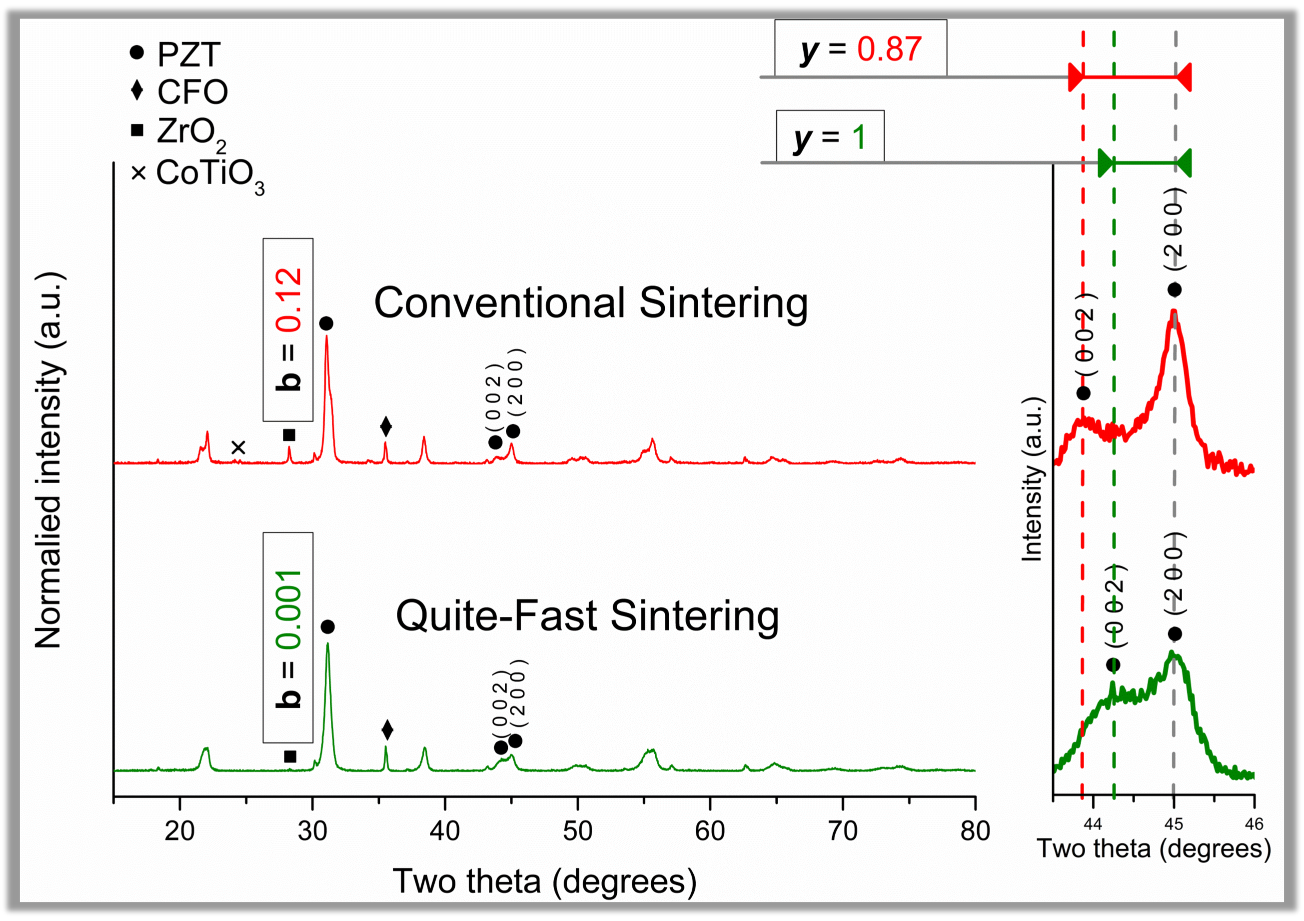
X-ray diffraction analysis has been used as *"chemical analysis"* to calculate the PbO loss [2]

Once the baddeleyite molar fraction (**b**) and the change of the amount of Zr in the produced perovskite (***y***) has been quantified by quantitative XRD analysis, the PbO loss $\delta = \boldsymbol{f} \cdot m_{Pb}$, expressed as molar fraction, can be calculated through the following equation [2]:

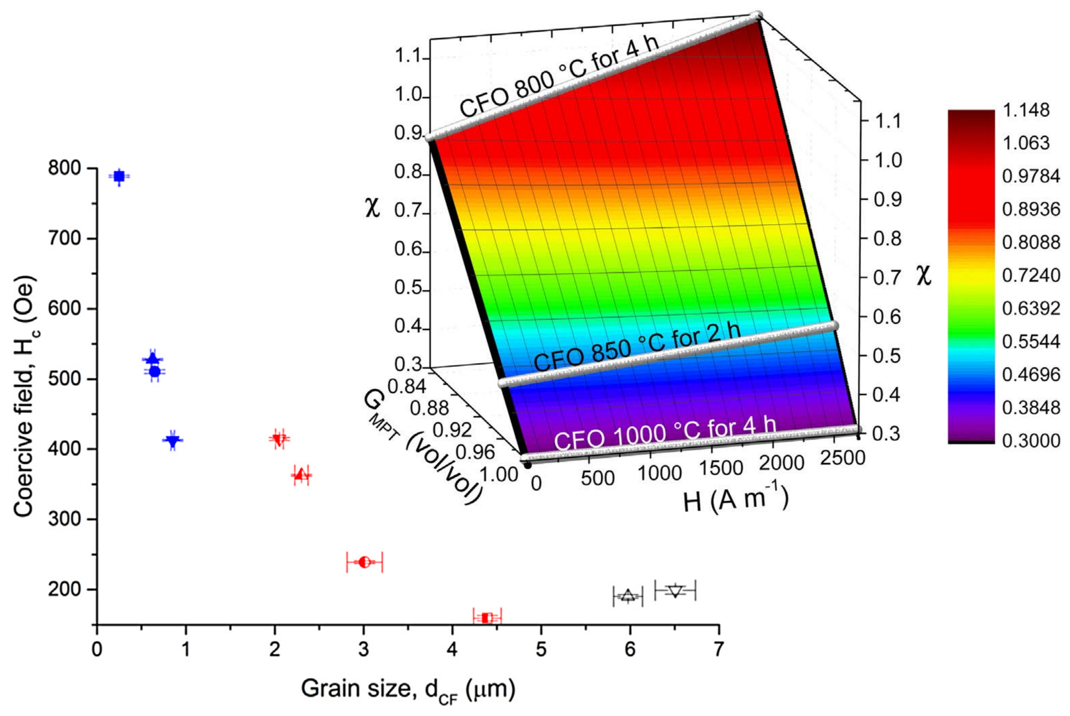
$$\delta = m_{Pb}(\mathbf{b}/m_{Zr} - 1 + \boldsymbol{y})/\boldsymbol{y}$$

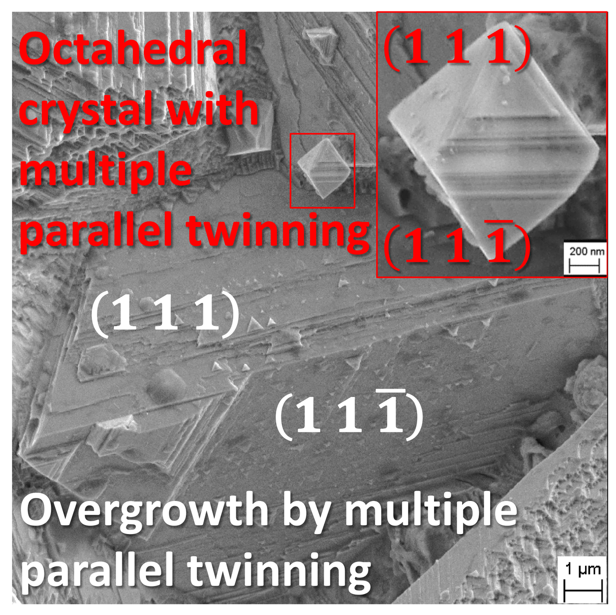
Galizia equation!

where m_{Pb} and m_{Zr} are the stoichiometric coefficients of lead and zirconium in the starting perovskite phase, respectively. In our case, m_{Pb} = 1 and m_{Zr} = 0.52



It has been demonstrated that twin boundaries on CFO {111} planes act as the effective pinning centers for the hindrance of domain wall movement [2, 3]





Globus model extension [3]

In the Globus model the linear correlation between the initial susceptibility (χ_i) and the mean grain diameter (D_m) is expressed as:

$$\chi_i = 2\pi\, M_S^2\, D_m / K$$

where M_s is the saturation magnetization, and K is the global anisotropy. But, where the domain walls are pinned at twinning boundaries, D_m should be interpreted as the distance between the twinning boundaries, i.e. the span of the domain wall [3].

References

[1] G Schileo, Recent developments in ceramic multiferroic composites based on core/shell and other heterostructures obtained by sol-gel routes. *Prog Solid State Ch* 41 (2013) 87–98.

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[3] P Galizia, C Baldisserri, C Capiani, C Galassi, Multiple parallel twinning overgrowth in nanostructured dense cobalt ferrite. *Mater Design* 109 (2016) 19–26.

[4] P Galizia, C Baldisserri, C Galassi, Microstructure development in novel titania-cobalt ferrite ceramic materials. *Ceram Int* 42:2A (2016) 2634-2641