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Oxygen Firing of Chem-Prep PZT 95/5

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Background

Extrinsic pore formers are added:

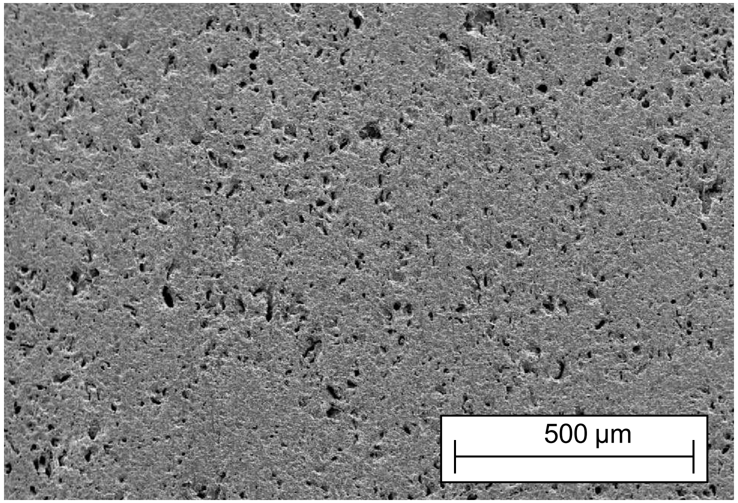
- Control (limit) density
- FE properties are effected by pore former type

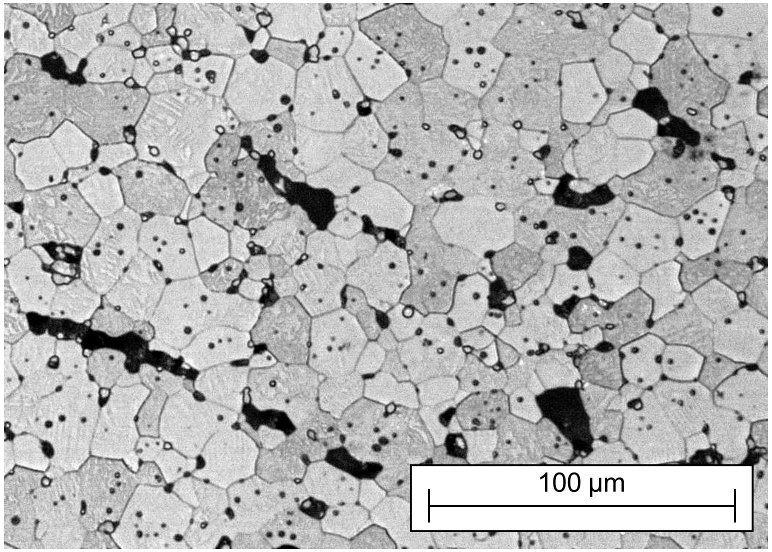
PZT also contains Intrinsic porosity

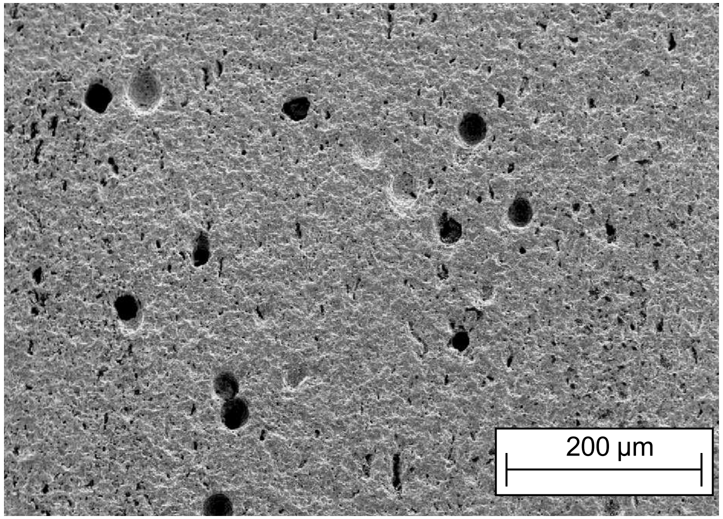
- Intergranular
- Intragranular
- Effect of Intrinsic porosity is not understood

Oxygen firing promotes density in other PZT compositions

- Increased grain boundary and lattice diffusion rates







Sample Fabrication, Testing, and Analyses

Chem-Prep PZT 95/5:

- Metal acetate/alkoxide solution process*
- Avg. particle size: 5 μm, typ.
- Particle size range: <0.1 μm to 40 μm
- Surface area: 1.3 m^2/g, typ.

Powder Granulation and Compaction :

- 2 wt.% acrylic binder (Glascol HA4, Ciba Specialty Chemicals)
- Twin-shell blender
- Die pressed at 14,000 psi, Green density: 4.4 g/cm^3, typ.

Bisque and High Firing:

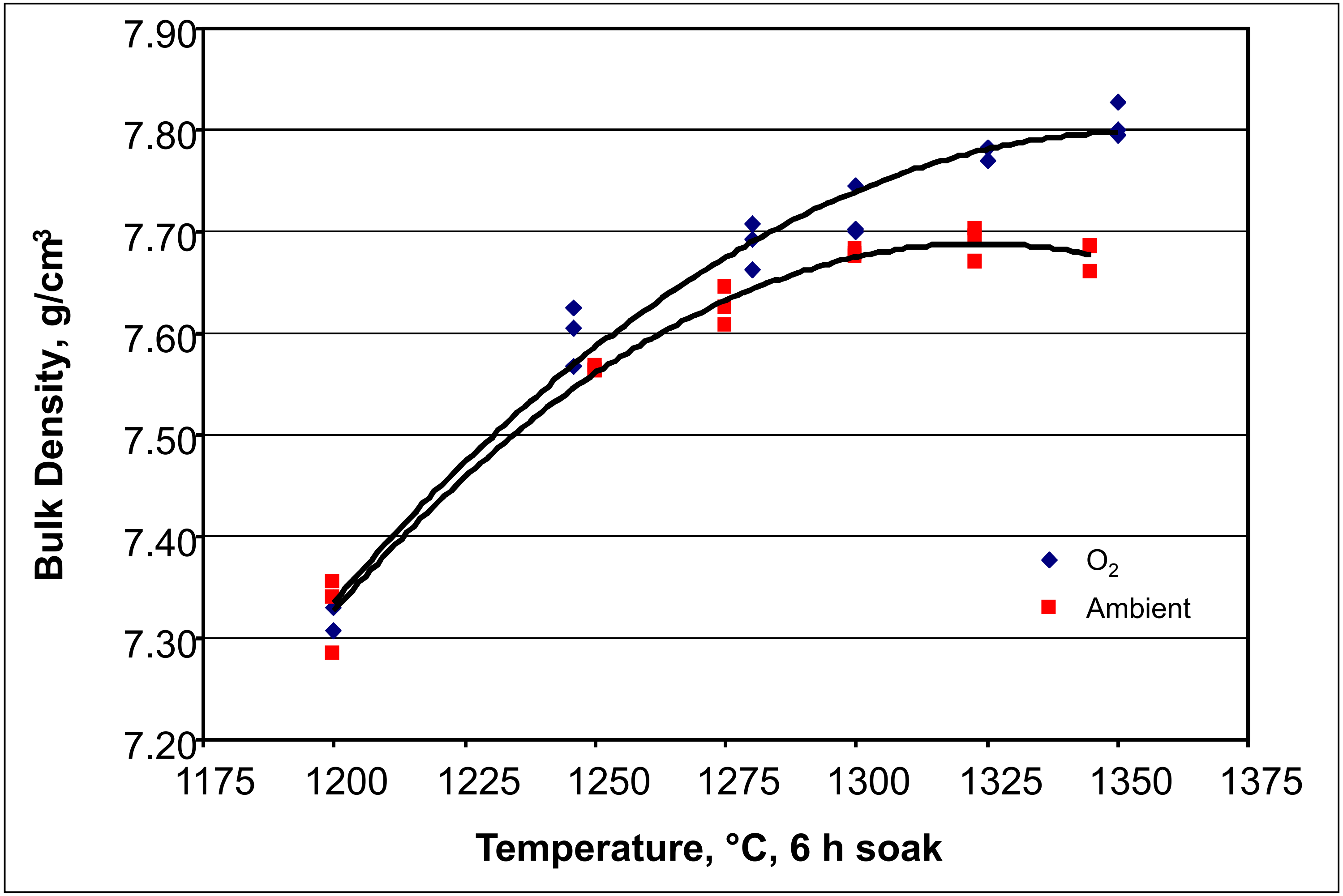
- Bisque at 750°C/4 hr soak, flowing air, density: 4.35 g/cm^3, typ.
- Tube furnace, 1200 - 1350°C, with soak times up to 12 h.
- Flowing O_2 or ambient environments
- Double alumina crucible system, Wt. Loss range: 0.2 – 1.2 wt.%.

Testing and Analyses:

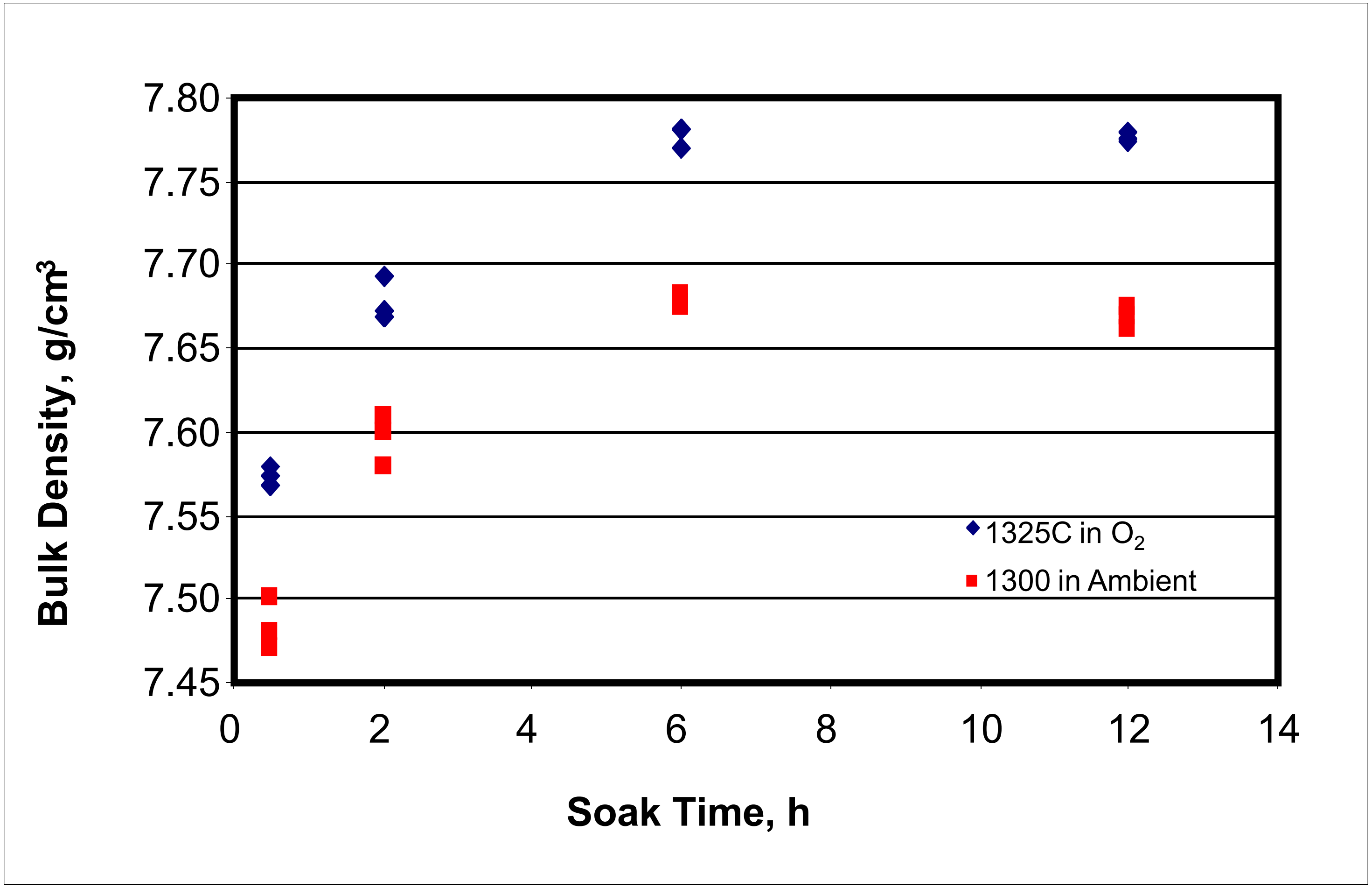
- Bulk Density (immersion)
- Ag Metallize, and polarize
- Ferroelectric hysteresis loop
- Hydrostatic depoling pressure
- Microstructural analysis (polish, etch, image analyses)

*J. A. Voigt, D. L. Sipola, B. A. Tuttle, M. T. Anderson, "Nonaqueous solution synthesis process for preparing oxide powders of lead zirconate titanate and related materials," U.S. Patent No. 5,908,802, June 1, 1999.

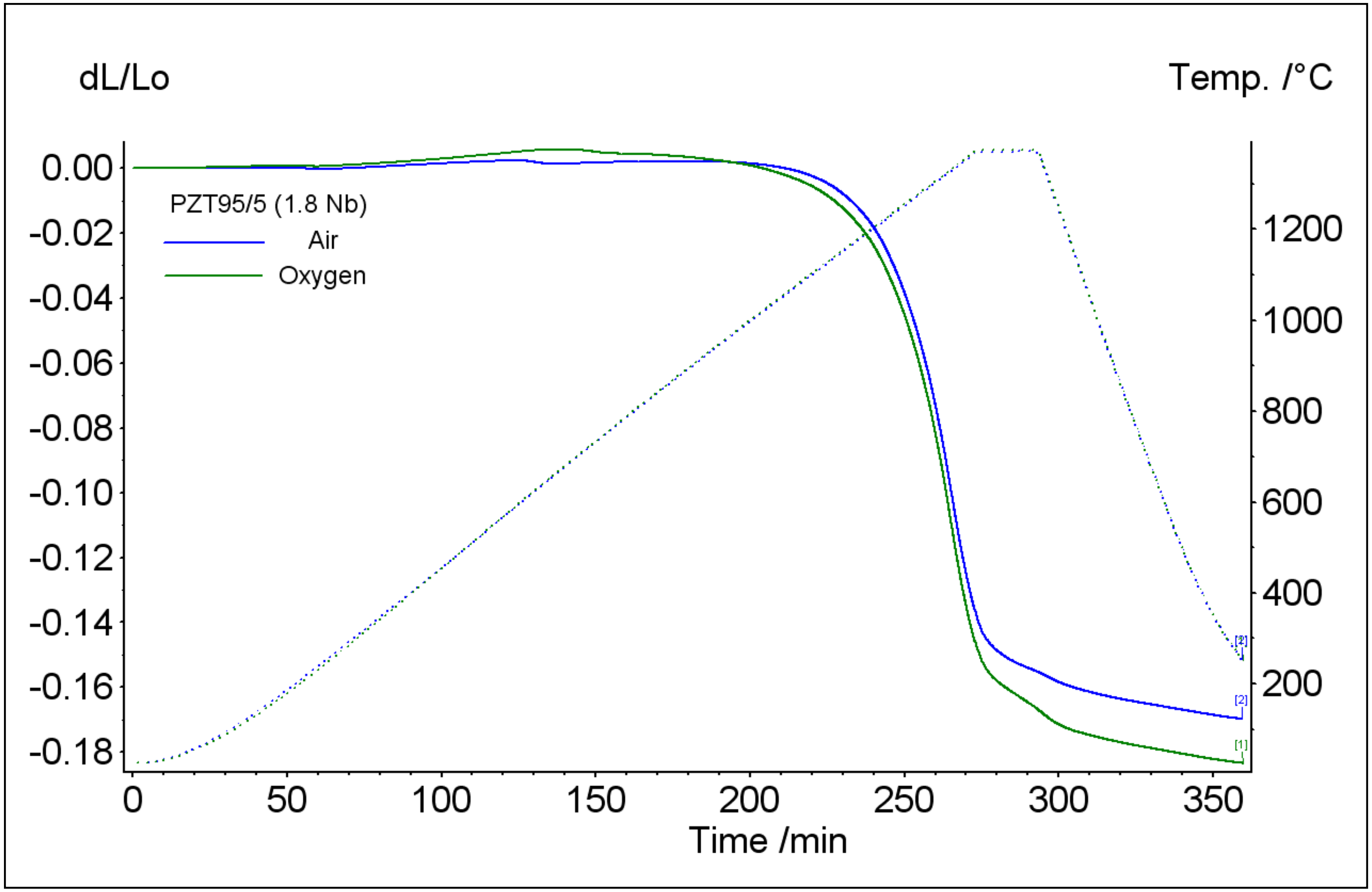
O_2 Environments Significantly Increase the Bulk Density of PZT 95/5



Six Hour Soak Periods are Required to Reach Maximum Density



O_2 Promotes Density during Final Stage Sintering



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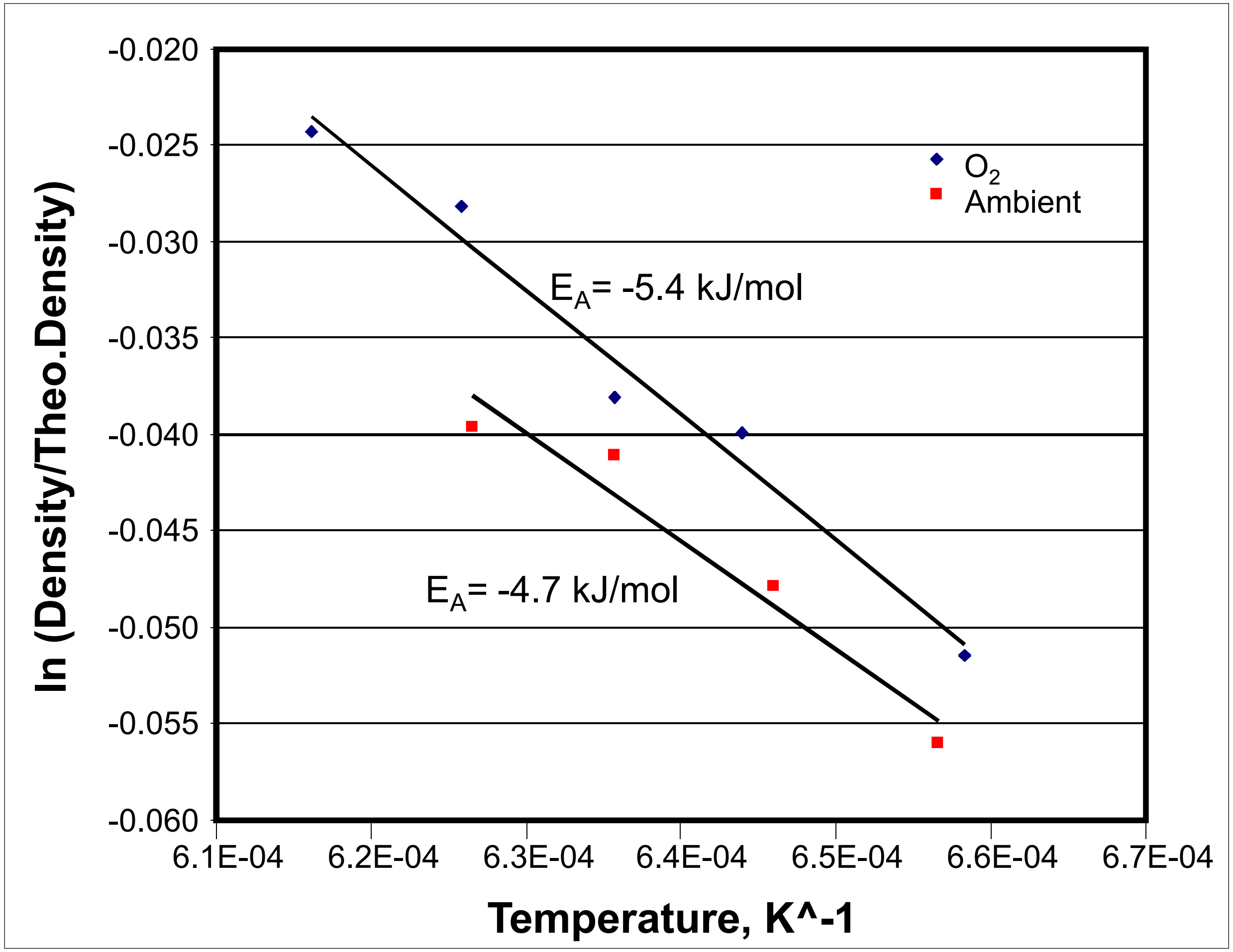
Activation Energy for Sintering is Comparable Between the Two Atmospheres

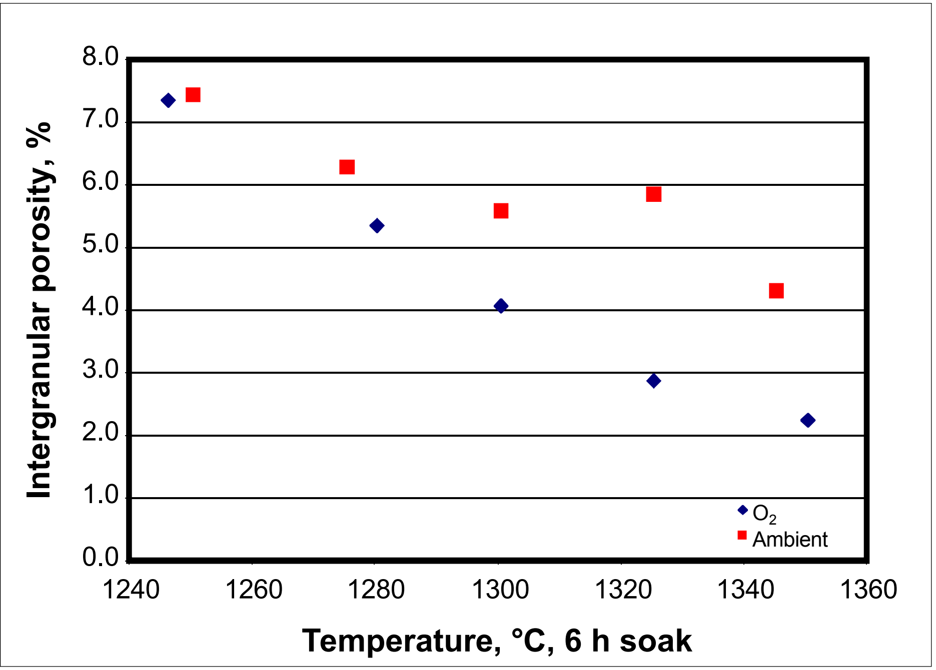


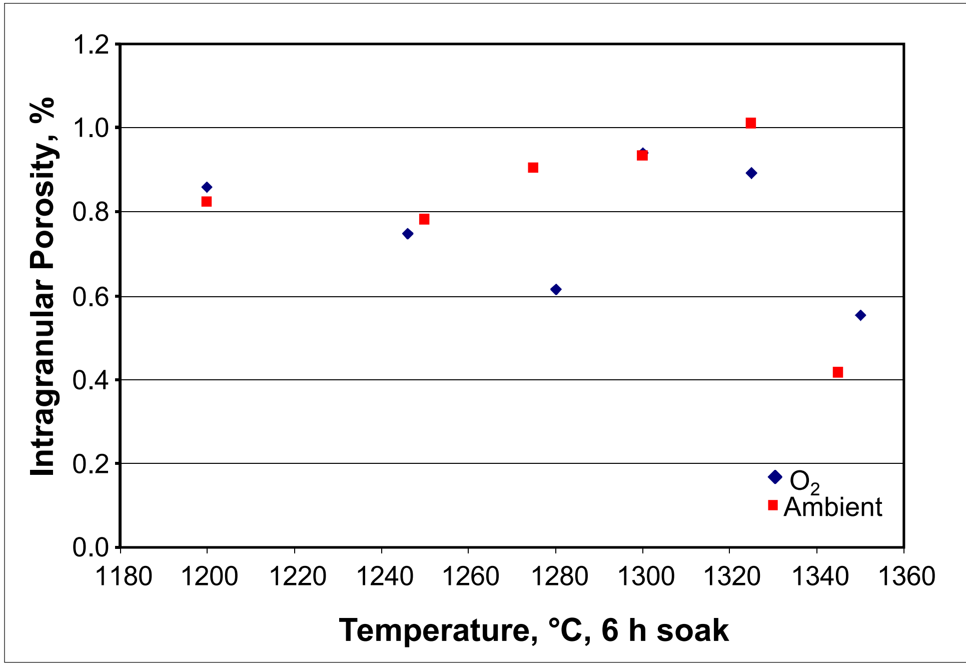
From the Arrhenius Equation:

$$k = Ae^{-\left(\frac{E_a}{RT}\right)}$$

$$E_a \equiv -R\left[\frac{\partial \ln\left(\frac{D}{D_{Th}}\right)}{\partial T^{-1}}\right]$$

Image Analysis Measurements of Inter- and Intra-Granular Porosity

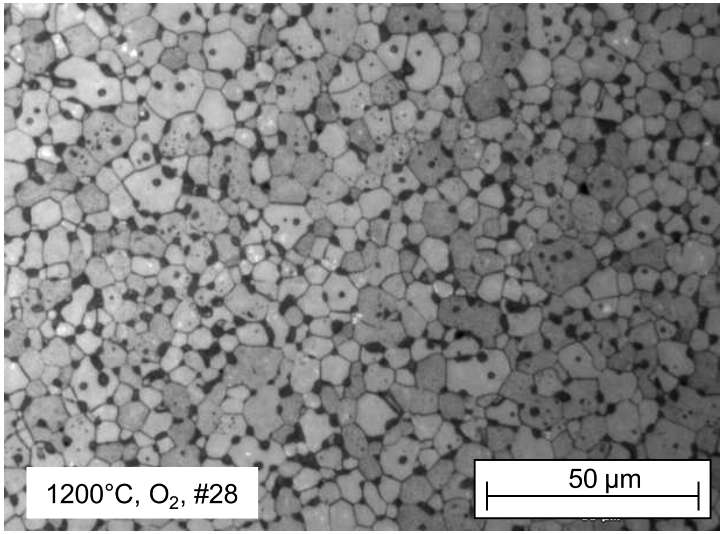


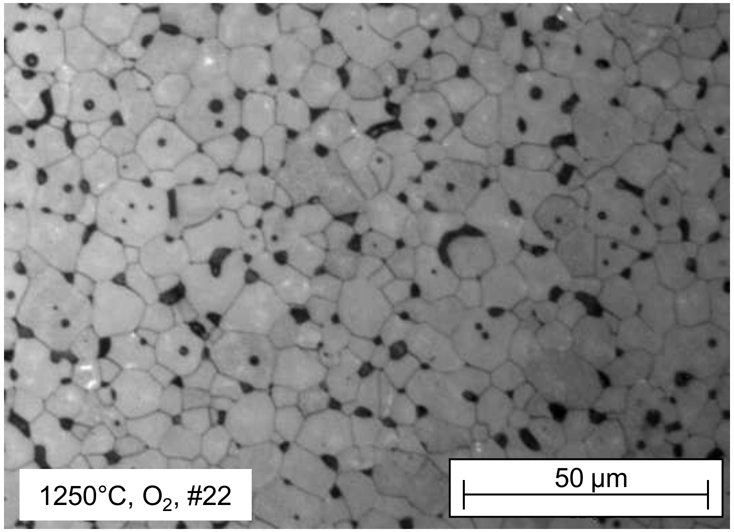


- Samples polished and etched (HCl, 70°C, 15 sec)
- analySIS FIVE (www.olympus.co)

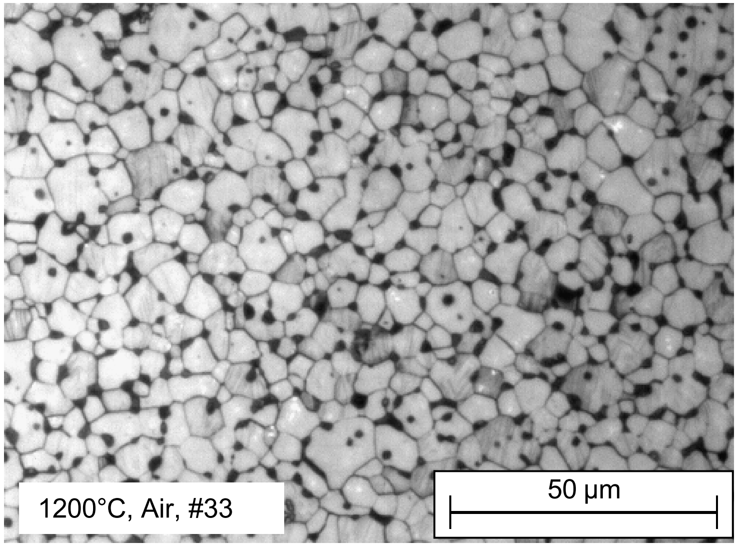
Oxygen and Ambient Fired Samples

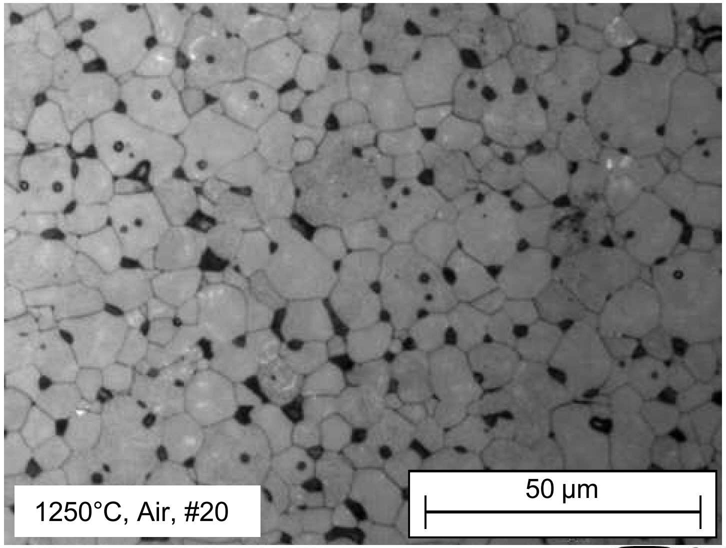
O_2





Ambient

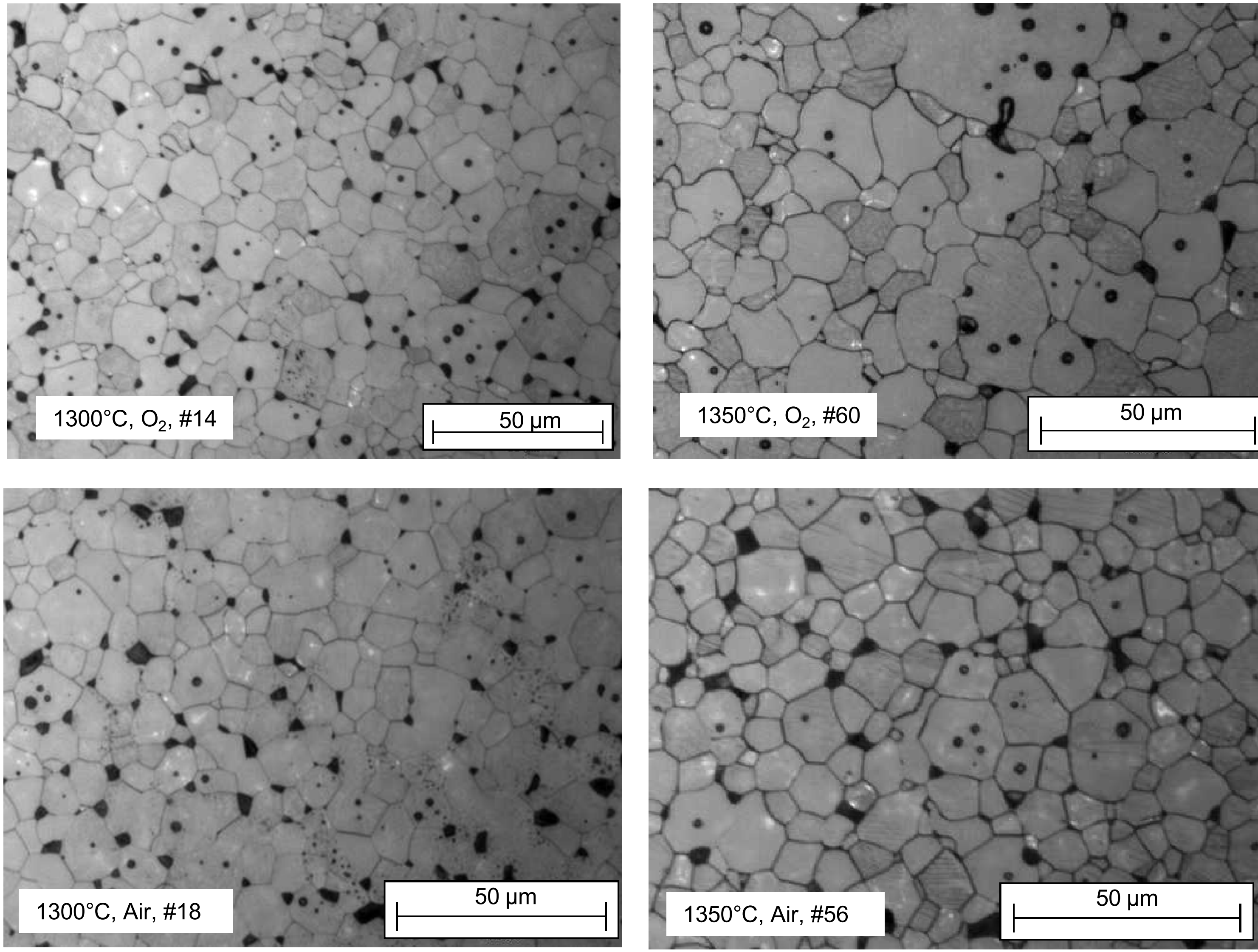




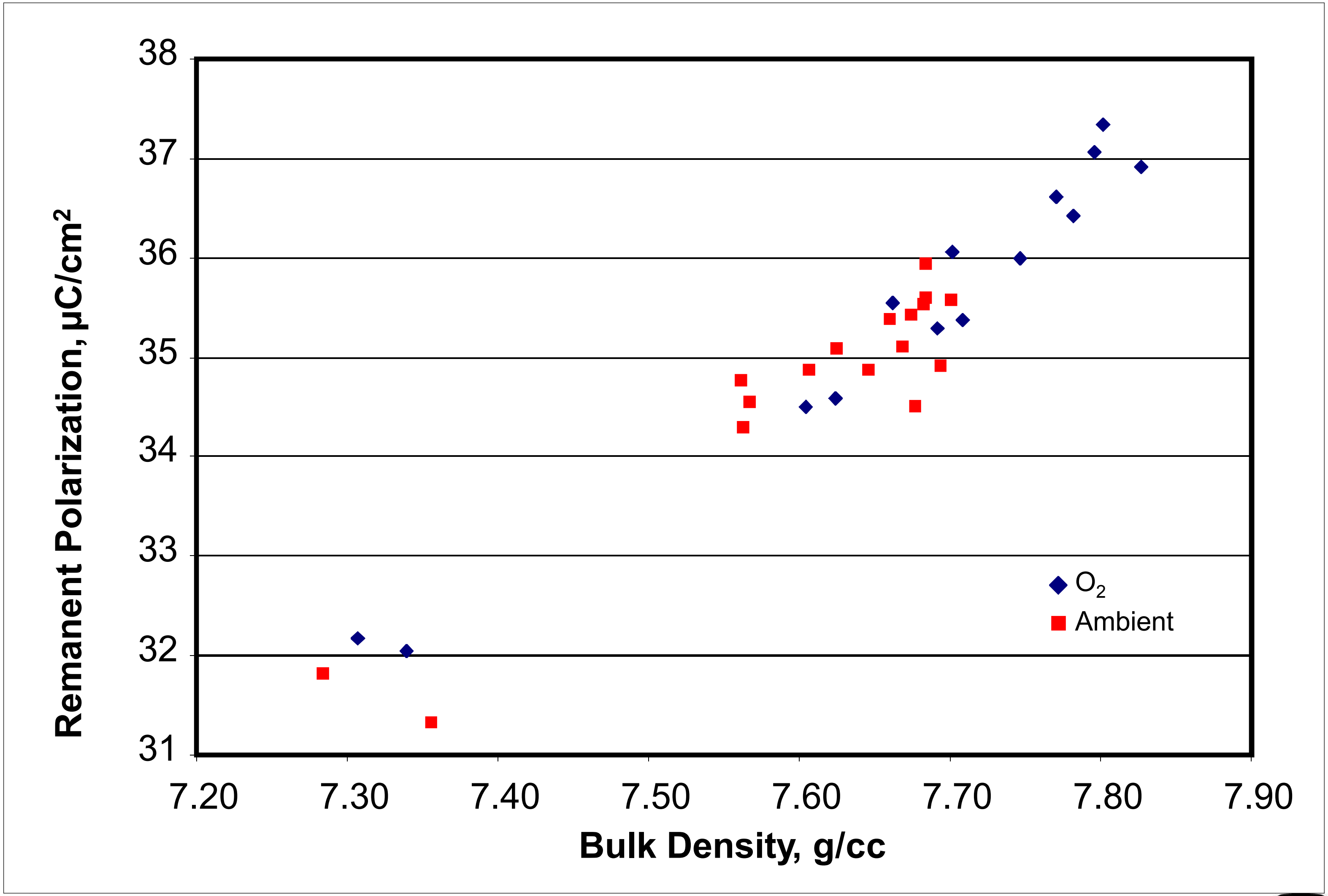
O_2 Atmosphere is More Effective at Removing Intergranular Porosity

O_2

Ambient



Polarization Increased with Density, Regardless of Atmosphere



Summary

- Firing PZT 95/5 under O_2 atmospheres increases bulk density by 0.1 g/cm^3
- Increased density leads to ~4% increase in polarization
- Firing shrinkage, density, and microstructural analyses show that the onset and progression of sintering are very similar.
- However, with oxygen, more intergranular porosity is eliminated during the final stage of sintering, most likely due to the higher diffusion rate of oxygen in PZT.
- Intragranular porosity varies little with firing atmosphere and persists regardless of firing conditions.

<u>Acknowledgements</u>

- George Burns
- Ted Montoya
- Tom Pehr

$$E_a \equiv -R\left[\frac{\partial \ln\left(\frac{D}{D_{Th}}\right)}{\partial T^{-1}}\right]$$

From the Arrhenius Equation:

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Activation Energy for Sintering:

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$$E_a \equiv -R\left(\frac{\partial\left(\frac{lnD}{D_{Th}}\right)}{\partial(T^{-1})}\right)$$

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