Stability of Perovskite Hydrogen Separation Membranes

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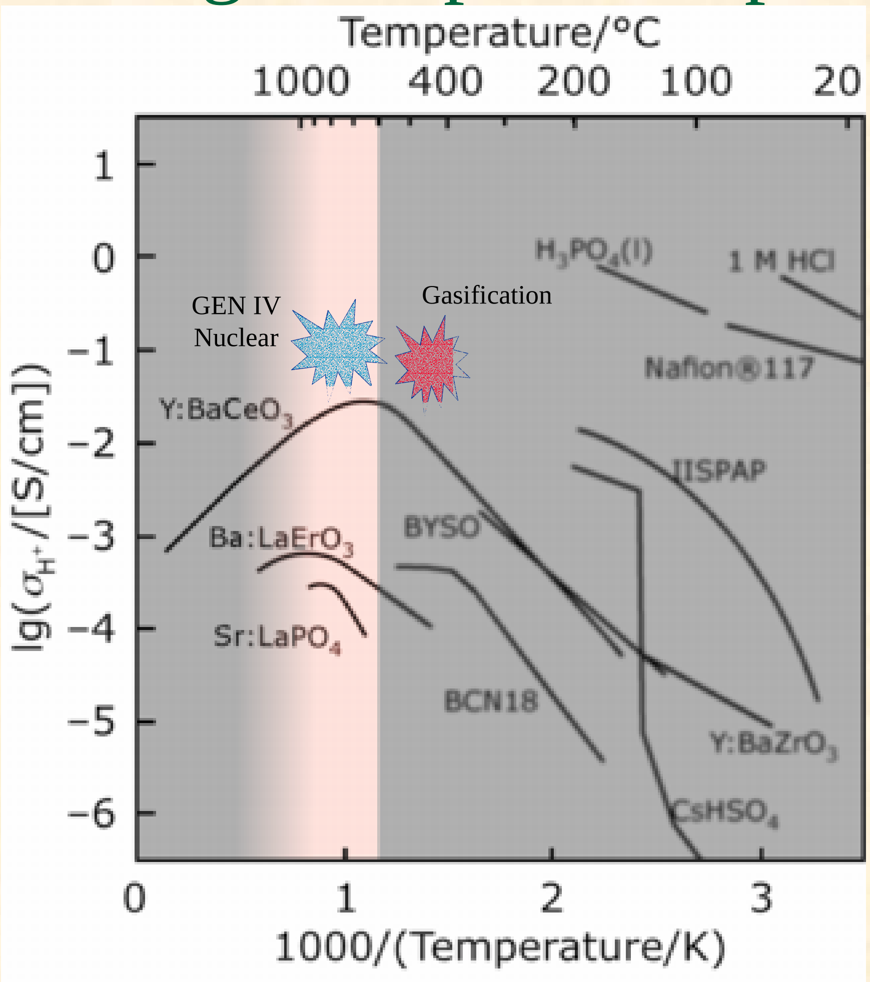
Many industrial process streams require absolutely pure hydrogen

- Three options exist to generate pure hydrogen
  - Microporous membranes coupled with pressure swing adsorption
  - Pd membranes
  - Ion transport membranes

- *Ion transport membranes have the potential to extract 100 % pure hydrogen from a mixed gas stream and be low-cost*

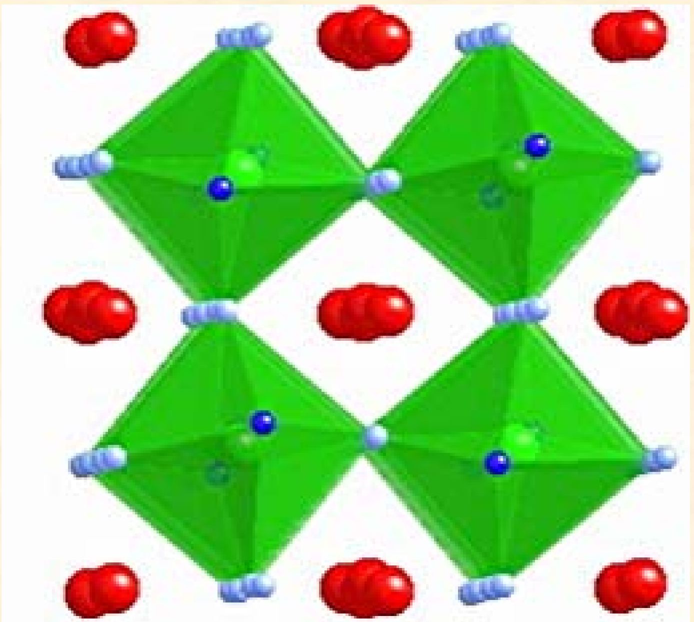
Industrial applications require improved high-temperature proton-conducting materials



T. Norby, "Solid-State Protonic Conductors: Principles, Properties, Progress, and Prospects," *Solid State Ionics*, **125** 1–11 (1999)

- Two mechanisms of hydrogen transport through solid membranes:
  - Vehicle mechanisms conduct hydrogen as a component of other assembly species (OH^-, H_2O, H_3O^+, NH_4^+, HS^-).
  - Free-proton mechanisms conduct hydrogen ions through a rigid host.
- Current HTPCs are oxide ceramics . . .
  - based on perovskite structure
  - acceptor-doped
  - low proton conductivity
  - intolerant of CO_2 and sulfur

Defect-perovskite structures enable proton conductivity at high temperature



Ba = red; Ce/Y = green; O = blue

- Development of oxide-based HTPCs has focused almost exclusively on perovskite ceramics, acceptor doped to enhance solubility
  - Mainly II–IV perovskites ($A^{2+}B^{4+}O_3$) (i.e.$BaCeO_3$ and $SrZrO_3$) doped with trivalent cations (Y^{3+}) to introduce oxygen vacancies
- Defect structure ceramic oxides are well suited for high temperature applications:
  - Protons diffuse into interstitial or vacant sites
  - Free-proton transport mechanisms are facilitated by interstitial hopping

Determination of Chemical Stability

- **Initially experiments were carried out baseline standard -** $BaCe_{0.8}Y_{0.2}O_{3-d}$
- **Several routes were pursued to improve stability**
  - **Composition modification:**
    - **adjusting Ba stoichiometry to produce A-site deficient composition**
    - **Adding Zr to replace Ce**
- **Characterization**
  - **high-temperature x-ray diffraction in pure** CO_2 **to determine worst-case-scenario decomposition temperatures.**
  - Mechanical property determination
  - Additional testing in S and H_2O environments

High-Temperature XRD Results—Stability in CO_2

Figures show $\log_{10}$ of the ratio of diffraction peaks due only to perovskite phase vs. peaks due only to non-perovskite phase.
Values > 0 indicate single-phase perovskite, values < –0.5 indicate significant decomposition; yellow highlighted region indicates transition region.

Top: stoichiometric doped composition

- **nearly total decomposition**

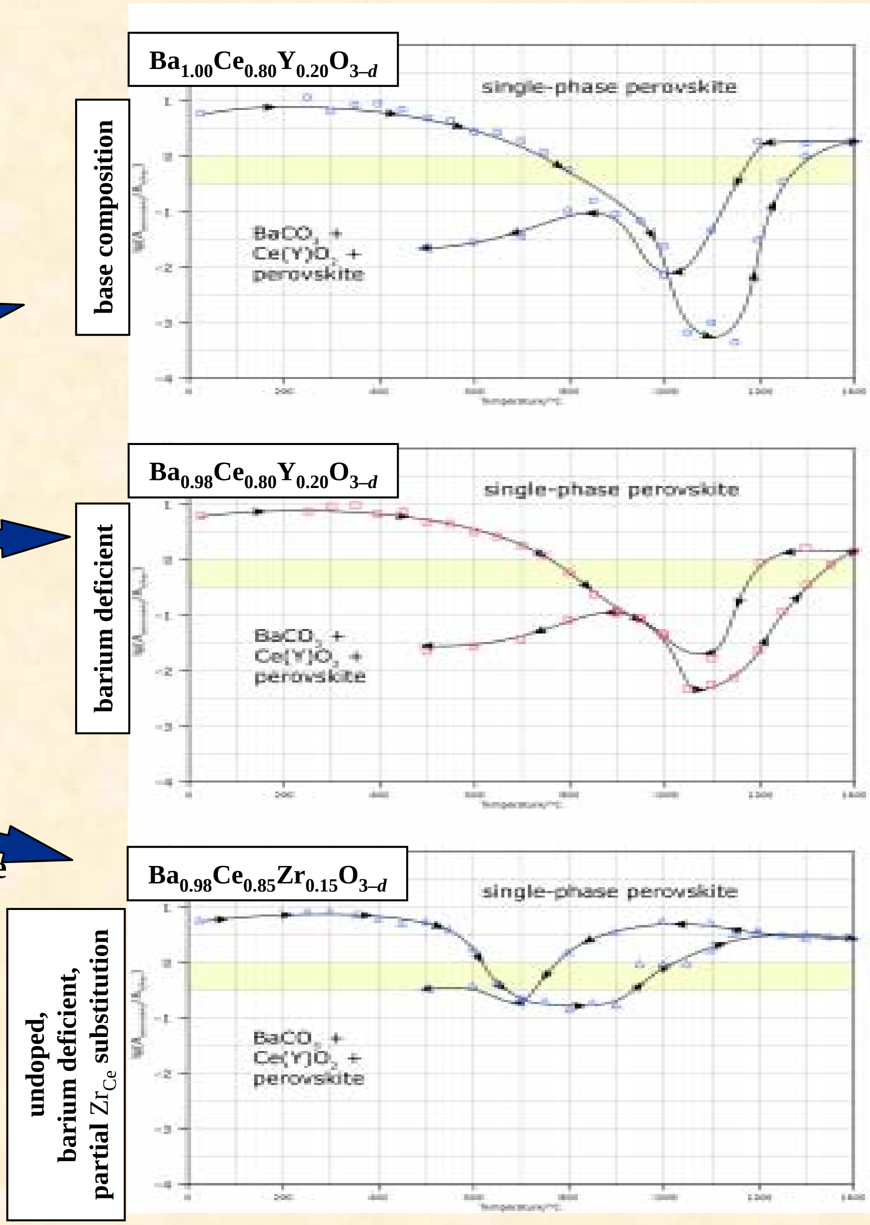
Center: barium-deficient doped composition

- **significantly less reaction**
- **transition temperatures unaffected**

Bottom: barium-deficient, undoped, partially Zr_{Ce} substituted composition

- **very little decomposition**
- **transitions shifted to lower temperatures**
- **hysteresis (difference of transition temperature between heating and cooling) in high-temperature transition temperature nearly doubled**

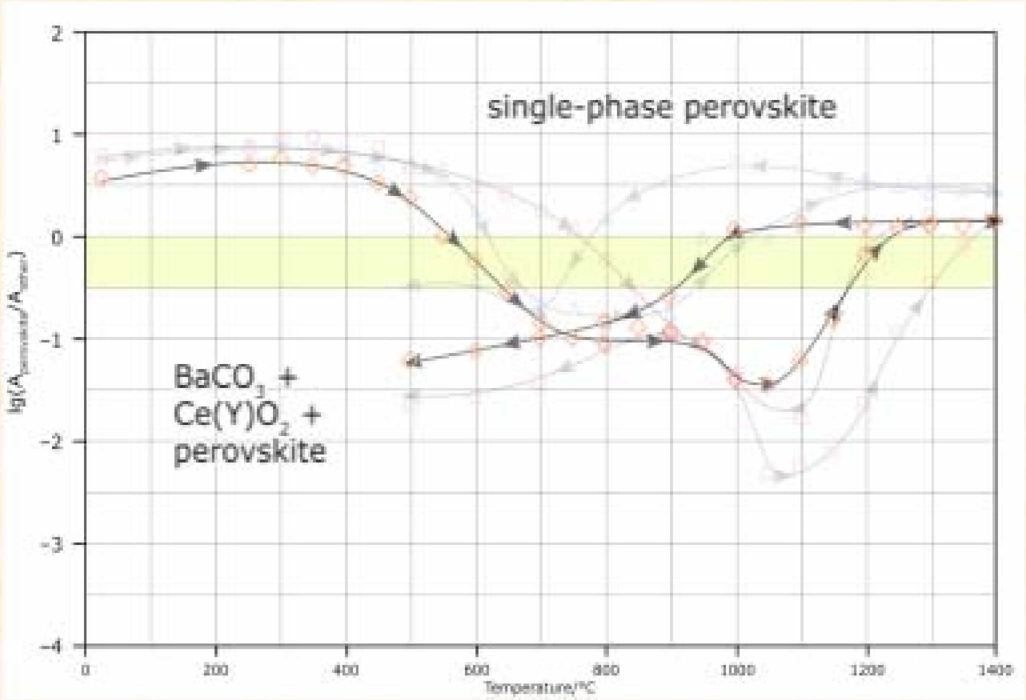
  lower reaction rates



Zr_{Ce} substitution in doped composition results in intermediate behavior

$Ba_{0.98}Ce_{0.65}Zr_{0.15}Y_{0.20}O_{3-d}$ **possesses characteristics of both the undoped** Zr_{Ce}**-substituted composition and the doped** Zr**-free composition:**

- **slight decomposition at low temperatures (650 °C to 900 °C);**
  like $Ba_{0.98}Ce_{0.85}Zr_{0.15}O_{3-d}$
- **more extensive decomposition occurring above 1000 °C;**
  like $Ba_{0.98}Ce_{0.80}Y_{0.20}O_{3-d}$
- **large hysteresis range (250 °C);**
  like $Ba_{0.98}Ce_{0.85}Zr_{0.15}O_{3-d}$
- **intermediate maximum peak ratio of ca. 1:30**
  (perovskite to decomposition product peaks ratio)



Dark curve: Y-doped and Zr_{Ce} **substituted composition,** $Ba_{0.98}Ce_{0.65}Zr_{0.15}Y_{0.20}O_{3-d}$

Phantom curves: Data from previous slide (center & bottom)

Summary & Conclusions

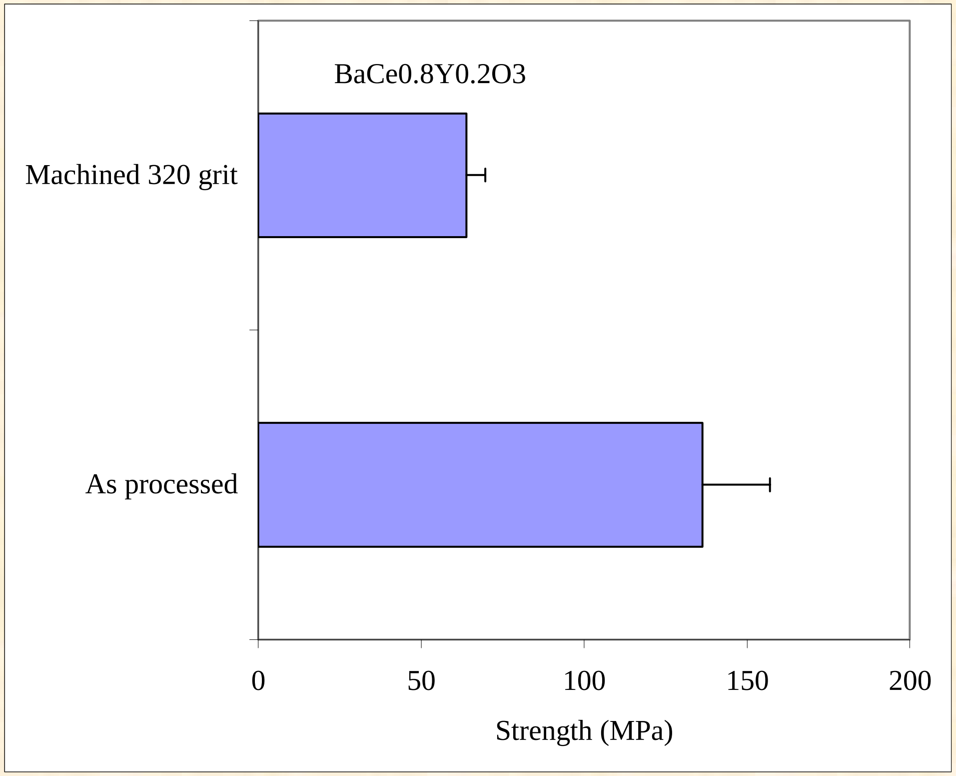
CO_2 Stability of Barium Cerate:

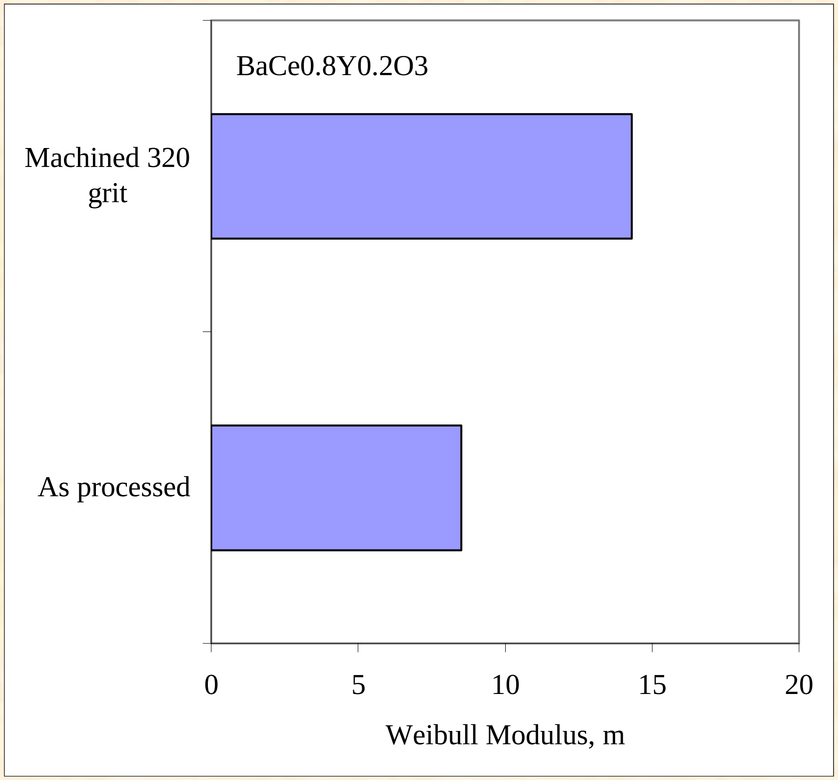
- ➪ **Stoichiometric BaCe0.8Y0.2O3 is unstable in CO_2 rich environments at the operating temperature**
- ➪ **Barium deficient compositions results in less decomposition-it is still not usable**
- ➪ **Additions of Zr to barium cerate nearly eliminated decomposition in Co2**
- ➪ **The combined effect of Zr additions and Ba deficiency resulted in nearly stable barium cerates**

Despite significant improvements in **CO_2** tolerance . .

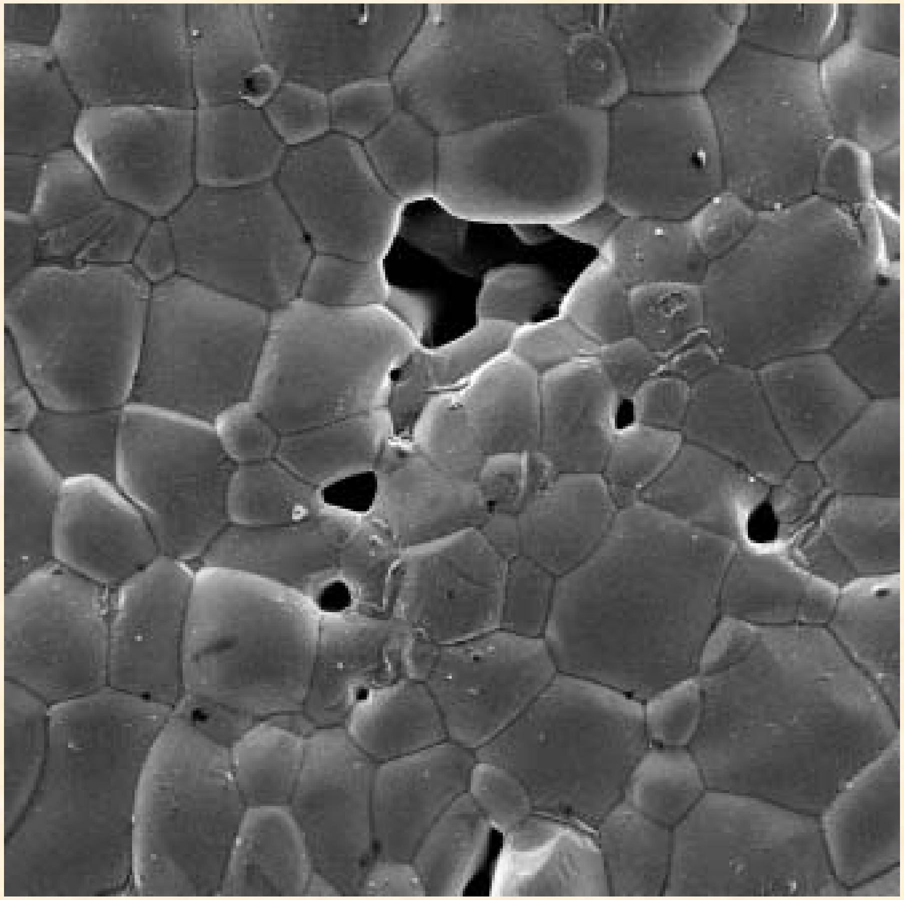
- ➪ Some tendency for chemical degradation persists
- ➪ The techniques used to improve stability - Zr additions and Ba deficiency-decrease electrical conductivity and H_2 flux
- ➪ Zr additions dramatically reduce the strength of the membrane

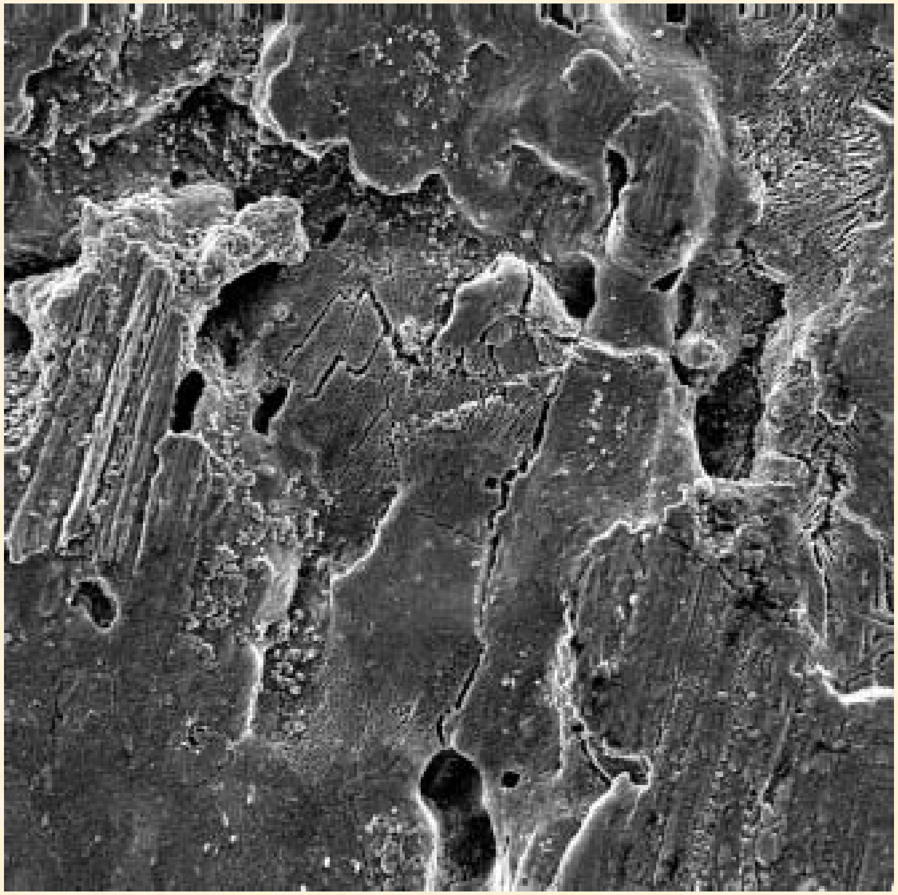
Specimens with Machined Surfaces Exhibit a Higher Weibull Modulus but Lower Strength than Specimens with As-Processed Surfaces





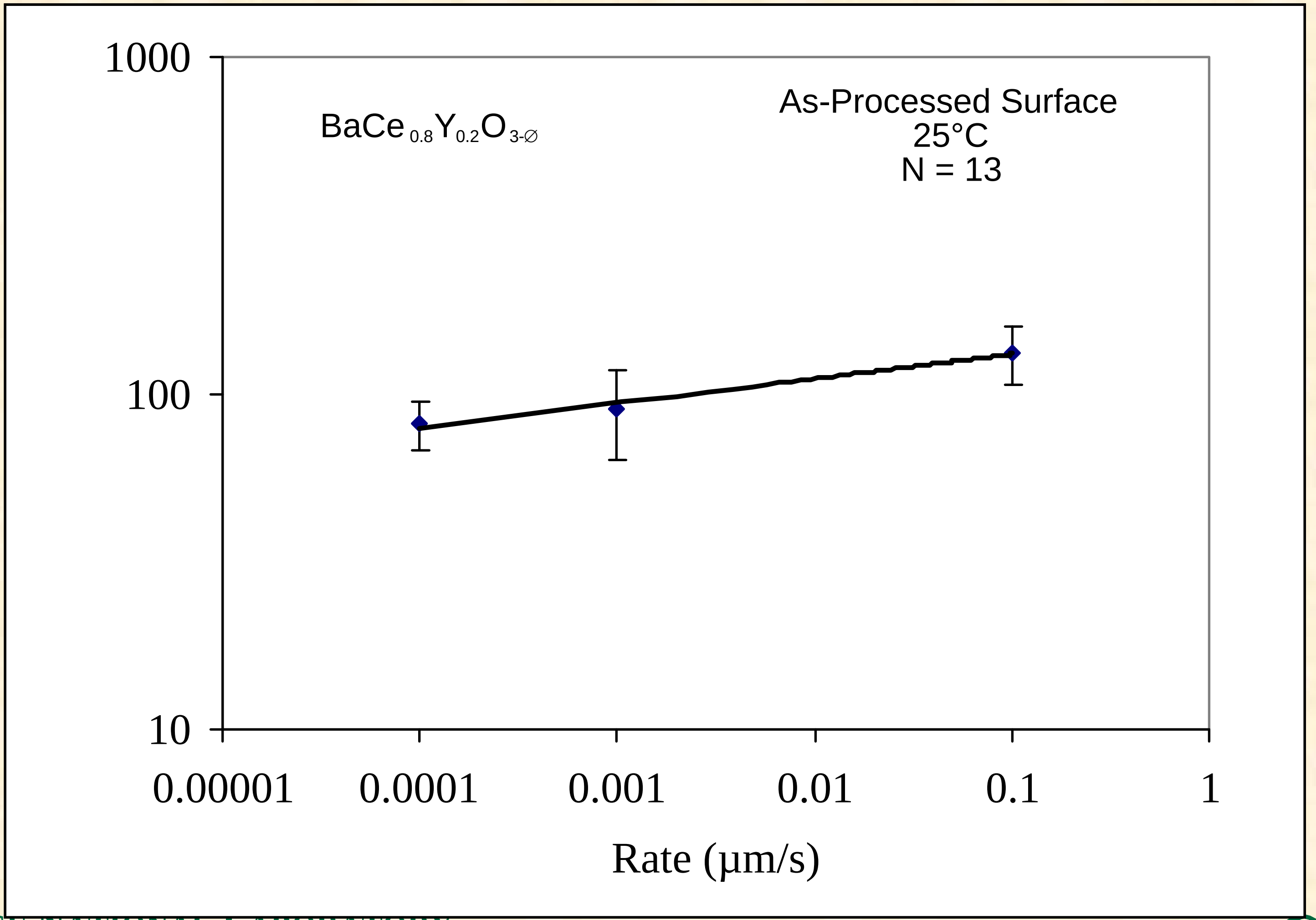
Machining Introduces Significant Damage





As-Processed 15 µm Dry Machined

Strength-Stressing Rate Tests Reveal Potential Problem with Slow Crack Growth



Microcracks are More Readily Observed for Specimens Tested at Slowest Rates

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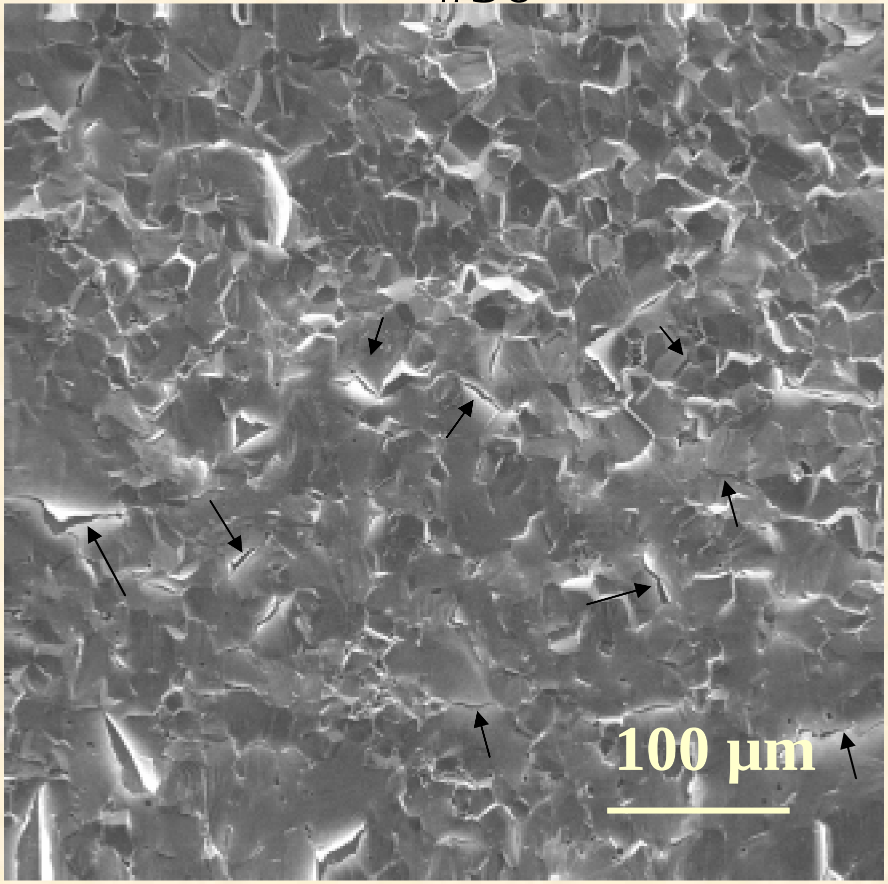

0.0001 mm/s

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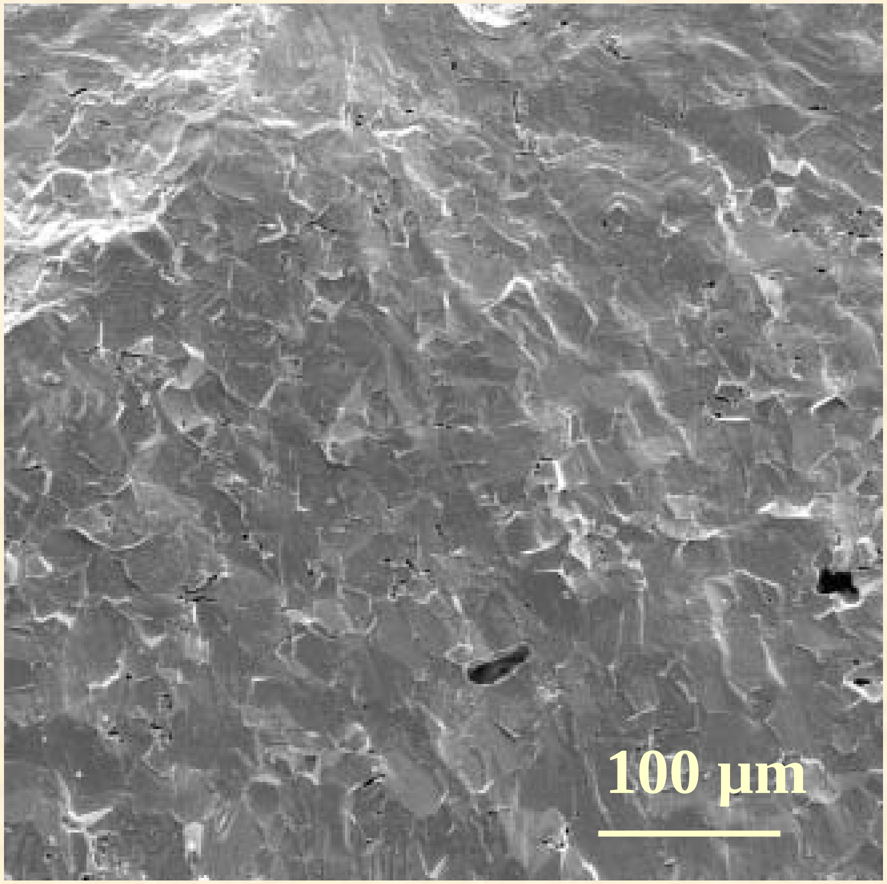
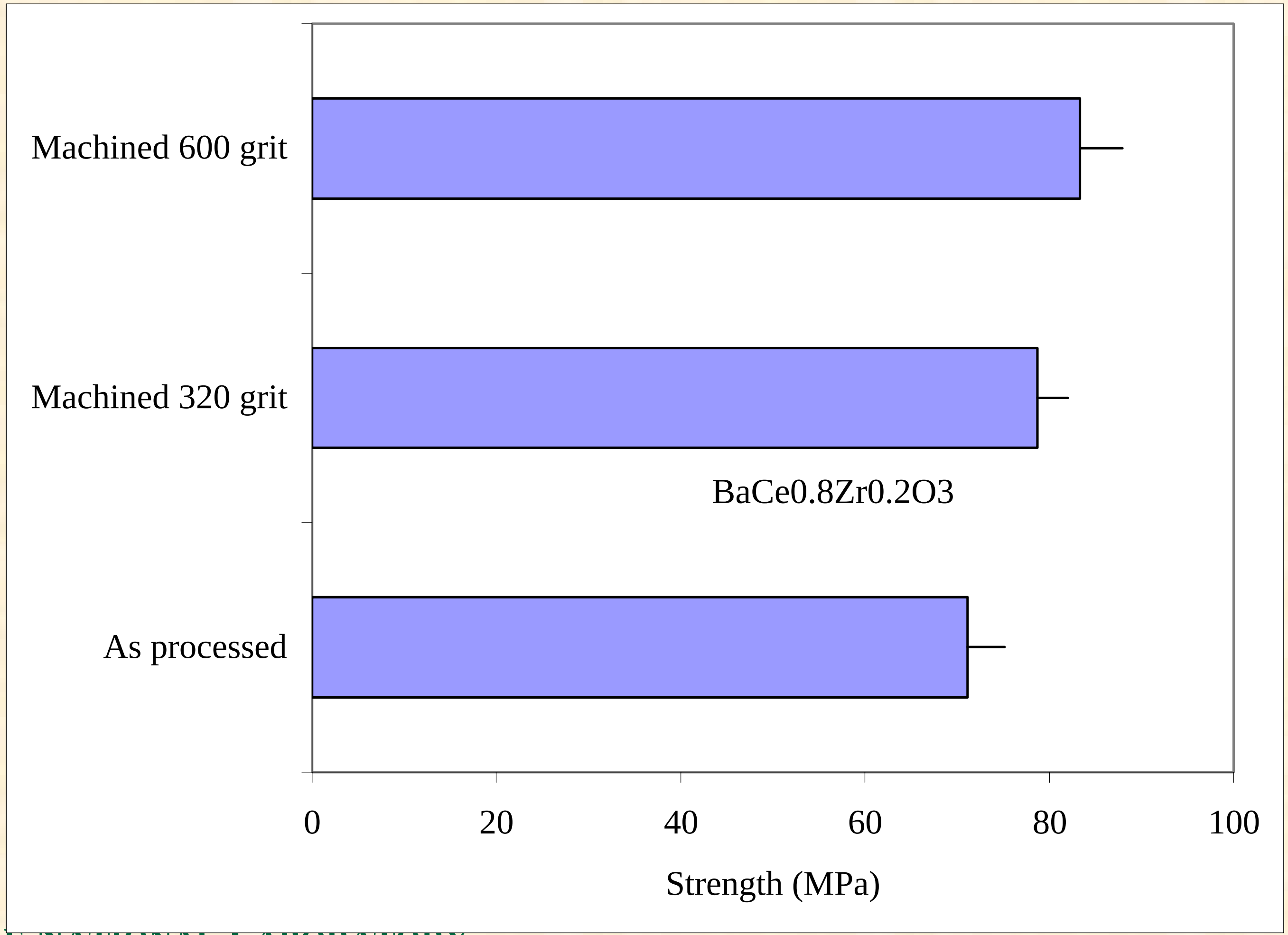


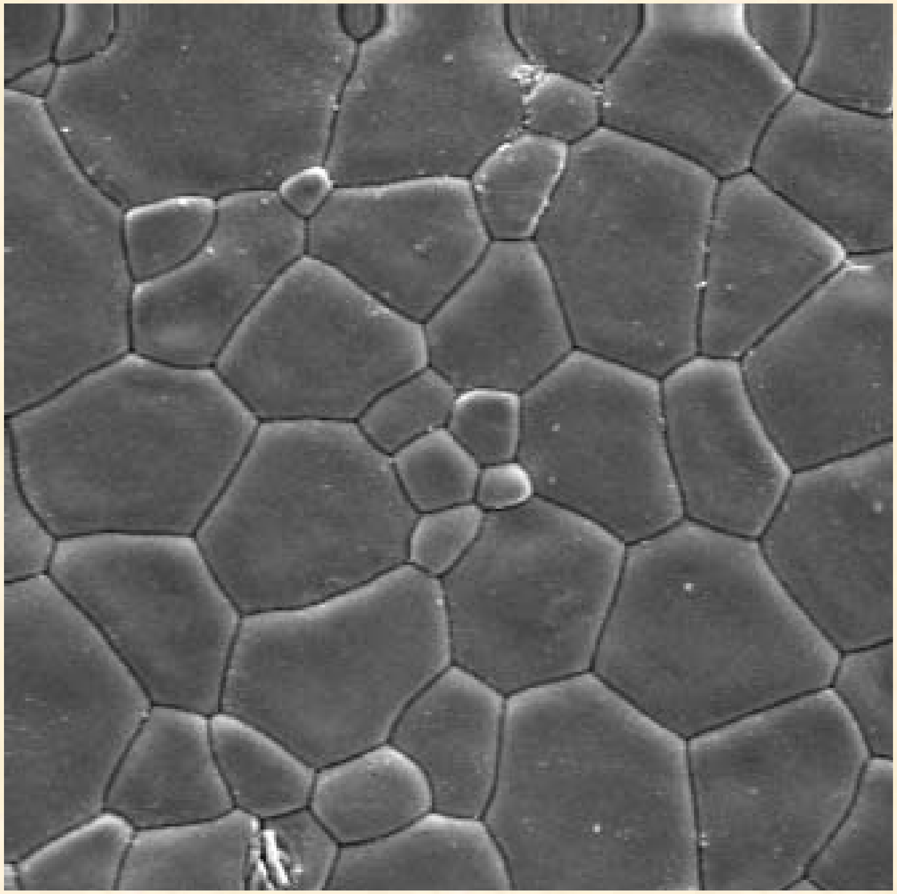
0.1 mm/s

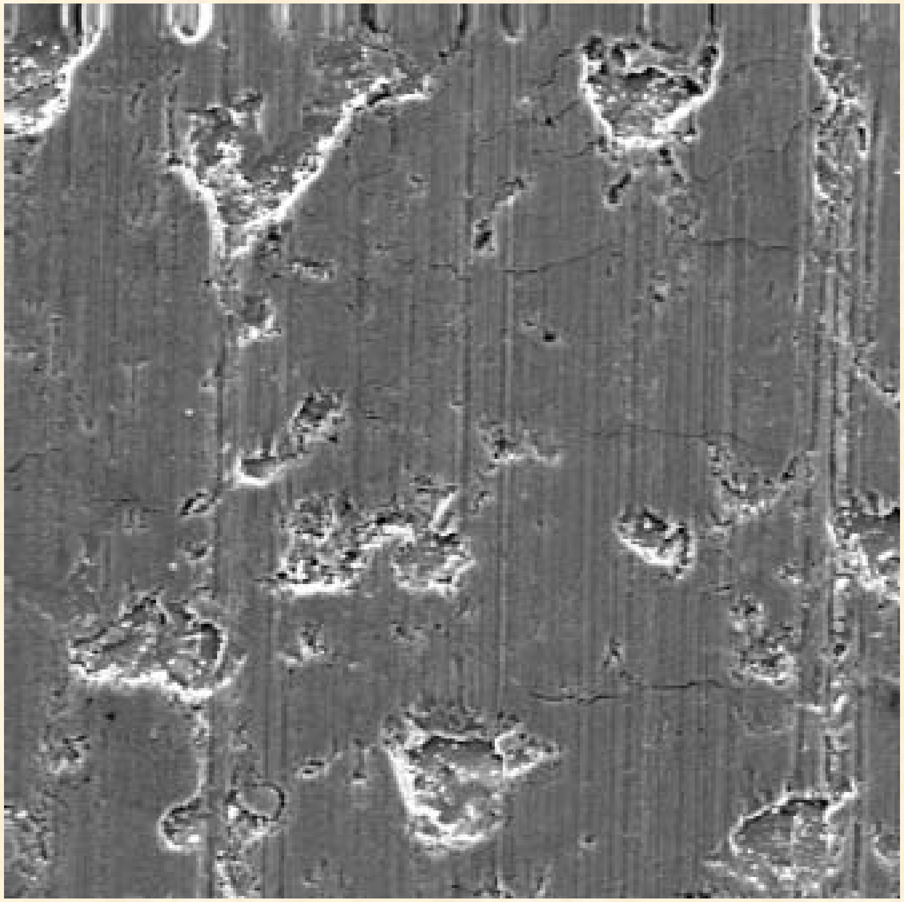
The Strength of $BaCe_{0.8}Zr_{0.2}O_3$ is Not Adversely Affected by Machining



Results-As Processed Versus Dry Machined Surfaces

$BaCe_{0.8}Zr_{0.2}O_3$
Surface Characteristics



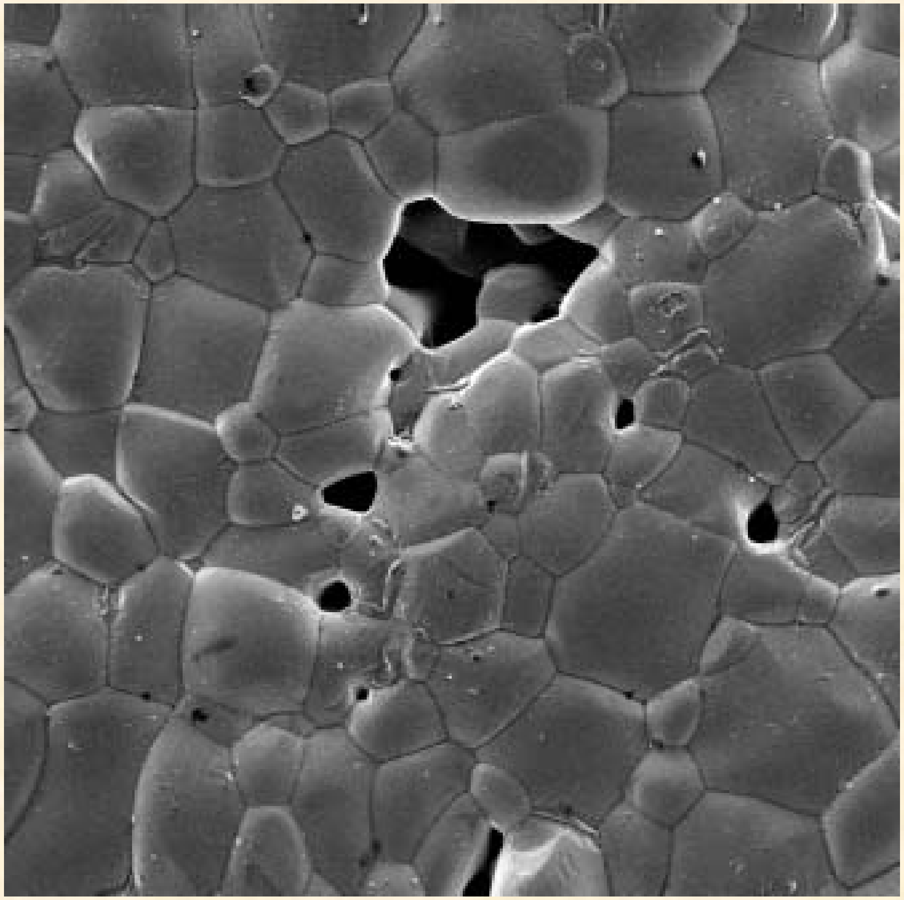


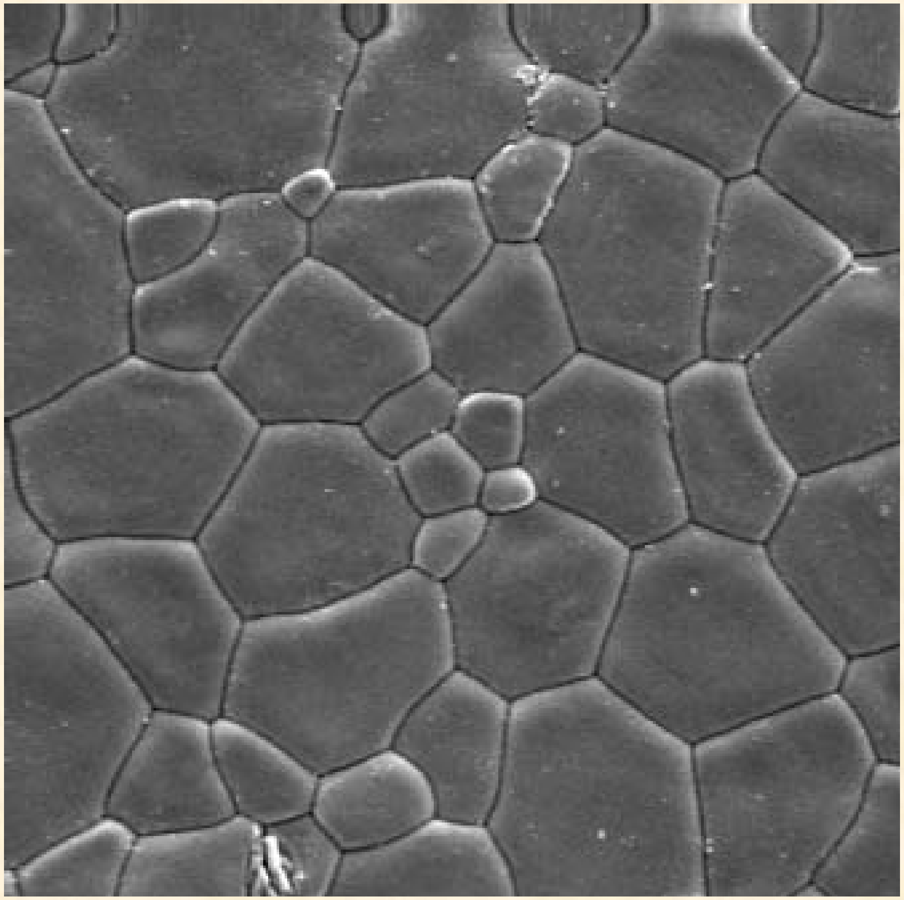
As-Processed   15 µm   Dry Machined

Mechanical Characterization of Ceramic Membranes for Hydrogen Separation

Comparisons

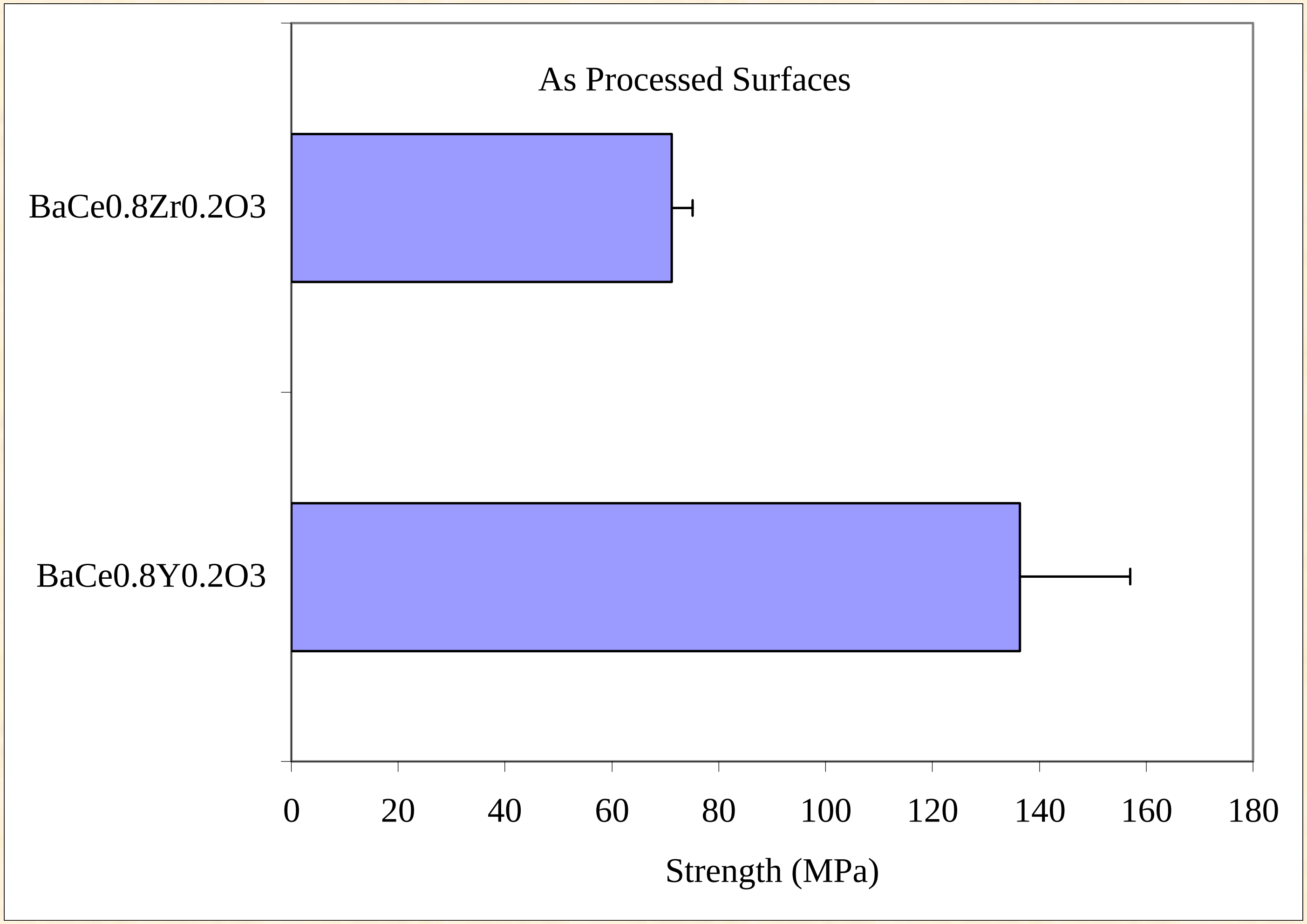
Grain Size of $BaCe_{0.8}Zr_{0.2}O_3$ is Larger than that of $BaCe_{0.8}Y_{0.2}O_3$



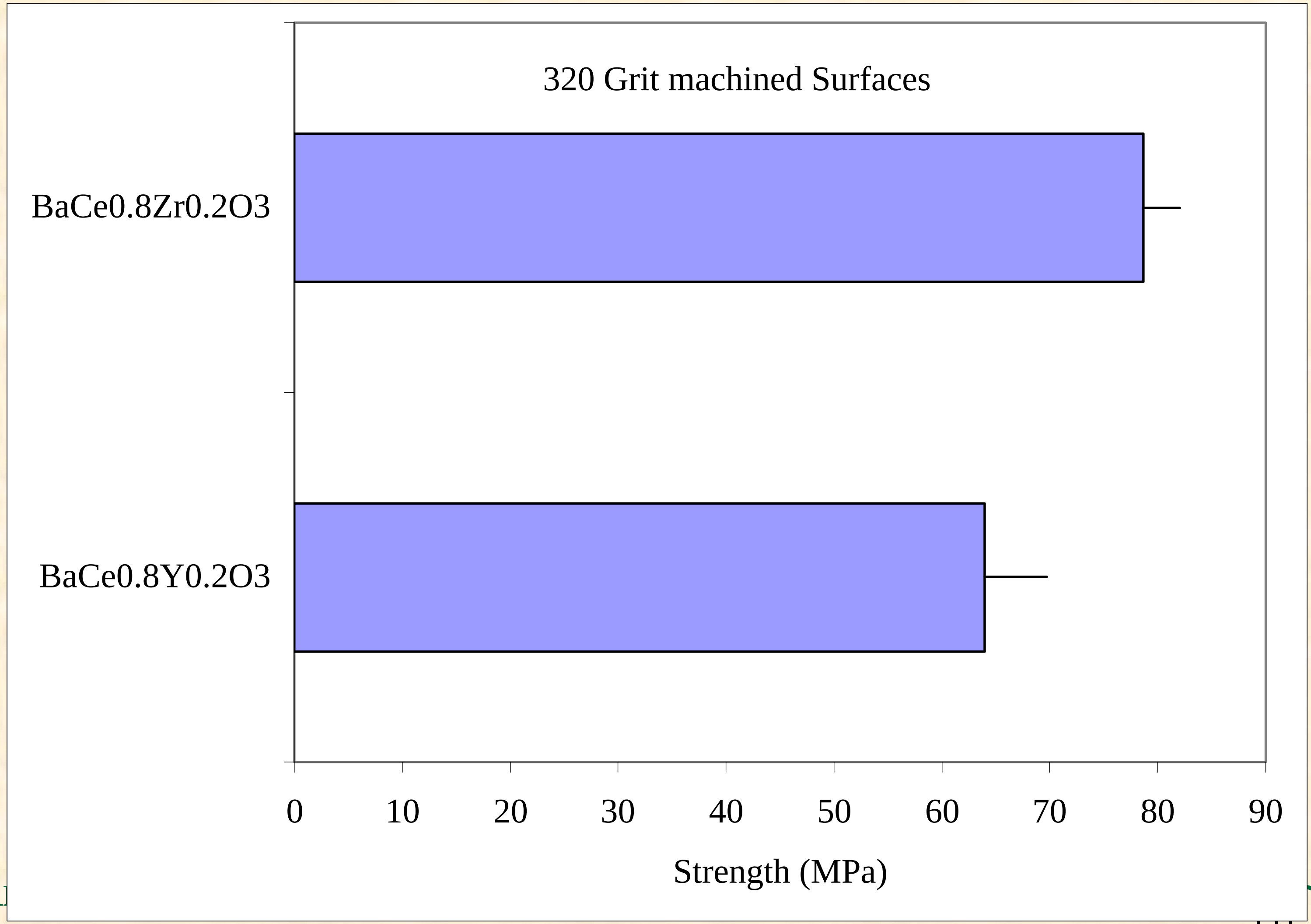


$BaCe_{0.8}Y_{0.2}O_3$ 15 µm **$BaCe_{0.8}Zr_{0.2}O_3$**

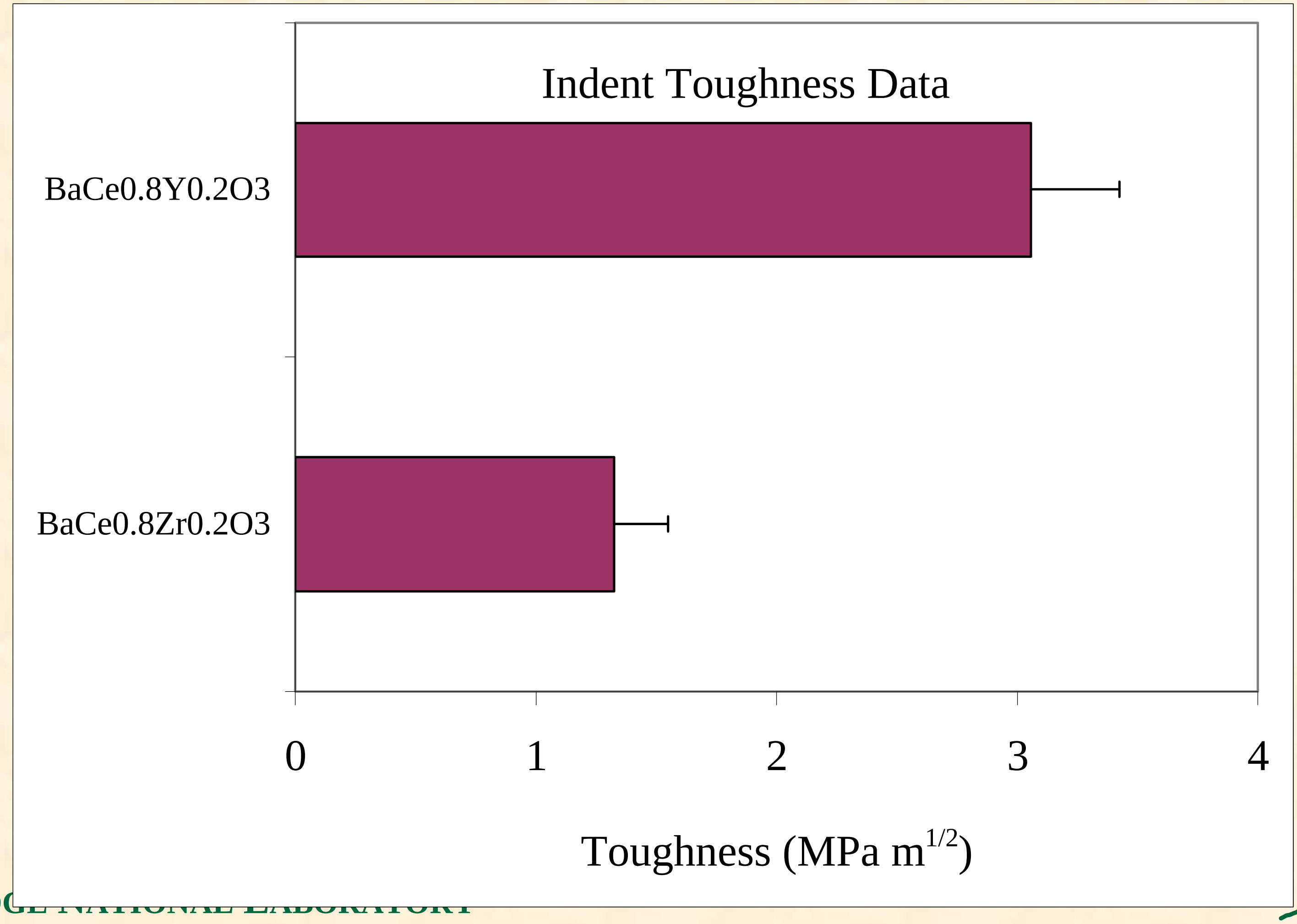
For Processed Surfaces the Strength of the $BaCe_{0.8}Zr_{0.2}O_3$ is Significantly Lower Compared with the $BaCe_{0.8}Y_{0.2}O_3$



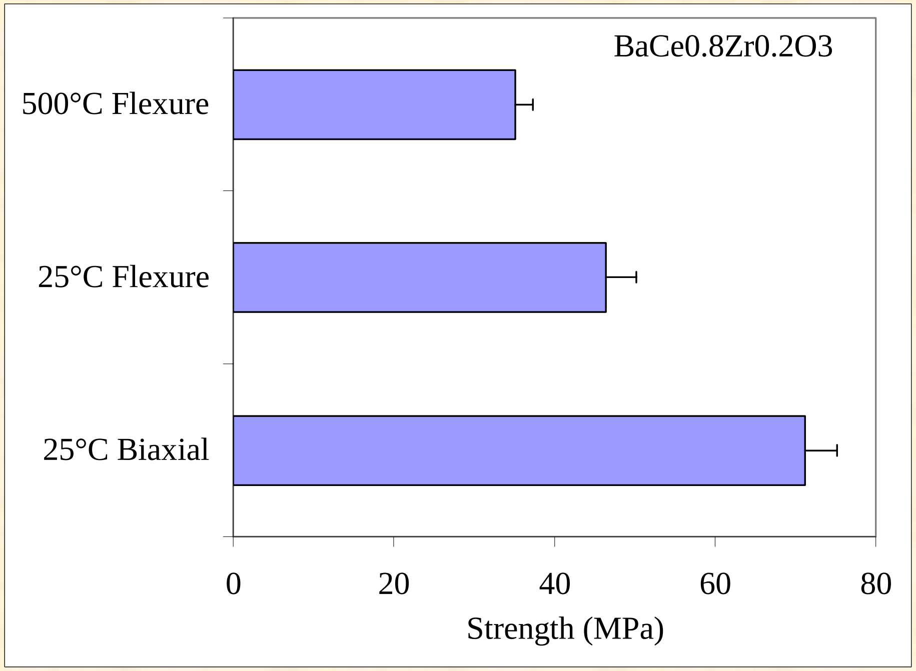
Strengths of 320 Grit Machined Specimens of Both Material Types are Similar

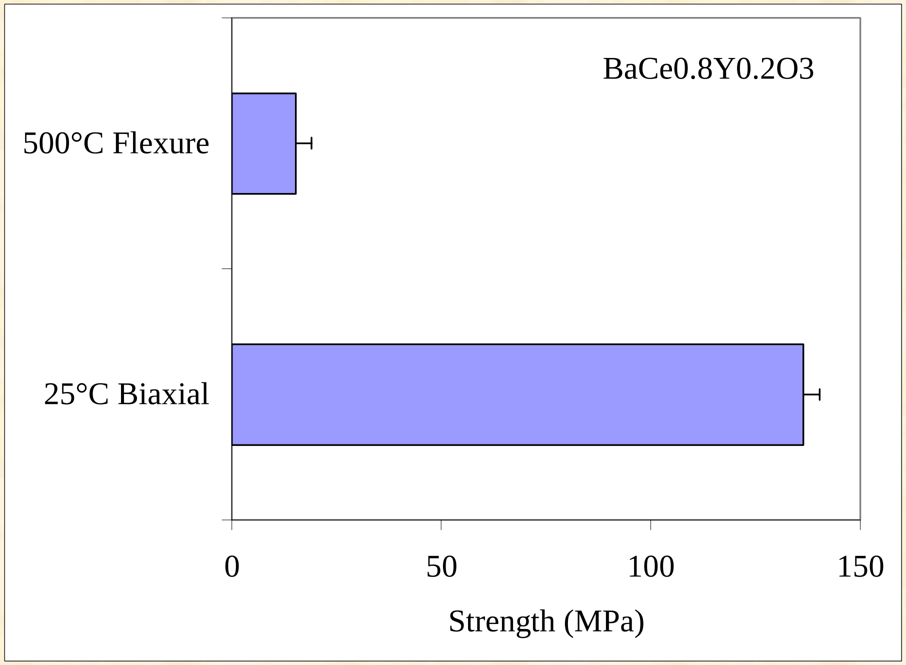


Toughness of the $BaCe_{0.8}Zr_{0.2}O_3$ is Significantly Lower Compared with the $BaCe_{0.8}Y_{0.2}O_3$



Preliminary Data Indicate that Strength Decreases with Increasing Temperature





Summary & Conclusions

H_2S Stability of Barium Cerate:

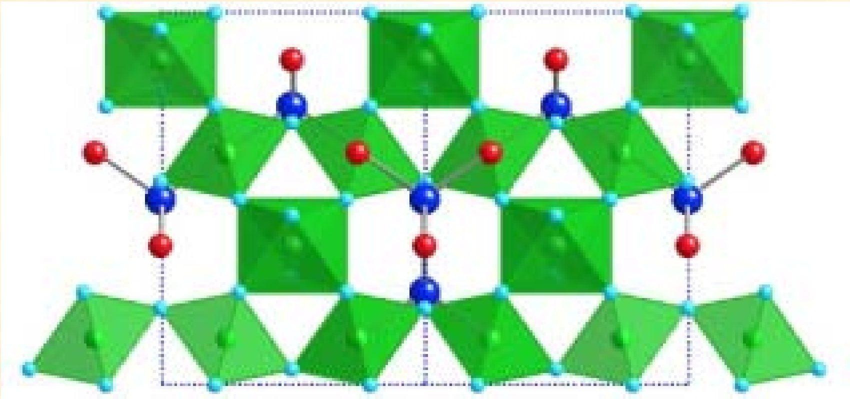
- **Stoichiometric BaCe0.8Y0.2O3 is stable**
  - **However, most materials contain some transition metal (Fe, Cu, Co...) to enhance mixed conduction**
  - **S binds easily to these metal oxides on surface of barium cerate**

H_2O Stability of Barium Cerate:

- **Optimized materials with Zr and barium deficiency showed increasing instability to steam at high-temperature**

The pyrochlore structure can facilitate enhanced proton conduction

- The pyrochlore $La_2Zr_2O_7$ has important advantages:
  - **greater inherent proton solubility**
  - **larger free cell volume for proton migration**.
  - **two distinct oxygen sites**, so vacancies may be introduced preferentially onto one or the other site.
- Proton conduction has been confirmed in $La_2Zr_2O_7$



La=red; Zr=green; O=blue

"There can be no denying that the quest for efficient separation of hydrogen is one of the most important challenges for the future of energy supply and the whole hydrogen economy."

Prof. Julian Gale

Imperial College, London