GRAIN BOUNDARY CHARACTERIZATION IN YTTRIA-STABILIZED ZIRCONIA BY TEM SPECTRUM LINES

N. D. Evans,*† P. H. Imamura,‡ and M. L. Mecartney‡

* Oak Ridge Institute for Science and Education, Oak Ridge, TN 37831-0117
† Metals and Ceramics Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6376
‡ Dept. Chemical and Biochemical Engineering and Materials Science, University of California, Irvine, CA 92697

The superplasticity exhibited by some fine-grained ceramics, notably 3-mol% yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP), offers interesting possibilities to lower manufacturing costs by near net shape forming. Both glassy and crystalline materials have been added to pure 3Y-TZP to limit grain growth and promote grain boundary sliding during sintering and isostatic pressing.[1] EDS spectrum lines have been used to characterize the distribution and extent of additive phases, but were not able to map some light-element components of additives (e.g., O and B in borosilicate glass). Additionally, quantification of the Si Kα peak was compromised by overlap with the Y L and Z L peaks.[2] To both improve light element sensitivity and investigate potential changes in oxygen bonding at the grain boundaries, undoped 3Y-TZP and 3Y-TZP powders processed with 1 wt% barium silicate have been examined with TEM spectrum lines.[3] Additionally, some elemental mapping has been performed. TEM specimens were examined in a 300 kV LaB_6 Philips CM30T equipped with a Gatan imaging filter (GIF) at the ORNL SHaRE User Facility. The configuration for elemental mapping was: incident beam divergence $\alpha = 2.9$ mrad, collection angle $\beta = 4.8$ mrad, energy selecting slit width $\Delta E = 30$ eV, 2× on-chip binning for 512 × 512 images, TEM magnification ~7400 (~148kX at the CCD camera), and 1 - 20 s exposure time. TEM spectrum lines were acquired as 1024 × 256 pixel images, 0.1 eV/pixel dispersion, and typically 20 s exposure time. Spectrum lines were acquired from areas selected with a 2 × 0.5 mm Au slotted washer located in the GIF entrance aperture; the washer is oriented normal to the energy dispersion direction. Grain boundaries were oriented “edge-on” and aligned normal to the area selecting slit with a tilt-rotate specimen holder. Subareas (~1024 × 3 pixels) from specific rows in acquired spectrum lines, corresponding to locations at and near the grain boundaries, were converted to Gatan EL/P spectra for comparison. Since spectrum lines are recorded in parallel mode, this procedure provides an unambiguous measurement of shifts in edge energy.

Jump ratio images revealed that barium is present both in triple points and along grain boundaries of doped 3Y-TZP, Fig. 1a. An intensity profile (from the location marked in Fig. 1a) reveals that the extent of the Ba is ~2 nm FWHM (Fig. 1b). This value is slightly smaller than that indicated by earlier EDS results. Si was not mapped as the Si L edge closely overlaps the Ba $N_{4,5}$. Fig. 2 is a core-loss image (oxygen post-edge) showing the edge-on grain boundary of doped 3Y-TZP, oriented normal to the area selecting slit, which was used to acquire spectrum lines for oxygen K (Fig. 3a) and barium $M_{4,5}$ (Fig. 3b) core losses. In Fig. 3, the TEM magnification, area selecting slit, and imposed spectrometer dispersion resulted in 0.8 nm pixel spacing. These figures readily reveal the O K excitation (Fig. 3a), but the Ba $M_{4,5}$ excitation is not obvious (Fig. 3b); the location of the grain boundary is denoted by the horizontal dark line in the approximate middle of the images. The resulting O K and Ba $M_{4,5}$ energy-loss spectra from subareas in Fig. 3 are presented in Fig. 4a (O K) and 4b (Ba $M_{4,5}$). The energies of the O K and Ba $M_{4,5}$ edges were not calibrated in this figure, but were assigned values of 532 eV and 781 eV, respectively. The spectra in Fig. 4a are from 3-pixel-wide (2.4 nm) subareas centered on the grain boundary and 3.2 nm on either side. For clarity, the intensities of spectra at +3.2 and -3.2 nm are vertically offset by 500 and -3000 counts, respectively. Additionally, a spectrum from a grain boundary of ‘Pure’ 3Y-TZP is presented for comparison. No shifts or additional features are observed, indicating that at this energy resolution, the energy-loss near edge structure of O K is not sensitive to the barium present in the grain boundary. This is perhaps a surprising result because the addition of 5 wt% silica to 3Y-TZP has been reported to change the oxygen bonding at grain boundaries.[4] Spectra in Fig. 4b are from subareas identical to those in Fig. 4a., but were acquired with the energy offset corresponding to the Ba $M_{4,5}$ excitation. An additional spectrum, further from the grain boundary (4.8 nm), is also shown in Fig. 4b. The intensities of spectra at +3.2, -3.2, and -4.8 nm are vertically offset by -1000, 500, and -1500 counts, respectively. The spectrum line analysis shows that the barium is confined to within a few nanometers of the grain boundary. Additional studies of both cubic and tetragonal zirconia, doped with silica and alumina, are planned.[5]

References

1. A. A. Sharif et. al, *Mat. Science Forum* 304-306 (1999) 443.
2. N. D. Evans et. al, *Microscopy and Microanalysis* 4(suppl. 2) (1998) 584.

3. J. Bentley and I. M. Anderson, Microscopy and Microanalysis 1996, San Francisco: San Francisco Press (1996) 532.
4. Y. Ikuhara, P. Thavorniti, and T. Sakuma, Acta Mater., 45 (1997) 5275.
5. Research at the SHaRE User Facility is sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., and through the SHaRE Program under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities. Discussions with Dr. Jim Bentley are gratefully acknowledged.

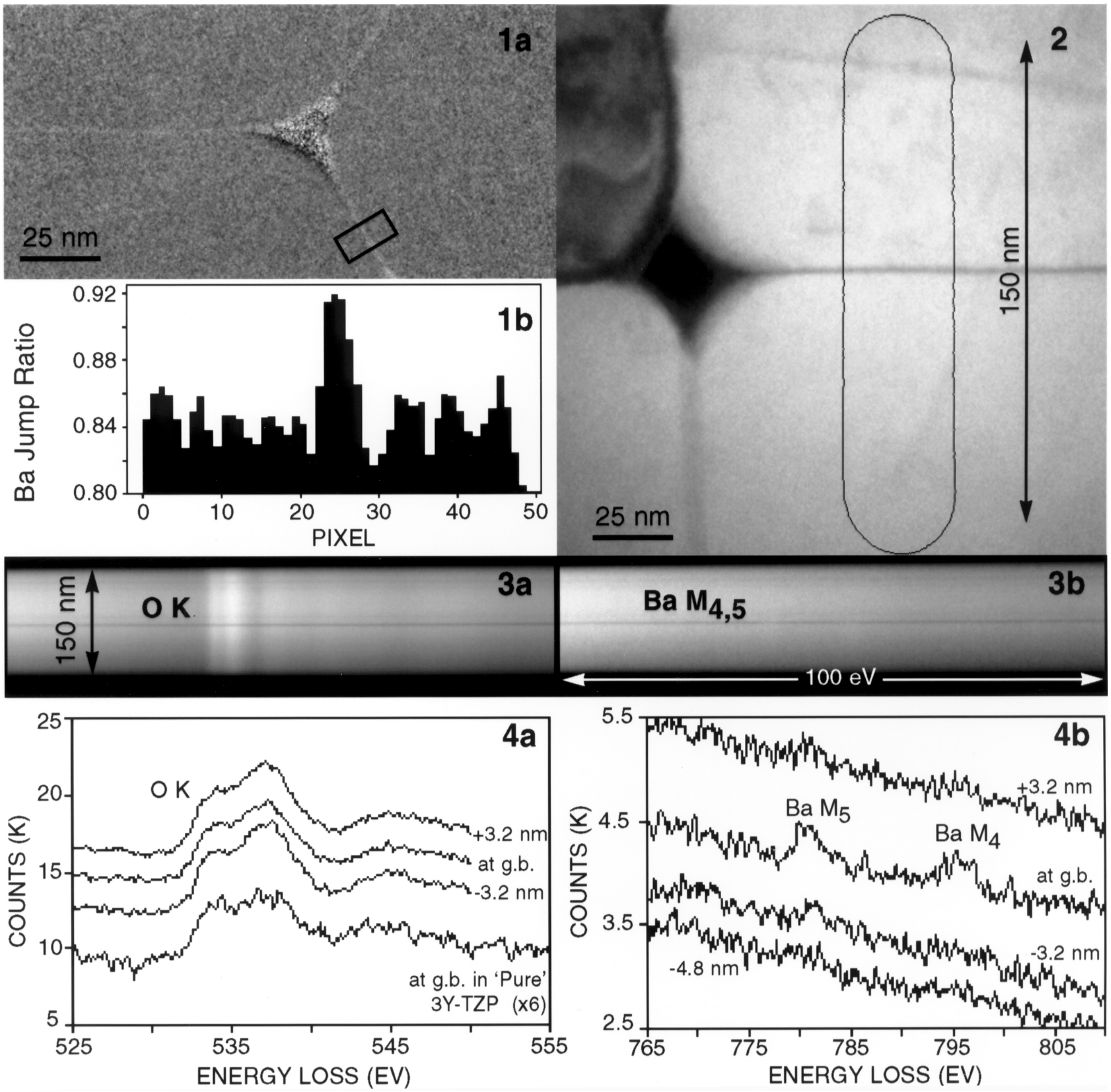

Fig. 1. a) Ba $M_{4,5}$ jump ratio image, and b) intensity profile across grain boundary (0.324 nm pixels).
Fig. 2. Edge-on grain boundary is oriented normal to slotted washer for acquisition of spectrum lines.
Fig. 3. Spectrum lines acquired with energy offsets for a) O K and b) Ba $M_{4,5}$ core-loss excitations.
Fig. 4. Energy-loss spectra extracted from spectrum lines of Fig. 3.