Probing the improbable: imaging C atoms in alumina

The ability to probe the three-dimensional atomic structure of materials is an essential tool for material design and failure analysis. Atom-probe tomography has proven very powerful to analyze the detailed structure and chemistry of metallic alloys and semiconductor structures while ceramic materials have remained outside its standard purview. In the current work, we demonstrate that bulk alumina can be quantitatively analyzed and microstructural features observed. The analysis of grain boundary carbon segregation – barely achievable by electron microscopy – opens the possibility of understanding the mechanistic effects of dopants on mechanical properties, fracture and wear properties of bulk oxides.

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Microstructure characterization is an essential step in the design of materials and optimization of their properties. In the case of bulk polycrystalline Al2O3, dopant distribution, concentration, and segregation to structural features can significantly impact mechanical properties such as high temperature creep, wear resistance and fracture behavior. These properties control the performance of ceramics in applications such as aerospace, fuel cells, nuclear materials, etc. In alumina, for instance, it has been shown that the presence of rare earth impurities (such as yttrium or lanthanum) at grain boundaries substantially reduces the grain boundary diffusion coefficient, as demonstrated by reduced rates of creep or grain boundary sintering1-3. At room temperature, alumina/SiC nanocomposites exhibit a change in fracture mode, from inter- to trans-granular, and better wear resistance compared to un-reinforced alumina4-6. Although direct crack-particle interactions may be important7, these changes are observed at such low SiC volume fractions that most alumina grain boundaries are not in contact with a SiC particle, indicating that impurities introduced with the SiC may play a key role in controlling grain boundary properties. An obvious possibility is carbon, but unlike yttrium that can be probed by high resolution z-contrast scanning transmission electron microscopy8, carbon surface contamination during analysis prevents the quantification of carbon at grain boundaries by electron microscopy. Atom-probe tomography has been successfully applied to reveal the atomic scale structure of a wide range of metals, for the detailed study of grain boundary segregation, dislocation analysis, or fine cluster and precipitate structures, e.g.9. Theoretically, it is therefore an attractive
technique to image and quantify carbon atoms at Al₂O₃ grain boundaries.

Atom-probe tomography, however, requires some minimum electrical conductivity (typically σ = 10⁻² Ω⁻¹.cm⁻¹) if electrical pulses are used to remove atoms from the specimen by a field ionization process. Laser pulsing has opened the field of three dimensional atomic scale analysis to semiconducting materials and oxide thin films revealing chemical and structural information previously unattainable in such non-conducting materials. The very first analysis of bulk insulators was performed by Kellogg about thirty years ago on pyrex and quartz using 337 nm ns laser pulses, but the field remained limited by the lack of reliable specimen preparation methods and laser systems. More recently, with the development of reliable lasers, atom-probe tomography has been used selectively for the analysis of oxide films on metallic substrates, such as surface oxides, thin films in magnetoresistive type structures, e.g., SiO₂ layers for optical devices, or oxidized stainless steel surfaces. These studies used <550 nm wavelength laser pulses with 355 fs, ~10 ps or ~500 ps duration. Hono et al. analyzed a bulk yttria-stabilized zirconia spinel. The results showed relatively large deviations from the expected stoichiometry for reasons that were not clear. Despite these isolated studies, the class of highly resistive, large band gap bulk materials examined by atom probe tomography, has remained to date a largely un-explored field.

To demonstrate the feasibility of analyzing selected microstructural features in bulk oxides, dense polycrystalline alumina doped with 0.036 wt% C and having an average grain size of 1.5±0.1 μm was produced by sintering in vacuum. The resulting grain structure is shown Fig. 1a after exposure to a thermal grooving treatment and deposition of a thin Pt layer. Specimens for atom-probe tomography analysis were prepared by focused ion beam milling. A specimen with a grain boundary within 50nm of the apex is shown in Fig. 1b. Note that the development of high resolution dual beam focused ion beam instruments has allowed not only the reliable preparation of non-conductive needle-shaped specimens but has also enabled the specificity of the specimen location with respect to the material microstructure.

Atom-probe analyses were performed on LEAP-3000XHR and LEAP-4000XHR instruments equipped with a 532 nm – 10 ps or a 400 nm – 500 fs pulsed laser respectively. A mass spectrum obtained with the 532 nm laser is shown in Fig. 2. Both experimental conditions yield an Al-rich matrix measured composition of 43.5±1 at.% Al-56.5±1 at.% O with less than 2 at.% H. The measured Al/O ratio is therefore 0.77±0.3 as compared to the expected value of 0.67. While the oxide may be oxygen deficient, the small deviation from the stoichiometry can also be explained by a possible loss of oxygen atoms in the high number of multiple hits (>50%) and/or by the overlap between O₂²⁺ and O⁺ peaks leading to an underestimation of the amount of O. A three-dimensional reconstruction of a dataset containing a grain boundary decorated with carbon atoms is shown in Fig. 1c. The level of carbon segregation at this particular grain boundary is 1.5±0.5 atom/nm² (corresponding to the shaded area in Fig. 1d). No measureable carbon is found within the alumina grains – note that the apparent presence of carbon atoms (at a level of about 40 ppm) in the grains corresponds to random noise.

Following the 1982 results by Kellogg using ns laser pulsing, Larson et al. demonstrated that ps laser pulses yields sufficient yield and mass resolution for the analysis of bulk Al₂O₃ or SiO₂. However, at that time, it was unclear whether near atomic resolution could be attained allowing the generation of three-dimensional atomic maps. Recent theories were then proposed that short laser pulse wavelengths...
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(in the UV range) with femto-second duration are advantageous and even necessary for the analysis of large band gap materials\(^\text{16}\). However, the present results clearly demonstrate that such analysis is indeed achievable using green or blue wavelength with ps or fs duration and that the analysis of bulk insulators does not require any specific laser operating space, in agreement with the previous surface oxide or oxide thin film studies. The difference in mass spectra between blue and green lasers (as shown in inset of Fig. 2) resides mainly in the level of the tails after the main peaks. The mass resolving power achieved with the blue laser is FWHM>820 and FWTM>320, while the green laser yields FWHM~580 and FWTM~250. The relative ratio of the different mass spectrum peaks and the multihit behavior are otherwise comparable.

These observations question our understanding of field evaporation and laser/matter interactions for the case of large band gap materials. Previous ab-initio calculations suggest that the band gap of crystalline alumina is reduced from ~8 eV in the bulk to 2.5 eV at the surface\(^\text{19}\), which is within reach of the photonic energy of a 532 nm laser pulse (2.3 eV). The presence of Ga and the possible amorphisation of the oxide surface by the 3 keV gallium beam during sample preparation in the focused ion beam instrument may also contribute to a modification of the surface states and thus a charge-draining path, much like coating with a thin metal layer\(^\text{11}\).

The feasibility of field evaporating bulk large band gap materials such as alumina and analyzing microstructural features at the near atomic scale opens an entire new field of experiments. Beside the technological importance of understanding the contribution of microstructural features and dopants to the behaviour of bulk oxides, it may also provide some essential clues as to the electronic structure of oxides in the one-dimensional nanoscale configuration such as that of a sharp needle geometry required for field evaporation.

The realm of oxides is now open for atomic scale probing.

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REFERENCES