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Laser and Material Effects on Laser Pulsed Atom Probe Analysis of Oxide and Nitride Ceramics

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Atomic scale characterization of internal interfaces in ceramics such as grain boundaries and thin films is needed in order to fully understand the electronic, ionic, mechanical, magnetic, and optical properties of the engineered material. High resolution analytical TEM has given a significant amount of new information about these interfaces, but lacks chemical sensitivity below ~1 at% as well as 3-D information and light element sensitivity. Atom probe tomography in ceramics has shown that atomic scale, 3-D characterization is possible with 10 ppm chemical resolution [1], but a thorough understanding of the laser assisted field evaporation process is needed.

As an example, Figure 1 shows the anion stoichiometry for a nitride ceramic where the cation / anion ratio should be 50 / 50. As can be seen, the atom probe quantification results in a highly sub-stoichiometric analysis for high laser power densities, a result which is observed in nearly every ceramic. Determining the origins of this sub-stoichiometry requires a more fundamental understanding of the optical absorption process as well as the resulting thermal pulse duration and magnitude.

During these experiments, a LEAP 4000XSi (Cameca Instruments, Inc., Madison, WI, USA) was used for data collection. The instrument uses a standard, 355 nm (3.5 eV) laser with < 10 ps pulse width and approximately 0.5 μm spot diameter at 0.8 σ. During the laser pulsing process, it is widely assumed that the laser is absorbed by the specimen, producing electron-hole pairs which are subsequently thermalized to the lattice. However, the ceramics demonstrated in this work all have bandgaps larger than 3.5 eV, implying transparency to the laser used. The fact that the laser pulse results in field evaporation for these materials suggests sub-gap energy states or multi-photon absorption processes.

Following absorption, the thermal energy produced is widely agreed upon to bring the specimen above the field / temperature evaporation threshold for a certain ion species. Peak specimen temperatures and the temporal dependence of specimen cooling are highly dependent upon the temperature dependent thermal diffusivity of the material as well as the mass (geometry) of the specimen. Figure 2 is a finite element simulation of the laser pulse atom probe process, illustrating the temporal and spatial temperature distribution for an oxide specimen pulsed with 1 pJ laser energy in the LEAP 4000X configuration.

Ultimately, understanding the optical absorption and thermal conductance of ceramics in the atom probe can give rise to stoichiometric, atomic scale analyses of internal interfaces in 3-D. This is demonstrated in engineered oxides and nitrides as well as natural terrestrial and lunar oxides.

References:
[1] Rita Kirchhofer, Melissa C. Teague, Brian P. Gorman, “Thermal Effects on Mass and Spatial Resolution During Laser Pulse Atom Probe Tomography of Cerium Oxide”, *J. Nuc. Mat.*, **436**, Issues 1–3, p. 23–28
[2] This work was supported by the National Science Foundation under grant #1040456

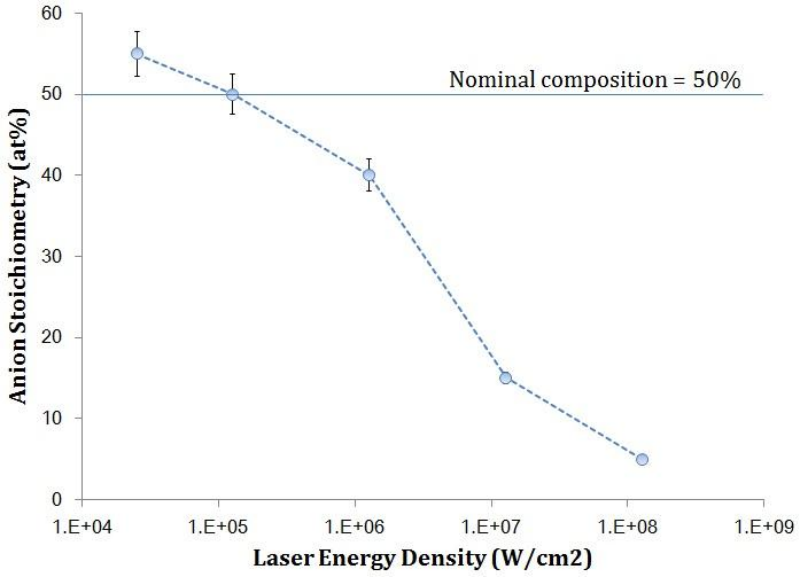

Figure 1. Anion stoichiometry as measured in a wide-bandgap ceramic as a function of laser energy density using atom probe tomography in a LEAP 4000XSi. Note the sub-stoichiometry measured at high laser energies.

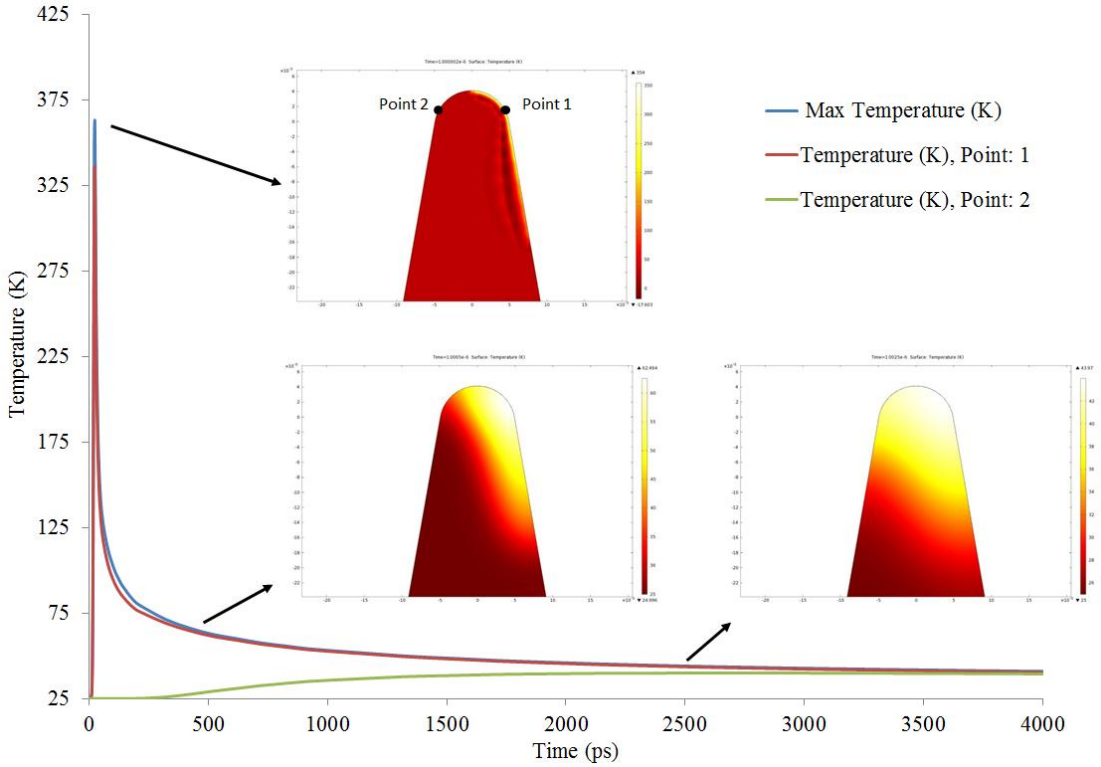

Figure 2. Finite element model of heat flow from an insulating ceramic atom probe specimen following laser pulsing with 1 pJ laser energy. Note the temperature maximum is reached in < 100 ps, followed by rapid quenching.

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