

Synthesis of Materials by Ultrafast Microexplosion

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Abstract: Microexplosions triggered by single femtosecond laser pulses tightly focussed inside a crystalline or amorphous host can be used to create high-pressure/density forms of nano-materials via an unconventional synthesis pathway: multiply ionized plasma, separation by diffusion, thermal quenching.

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Introduction. Tightly focused femtosecond (fs) laser pulses are widely used for surface and in-bulk structuring of materials. Due to localization of light into a spot size with cross sections comparable with the light wavelength, λ , and due to a short pulse duration, $t_p \simeq 100$ fs, a comparatively small pulse energy of ~ 100 nJ creates intensity/irradiance far exceeding the dielectric breakdown of crystals and glasses. Exploiting the threshold effect of material response, patterning of surfaces and bulk with super-resolution, i.e., with a feature size of modification smaller than the diffraction limit, become possible. Physical and chemical pathways of material modifications at the conditions close to and exceeding breakdown plasma formation provide unexplored new avenues to three-dimensional (3D) volume structuring, e.g., a cross linking of photo-polymers at the close-to-breakdown excitations by a controlled avalanche ionization provides a photo-initiation step even in a non-photo-sensitized monomer/oligomer-only resists [1]. This alters photo-chemical pathways of polymerization known at low-irradiance and one-photon excitation. Void-formation in crystals and glasses by single focused fs-laser pulses [2] is another example where 3D enclosure of dielectric breakdown and plasma formation provide a method to create dynamic-shock compression conditions characterized by high-pressure/temperature (high- p/T). Moreover, achievable heating and cooling rates are the fastest possible due to small volume and short pulse duration [3] providing efficient thermal quenching of the metastable and high- p/T phases.

Here, we report systematic structural study of modifications induced by fs-laser single-pulse-triggered microexplosions in α -Al₂O₃. The synchrotron X-ray diffraction (XRD) is used to map structural modifications induced by dynamic high- p/T microexplosions around the laser structured volumes. Formation of nano-crystallites of a high-density body centered cubic (bcc) aluminium inside sapphire is confirmed. We propose a new mechanism for spatial separation of Al and O ions as a result of microexplosion based on the difference of diffusion length of the ions in plasma. The estimated difference in the diffusion corresponds to the nano-crystallites size determined from the width of X-ray diffraction lines.

Experimental. Samples of α -Al₂O₃ (Shinkosha, Co. Ltd.) were structured by single tightly-focused fs-laser pulses (800 nm/150 fs) using an objective lens of numerical aperture $NA = 1.4$ as described elsewhere [1,3] and schematically shown in Fig. 1(a). The distinctive feature of structural modification was void formation at the focal region. The void-structure - the void with surrounding amorphous shell - was earlier observed by mechanical or focused ion beam cross-sectioning of the irradiated micro-volume. In this study we observed and reconstructed the modified volume by a 3D X-ray tomography (see, Fig. 1(b)). Images were obtained with the Xradia NanoXCT full-field X-ray microscope at beamline 6-2 at SSRL [4], at 8 keV in phase contrast. Tomography was obtained using the recorded images and reconstructed using Xradia software, and also via an in-house iterative method.

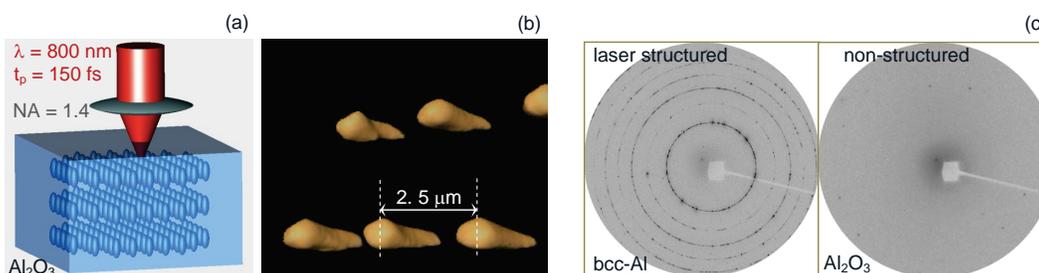


Fig. 1. (a) Schematics of an in-bulk modification of extended volumes by tightly focussed (a numerical aperture of an objective lens is $NA = 1.4$) fs-laser pulses; a single pulse per void-structure irradiation mode was used for fabrication of extended regions for XRD measurements. (b) 3D X-ray tomography view of a single pulse modified micro-volumes inside a $34\text{-}\mu\text{m}$ -thick sapphire slab; X-ray energy is 8 keV. (c) XRD image from an area of $5 \times 10 \mu\text{m}^2$ containing fs-laser modified micro-volumes; X-ray energy is 33 keV. The XRD pattern is indexed as bcc-Al.

High resolution X-ray diffraction (XRD) experiments were carried out at the HP-CAT sector's beamline 16-BM-D of the Advanced Photon Source, Argonne National Laboratory using X-ray energy of 33 keV ($\lambda_X = 0.37571\text{\AA}$) and the X-ray beam size of $5 \times 10 \mu\text{m}^2$ (width \times height). Data were collected in the transmission mode at different locations of laser-structured volume (see, Fig. 1(a)). The diffraction patterns were obtained using a MAR165 CCD, and the typical exposure time per image was 50-100 sec. X-ray diffraction data processing and data analysis were performed with FIT2D and Materials Studio (Accelrys Inc.) software packages. The simulated X-ray powder diffraction profiles were obtained using Materials Studio Reflex Powder Diffraction suite.

Results. Figure 1(c) shows experimental images obtained from the fs-laser structured and pristine regions in sapphire. The spot size of the X-ray beam was small and single-crystal of $\alpha\text{-Al}_2\text{O}_3$ ensured almost a background-free XRD detection (compare left and right images in panel (c)). Analysis of the experimental XRD data confirmed presence of ~ 20 nm crystallites of bcc-Al. This phase has density 41% higher as compared with face-centered cubic (fcc) Al known at normal conditions (20°C , 1 bar). Existence of this Al phase and pathways of its formation under static pressure has been predicted at >350 GPa [5], i.e., the pressure comparable to that at the center of the Earth. However, bcc-Al phase has not been confirmed experimentally. Analysis of the hydrodynamic motion of strongly ionized plasma during microexplosion and fast thermal quenching can explain separation of Al and O ions required for formation of bcc-Al nano-crystallites. The faster moving ions of oxygen are expected to form known oxygen rich forms of alumina at the outer regions affected by microexplosion.

Conclusions. We have identified presence of nano-crystallites of bcc-Al formed as a result of fs-laser single-pulse triggered spatially confined microexplosions and propose a mechanism of spatial separation of Al and O. The spatial XRD mapping confirms presence of the high-pressure phase of bcc-Al at the laser structured regions. We discuss application potential of the 3D fs-laser structuring in the field of high-energy-density physics [6] where matter subjected to pressures above 100 GPa is studied.

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