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Simultaneous multiple pulsed laser (SMPL) induced transformations in ZrO_2 ceramics

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This communication reports on the structural transformation from tetragonal to cubic ZrO_2 induced by excimer, YAG : Nd and CO_2 pulsed laser fluxes.

The idea that a laser pulse can cause reconstructive quenchable phase transitions was given an enormous boost by the discovery by Fedoseev and Derjaguin that graphite could be converted to diamond in the open air by dropping a fine powder through a 50 W CO_2 laser beam.[1–3] Hexagonal to cubic BN transformation was also claimed, but with less documentation, as was quartz (SiO_2) to stishovite. Confirmation and extension of the Fedoseev and Derjaguin experiments used a continuous wave CO_2 laser to reproduce the graphite–diamond transition and the quartz–stishovite transformation and obtain even higher-pressure phases of SiO_2 with the PbO_2 and Fe_2N type structures.[4–6] Kikuchi *et al.*[7] exposed various carbon materials to a continuous wave CO_2 laser beam in He and identified diamond crystals of some 10 µm in size; this was confirmed by Ogale *et al.*[8] In spite of these well-established facts, when, in 1995, Mistry *et al.*[9] announced their formation of diamond in a CO_2/N_2 atmosphere using lasers, they were greeted by universal disbelief from the community caught up in the narrow throes of the CVD approach, and a C–O–H diagram, which "demanded" the presence of hydrogen to make diamond.

In these various experiments,[1–6] the new (usually high-pressure) phases were fine (0.1–1.0 µm) powders, and in very low concentrations. Mistry *et al.*, on the other hand, made 30 µm thick continuous coatings on WC/Co substrates 1 cm × 1 cm in size. Also, in contrast to previous laser–material interaction work, they used three pulsed lasers of different wavelengths to simultaneously impact the work piece.[9]

Since then, simultaneous multiple pulsed laser (SMPL) exposure has been applied to diamonds, metals and polymers.[10–14] The most dramatic phase change recorded so far is in an 8 mm diameter, 2–5 mm thick fuel injector nozzle of ferrosilicon (3% Si) subjected to a *ca.* 30 s cladding and transformation treatment. Three layers form: a 1–2 µm clad layer of Ti(CN); a 10–15 µm layer transformed to a martensite-like phase inside the solid body; an inner 30–50 µm layer of metal transformed completely to a non-crystalline (glassy) state.[11] In this communication, we report for the first time the structural effects of the SMPL process on ceramic bodies in their final shape.

Given these data on ferrosilicon, we expected that many ceramics would also transform to glass. Samples of Si_3N_4 as ball bearings, Al_2O_3, and quartz were all examined but none, under the various experimental conditions tried, showed any substantial (*i.e.* 1 µm or more) layer of transformed material. The exception was ZrO_2. The starting material was a spherical ball bearing 5 mm in diameter.

It was exposed to the typical three-laser flux.[9] The lasers' parameters are as follows: excimer 248 nm, power 100 W, pulse length 30 ns, repetition rate 200 Hz, energy per pulse 440 mJ; Nd : YAG 1.06 µm, power 500 W, pulse length 8 ms, repetition rate 75 Hz; CO_2 laser 10.6 µm, power 750 W (CW). The 30 s laser exposure took place in the laboratory under ambient conditions with nitrogen as a shrouding gas. A plasma forms under such laser beam powers and its temperature can be in the range 5000–10 000 K, but the surface itself does not melt. The samples were sectioned and examined by optical, XRD and Raman spectroscopy, as follows.

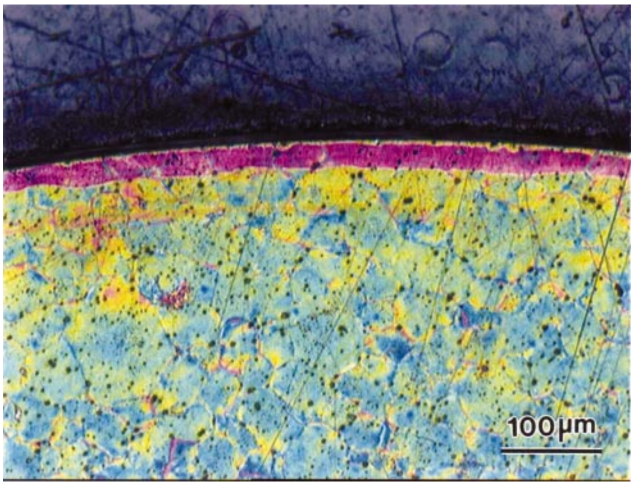

Fig. 1 Optical image of cross-section of the zirconia ball.

The optical microscope image of the cross-section of the zirconia ball shows the typical microstructure characteristic of such polycrystalline material. The outer edge of the ball shows a different contrast in a strip *ca.* 25 µm wide (Fig. 1).

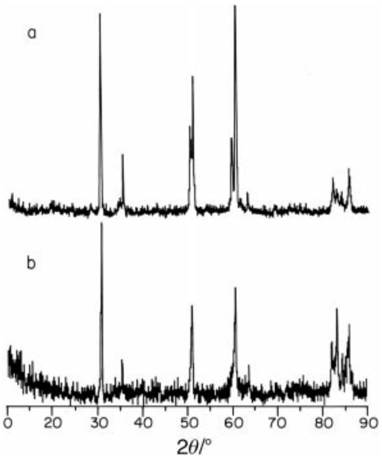

Fig. 2 X-Ray diffractometer traces taken with Cu-K radiation. (a) Diffractogram of the cross-section surface. (b) Diffractogram of the zirconia ball surface.

Table 1 Comparison of diffraction lines with JCPDS files

Main body		No. 14-534 Tetragonal			Surface layer		No. 27-997 Cubic		
D_{hkl}/Å	Intensity[a]	Tetragonal	Intensity	*hkl*	D_{hkl}/Å	Intensity	Cubic	Intensity	*hkl*
2.93	vs	2.949	100	111	2.911	100	2.93	100	111
2.57	vw	2.584	20	002					
2.54	m	2.542	60	200	2.536	20	2.55	25	200
1.81	ms	1.804	100	202					
1.79	s				1.795	50	1.801	50	220
1.55	vw	1.551	40	113					
1.53	s	1.535	80	311	1.527	58	1.534	20	311
1.47	w	1.474	40	222	1.465	15	1.471	5	222
1.29	vw	1.291	40	004					
1.28	vw	1.2869[b]	3	220					
1.27	w	1.270	60	400	1.25	5	1.270	5	400
1.175	w	1.1728[b]	3	114	1.180	15			
1.170	w	1.564[b]	2	222	1.161	45	1.167	5	331
1.153	w	1.151[b]	2	310	1.148	10			
1.135	w				1.133	35	1.135	5	420

[a] vs very strong, s strong, m medium, w weak, vw very weak. [b] No. 42-1164

Chemical analysis was conducted using an electron microprobe to see if there was any compositional change at the surface. Three spots were inspected: the center of the cross-section, the edge and the ball surface itself. The γ-PGT (Princeton, NJ) energy dispersive spectrometer showed the presence of Zr and O and, in addition, small amounts of C, Mg and Ca. The relevant finding was that there was no compositional difference and no matter was added or lost during the laser treatment.

Crystal structure information was obtained by X-ray diffractometry and the photographic Debye–Scherrer method. The main body and the outer spherical surface data are compared in Fig. 2. The diffractogram from the cross-section was identified as due to tetragonal zirconia. A comparison of diffraction lines and JCPDS file no. 14-534 is shown in Table 1. The table combines both diffractometer and photographic data taken with the Debye–Scherrer camera (114 mm in diameter, operated with Cu radiation filtered by a Ni foil placed before the film). The listed lines fit well with tetragonal ZrO_2, however, an orthorhombic lattice distortion can be suggested because of the presence of a weak line at 1.28 Å. The tetragonal phase has lattice parameters $a = 3.64$, $c = 5.27$ Å and space group D_{4h},[15] ($P4_2nmc$) according to JCPDS no. 24-1164.

The diffractogram taken on the hemispherical outer surface of the ball fits the cubic zirconia (JCPDS no. 27-997) data well, with a lattice parameter $a = 5.09$ Å and space group O_h^5 ($Fm3m$).

An attempt was made to compare the Raman spectra from the interior of the ball and from the surface. The spectra, which combine Raman and luminescence lines, are almost identical in respect of the positions of the lines but differ in intensity ratios. Overall, the intensity of the spectrum obtained from the surface is two orders of magnitude less than that from the interior.

The Raman signature at 460 cm^{-1}, characteristic of the cubic CaF_2 type structures, which was expected to show, was not detected at the surface.[15] We think that lattice disorder present in the transformed cubic phase prevents the appearance of vibrations typical for oxides with a fluorite-type structure.

An enormous body of literature exists on transformations in ZrO_2. However, laser treatment of ZrO_2 has received very limited attention. Simple exposure to a CW CO_2 laser has been reported by Chaim and co-workers. Of course, the laser caused surface melting, and rapid cooling and partial surface melting and reprecipitation of tetragonal ZrO_2 was observed.[16]

A recent review of surface modification of inorganic materials using excimer lasers considers only phase transformations when melting at the surface is involved. The review does not mention ZrO_2 or Si_3N_4. The report shows Al_2O_3 surface melting and re-solidification—partly to a 0.2 μm "amorphous" layer.[17]

In contrast to all previous work on ZrO_2 and other ceramic materials, our work employs three pulsed lasers. The treatment of ZrO_2 does not result in any surface melting. Nevertheless, the shock waves and the *p–t* conditions cause phase transitions while the macro-morphology is unchanged.

In conclusion this study is the first report on an *in situ* phase transformation within the outermost 25 μm layer of a finished ceramic body while retaining its net shape. It demonstrates the potential of multiple pulsed laser processing for post-formation modification of ceramics.

Acknowledgements

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