



AFRL-OSR-VA-TR-2014-0050

**LASER-INDUCED PATTERNING OF TRANSPARENT CERAMICS
AND METALLIC THIN FILMS FOR PHOTONIC AND SENSING
APPLICATIONS**

SANTIAGO CAMACHO-LOPEZ

CENTRO DE INVESTIGACION EN MATERIALES AVANZADOS, S.C.)

02/03/2014

Final Report

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14. ABSTRACT We developed novel laser processing of materials studies and techniques. Based on these we achieved demonstration of waveguides forming on transparent polycrystalline ceramics. Also, we demonstrated the formation of metallic oxides by very fast delivery of ultra low energy femtosecond laser pulses. Apart of scientific publications, we issued patent applications.					
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Laser-induced patterning of transparent ceramics and metallic thin films for photonic and sensing applications

US/MEXICO Basic Research Initiative

FINAL REPORT

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 - ❑ Scientific results
 - ❑ Infrastructure
 - ❑ Students/Postdocs
 - ❑ Journal Publications
 - ❑ Conference presentations and proceedings
 - ❑ Thesis, invention disclosures and patents
- ❑ Leveraging resources
- ❑ Future work
- ❑ Support Needed/Suggested
- ❑ Acknowledgements

Research team

Ultrashort Pulse Lasers and Materials Processing, CICESE



Laboratory of Transport
Phenomena, (LTP) UCR



Optics
Characterization
Laboratory
(OCL)

Advanced Materials Processing
and Synthesis, (AMPS) UCR



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Lidia Sanchez-Hernandez (BSc UAEM) #
Adela Reyes-Contreras (BSc UAEM) #

Postdocs:

Israel Perez (Postdoc, 4 months)

USA

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Javier Garay (UCR)

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Corey Hardin#
Yasaman Damestani#

Postdocs:

Dr. Pablo Martinez*
Dr. Daniel Garcia*

- partially supported through this project
* - not supported through this project

Motivation

Motivation

1. The DoD has identified transparent ceramics as promising replacements for glasses and single crystals.
2. Transparent ceramics may be used for laser host materials, opto-electronics applications (displays) and solar cells.
3. Transparency in ceramics is of great interest for optical-structural applications.
 - *Transparent ceramics may also become an integral part of President Obama's initiative known as BRAIN (Brain Research through Advancing Innovative Neurotechnologies), also commonly referred to as the Brain Activity Map (BAM) Project in order to understand complex brain processes.*
4. Metallic oxides are of great interest for applications such as displays and gas-sensing due to their photochromic, electrochromic, and/or gasochromic features. More recently, metallic oxides are mentioned as the new materials to impact the plasmonics field.

Proposal brief and logistics

The proposed work has three main directions:

Direction 1: Fabrication:

- a. polycrystalline transparent ceramics
- b. proton conduction ceramics
- c. metallic thin films.

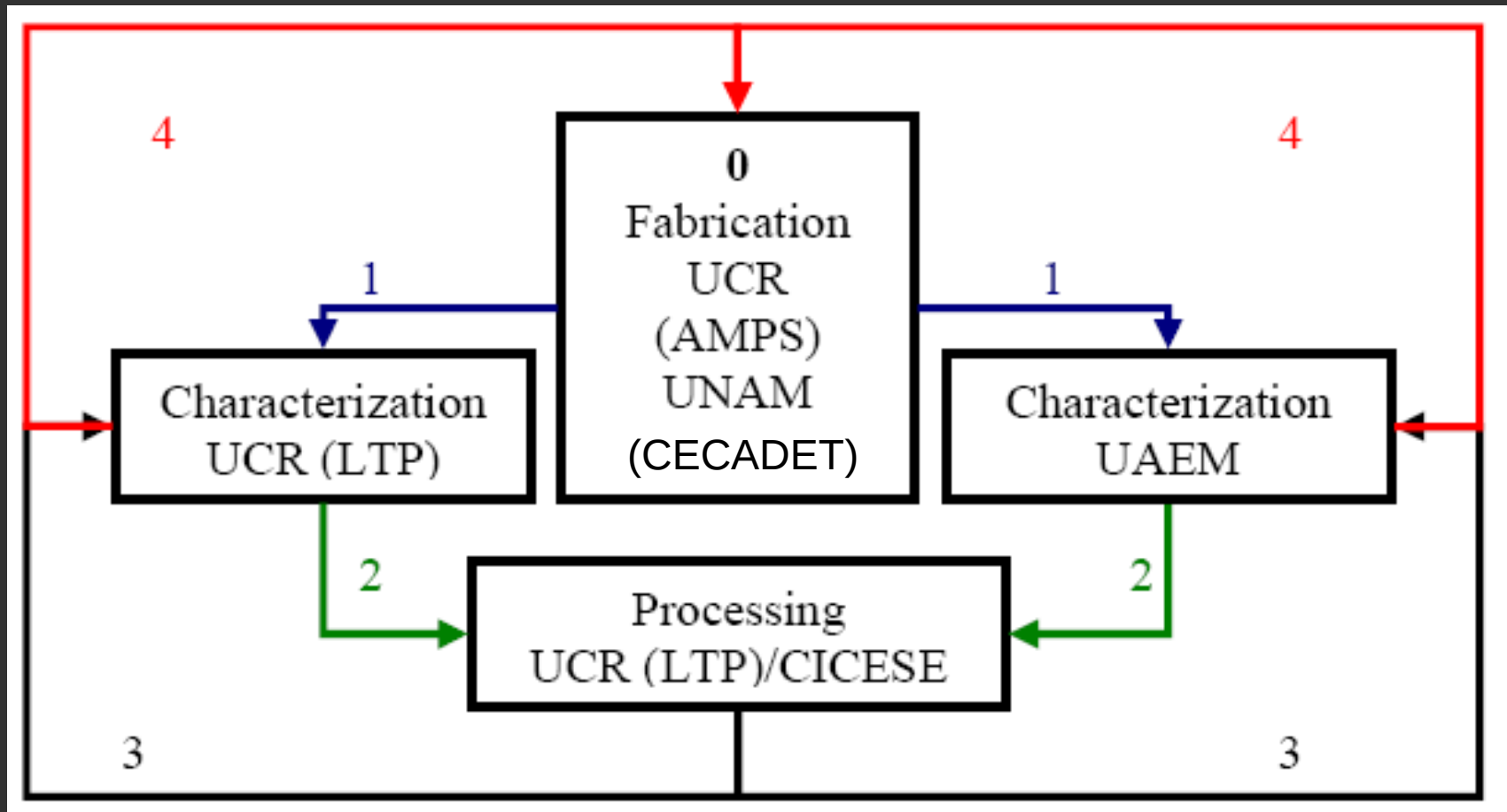
Direction 2: Laser Processing:

- a. Establish effect of pulsed lasers on phase changes.
- b. Establish effects of pulsed lasers on diffusion/doping of transparent ceramics.
- c. Use pulsed lasers to pattern complex structures in ceramics and metallic thin films.

Direction 3: Characterization:

- a. Optical properties (refractive index, absorption, reflectivity, transparency)
- b. Microstructural (Raman spectroscopy, XRD, SEM, TEM, AFM, EDS, Photoluminescence)

The diagram below shows the collaboration sequence we followed as we proceeded with this project:



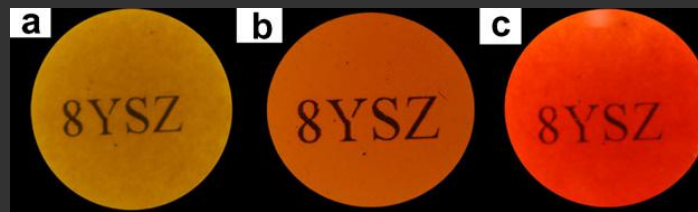
What was
accomplished?

	Metallic Oxides	Ceramics
Journal papers	1 (Opt Mat) 5 (in progress)	1 (Opt Mat Express) 1 (Nanomedicine) 6 (in progress)
Patent applications	1 full (USA)/1 full (Mexico)	2 provisional (USA)
Conference proceedings	1 – COLA2011 1 – RIAO2013 1 – MOPM2013	1 – COLA2011
Invited talks	1 – USAL (CLPU) 1 – CNyN 1 – CNCIM 1 – UGTO	1 – TMS 1 – MS&T 1 – UCSD 1 – CIMAV-Monterrey
Students	2 PhD (CICESE) 1 MSc (CICESE) 2 BSc (UAEMex) 1 MSc (UCR)	2 PhDs @ 50% (UCR) 1 PhD temporal for 3 months 1 MSc (CICESE)
Postdocs	1 (four month, CICESE) 1 UCR	2 UCR

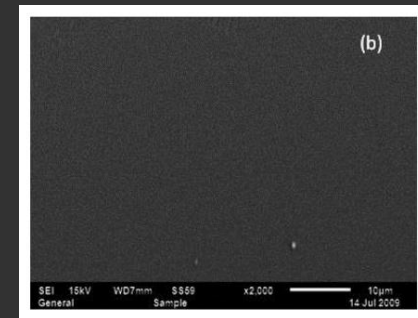
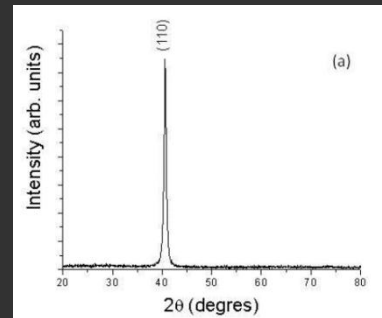
	Metallic Oxides	Ceramics
Joining collaborators	1 (King's College, UK)	2 (CLPU/USAL, Spain) 3 (UCR-interdisciplinary grp) 1 (UCSD – in vivo studies)
Upcoming proposals	3 (electronic vs thermal; plasmonic features; optical and electric properties)	3 (active media; multi- waveguide/multi-color lasers; cranial windows)

Scientific Results

1. We have successfully fabricated transparent zirconia with a wide range of linear and non linear absorption coefficients. The transparent zirconias were subsequently treated with *fs* laser pulses. We found that the absorption coefficients were affected by sample processing temperature and subsequent annealing in air.

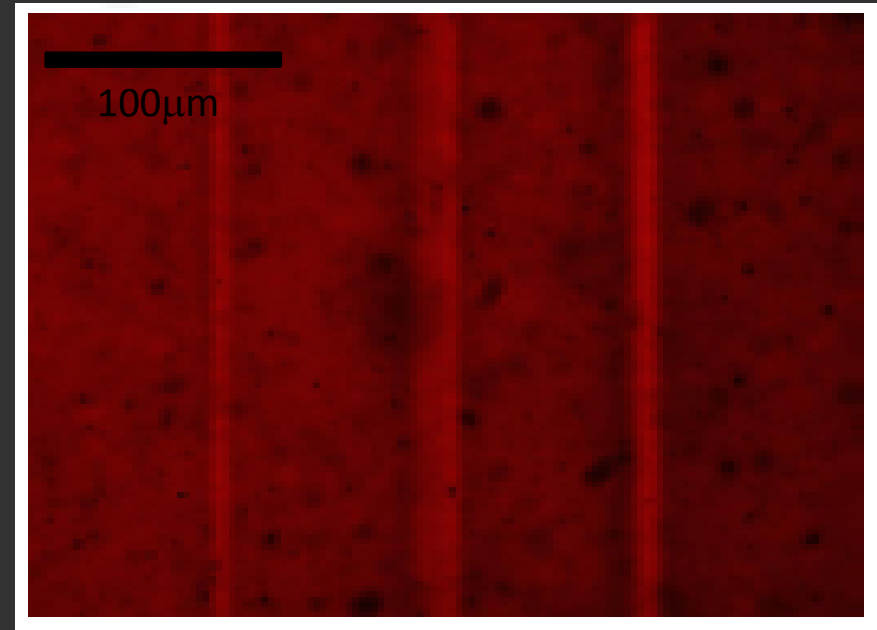
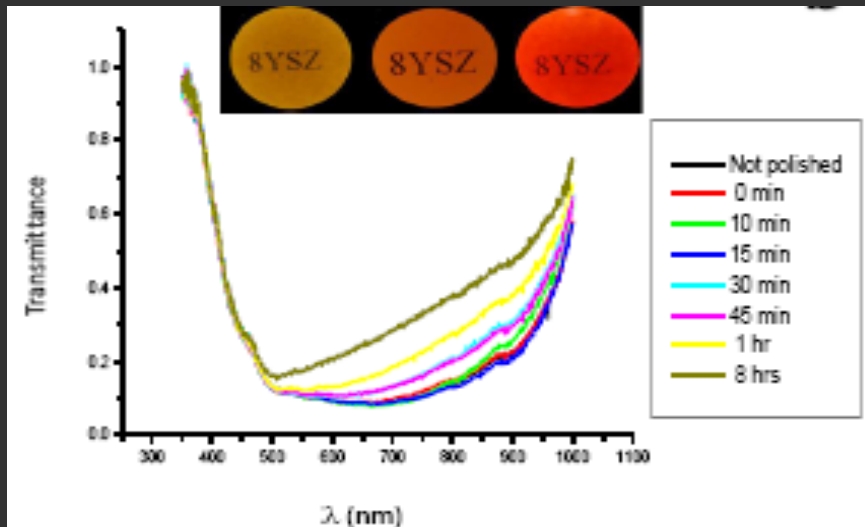
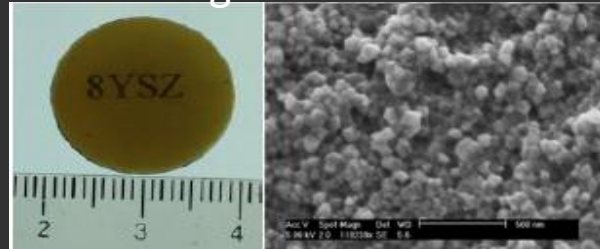


2. The sputtering deposition method proved itself to provide good quality metallic thin films for the synthesis of *fs* laser-induced metallic oxides – it works consistently for our choice of transition metals and substrates



1. Experimental demonstration of direct fs laser-writing of waveguides in YSZ – new laser-matter interaction mechanism → [Opt Mat Express, 2012](#)

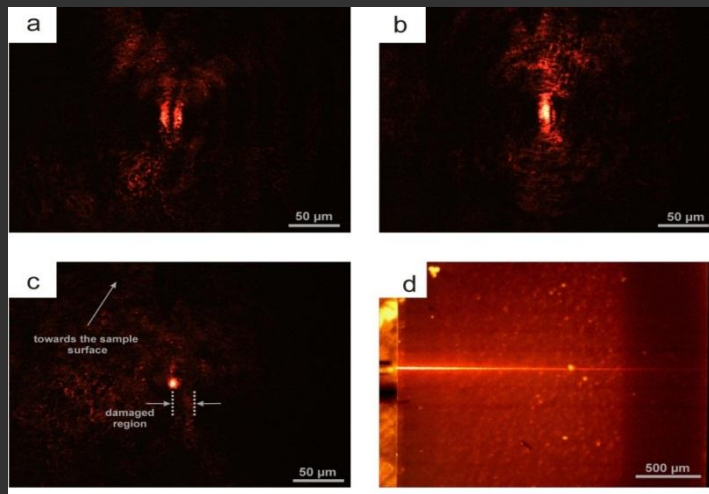
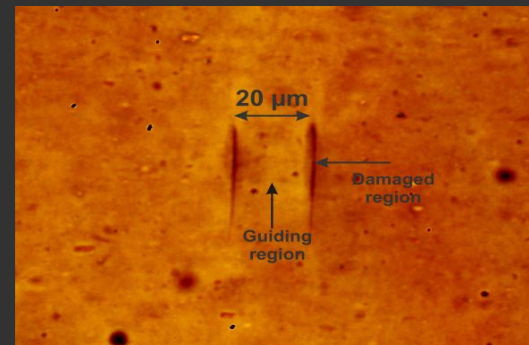
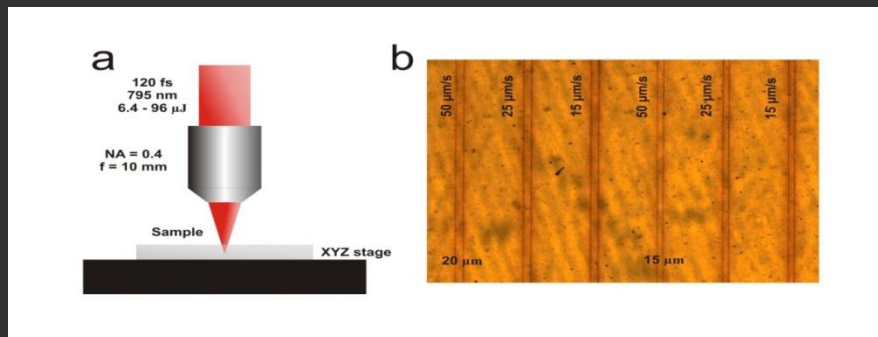
Spark sintering of nanostructured YSZ and annealing



fs laser-written waveguide-like structures. Energy per pulse up to 9nJ for a fluence per pulse of $\sim 70\text{mJ}/\text{cm}^2$ delivered at 70MHz

2. Experimental demonstration of direct fs laser-writing of waveguides at high fluences – first time in polycrystalline ceramics → [Manuscript in progress](#)

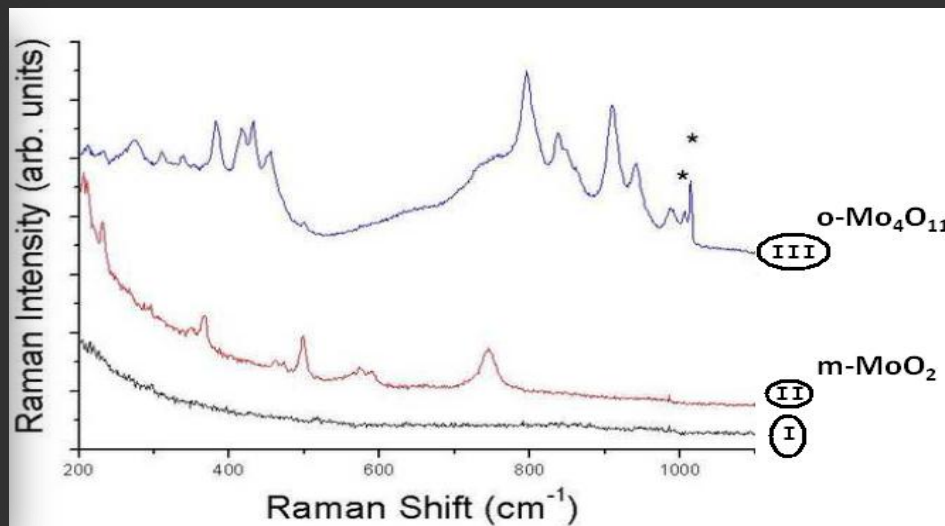
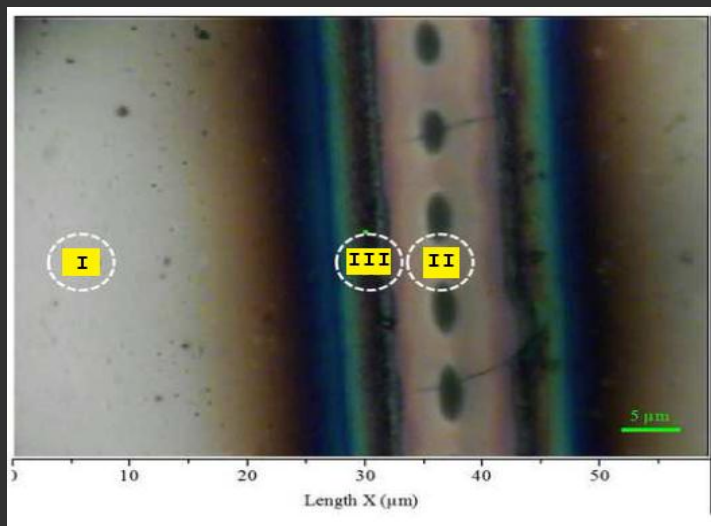
Channel waveguides written using amplified fs laser pulses in YSZ



3. Experimental demonstration of fs laser-induced metallic oxides synthesis – novel method for metallic oxides synthesis → [Optical Materials, 2011](#)

Molybdenum

60 fs lasers pulses at 800nm, up to 5nJ per pulse, and a rep rate of 70MHz
focusing with an aspheric lens (NA=0.5)
fluence per pulse of $\sim 30\text{mJ}/\text{cm}^2$ (below the ablation threshold)

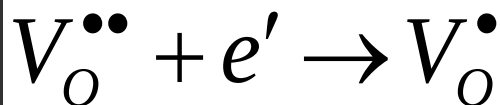
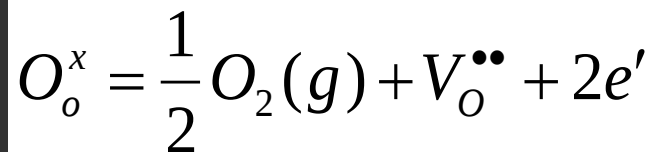


M. Cano-Lara, S. Camacho-Lopez, A. Esparza-Garcia, M. A. Camacho-Lopez, *Opt. Mater.* (2011), doi:10.1016/j.optmat.2011.04.029

4. Phenomenological model for explaining ultralow-fluence writing of waveguides in polycrystalline ceramics → In progress

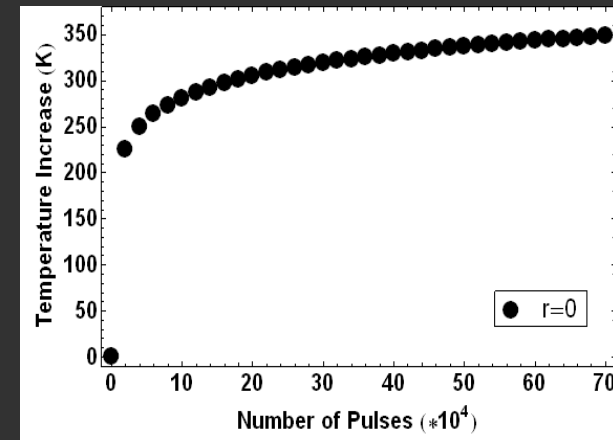
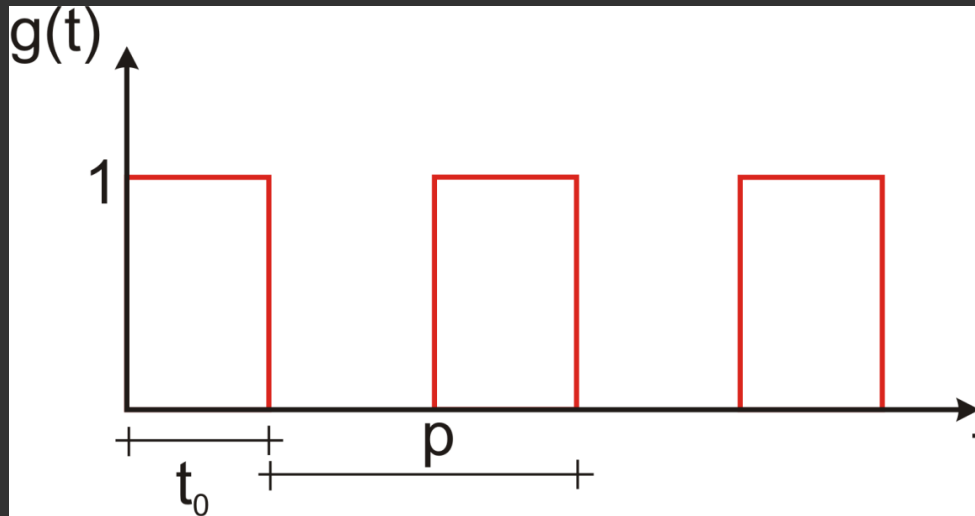
Processing causes changes in oxygen stoichiometry

A reduced (oxygen deficient) YSZ undergoes:



Oxygen vacancies with trapped electron causes blue-green absorption

5. Phenomenological model for explaining the synthesizing of metallic oxides through ultrashort laser pulses at ultralow fluence → In progress



$$g(t) = \sum_{m=0}^{M-1} [H(t - mp) - H(t - (mp + t_0))]$$

M = Total number of pulses in the train

$H(t)$ = Unit step function

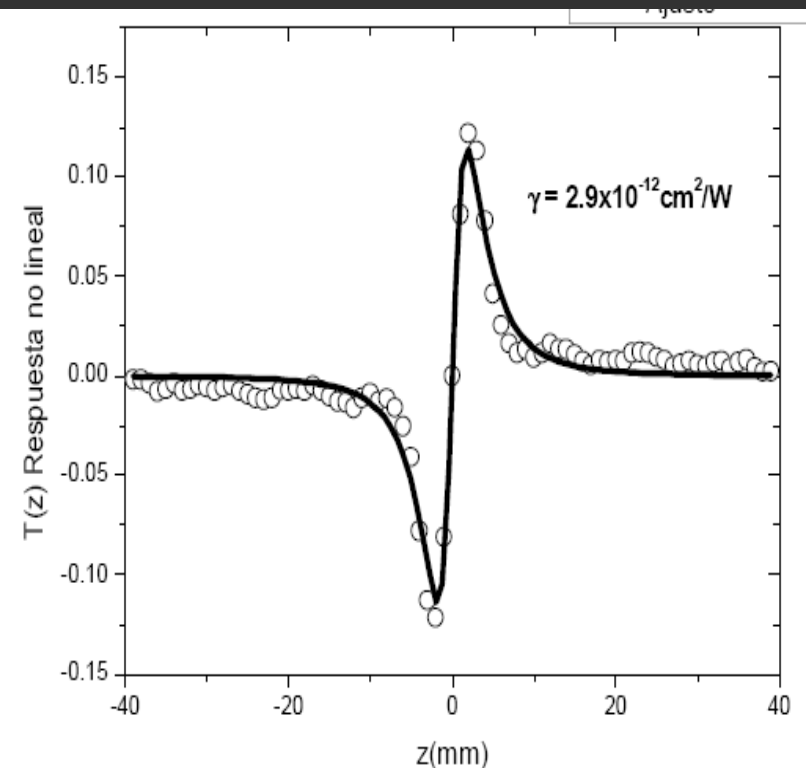
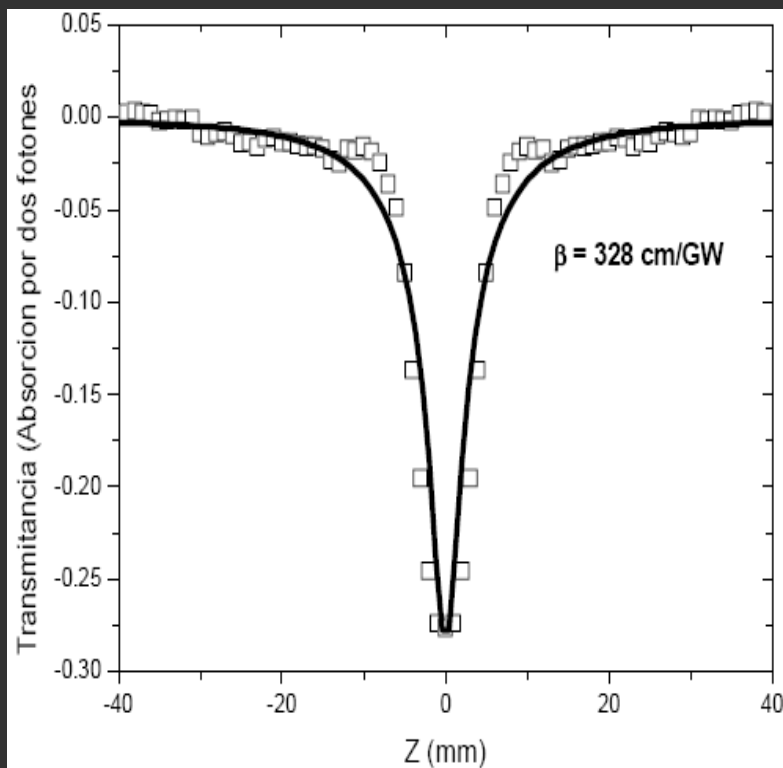
m = number of pulses

p = period

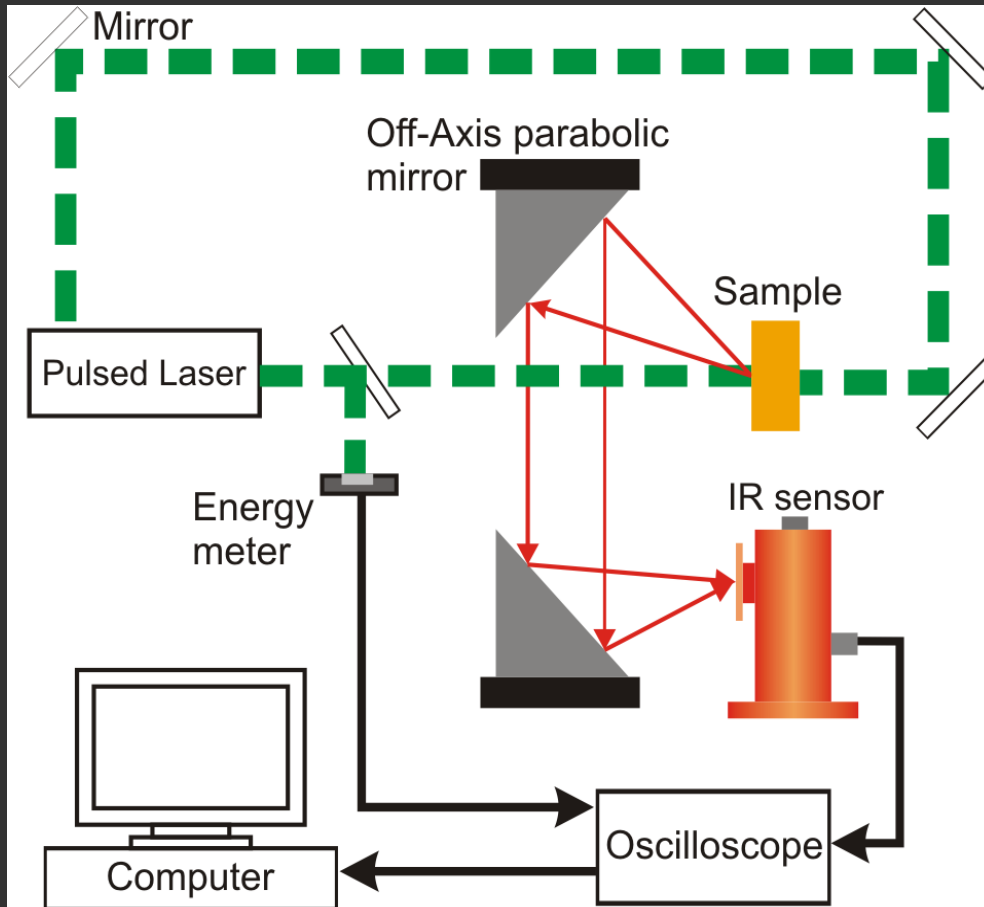
1. Preliminary results on the determination (z-scan) of the nonlinear optical properties of YSZ → for the first time to the best of our knowledge

Nonlinear optical properties of the nanostructured YSZ

Annealing time 10 min



2. Measurement of surface YSZ temperature increase during laser processing via pulsed photothermal radiometry (PPTR) to determine mechanism of waveguide writing → for the first time to the best of our knowledge



The temperature is function of time

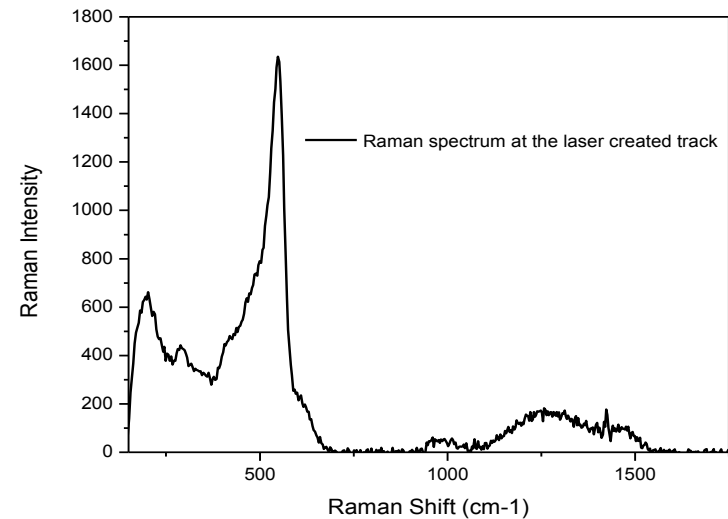
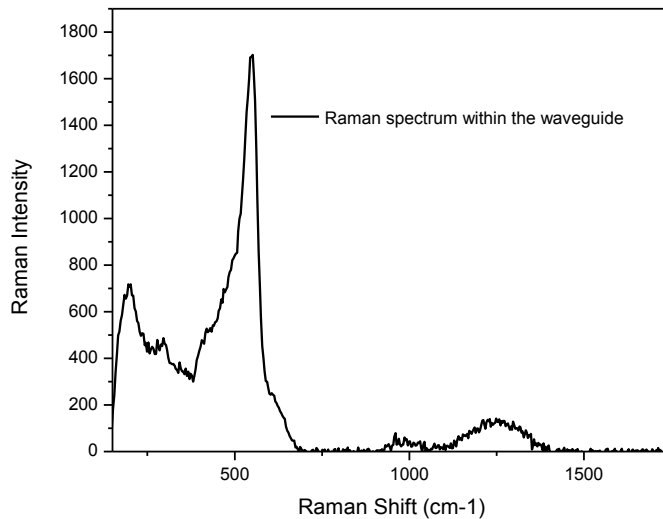
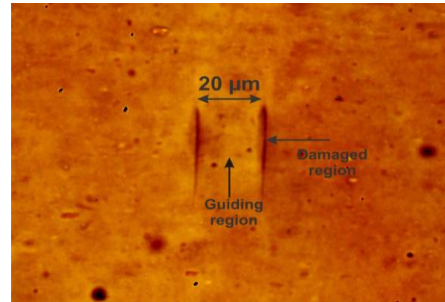
Signal:

Short-lived transient; magnitude decreases with time.

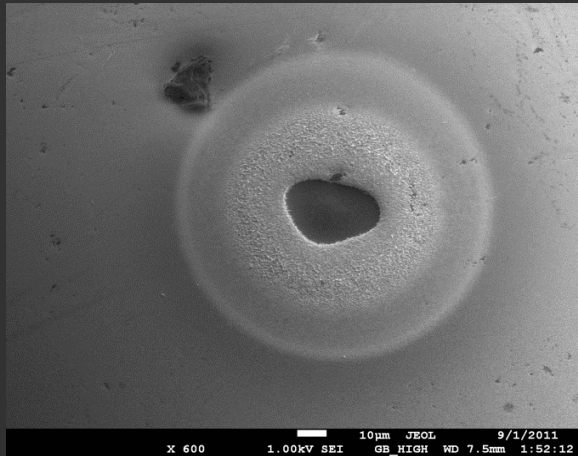
Detection:

Peak magnitude estimation and transient waveform analysis.

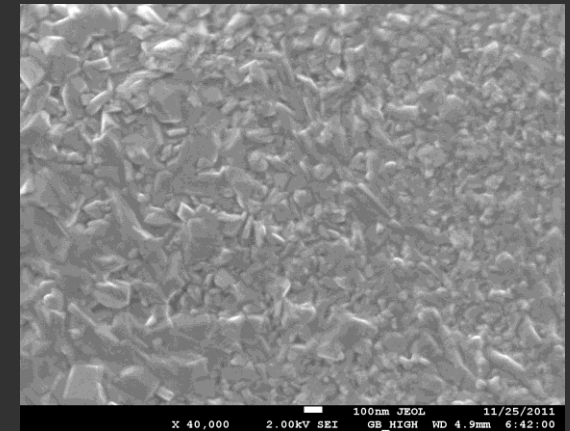
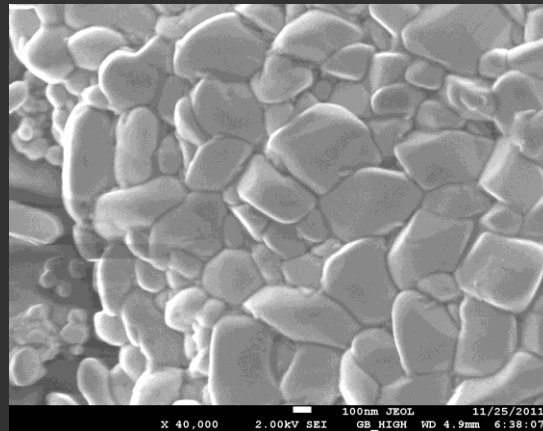
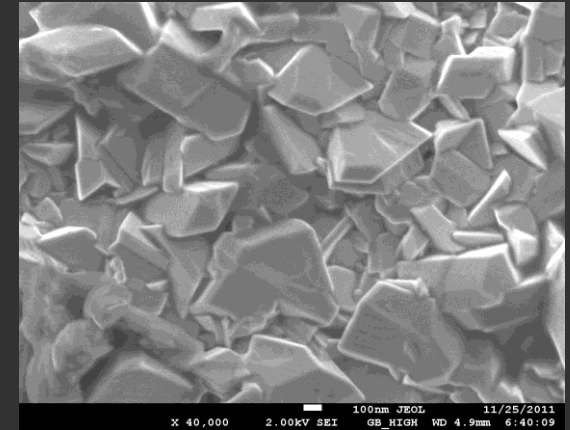
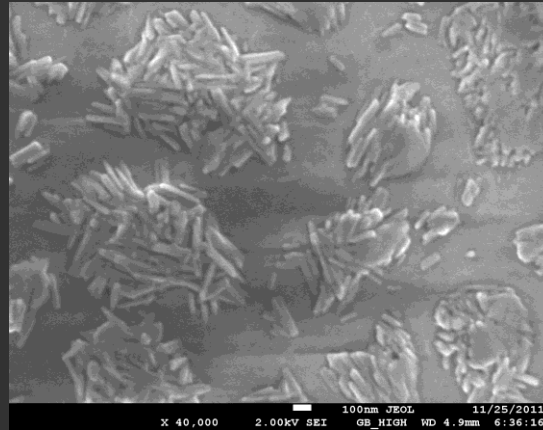
3. Investigation of the origin of the refractive index increase induced in the YSZ by the amplified fs laser pulses (microRaman spectroscopy) → for the first time to the best of our knowledge



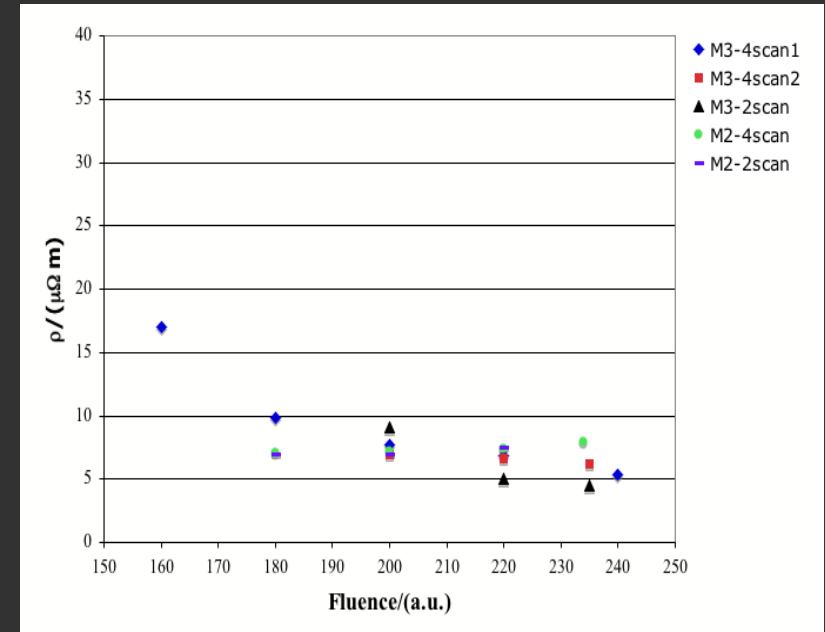
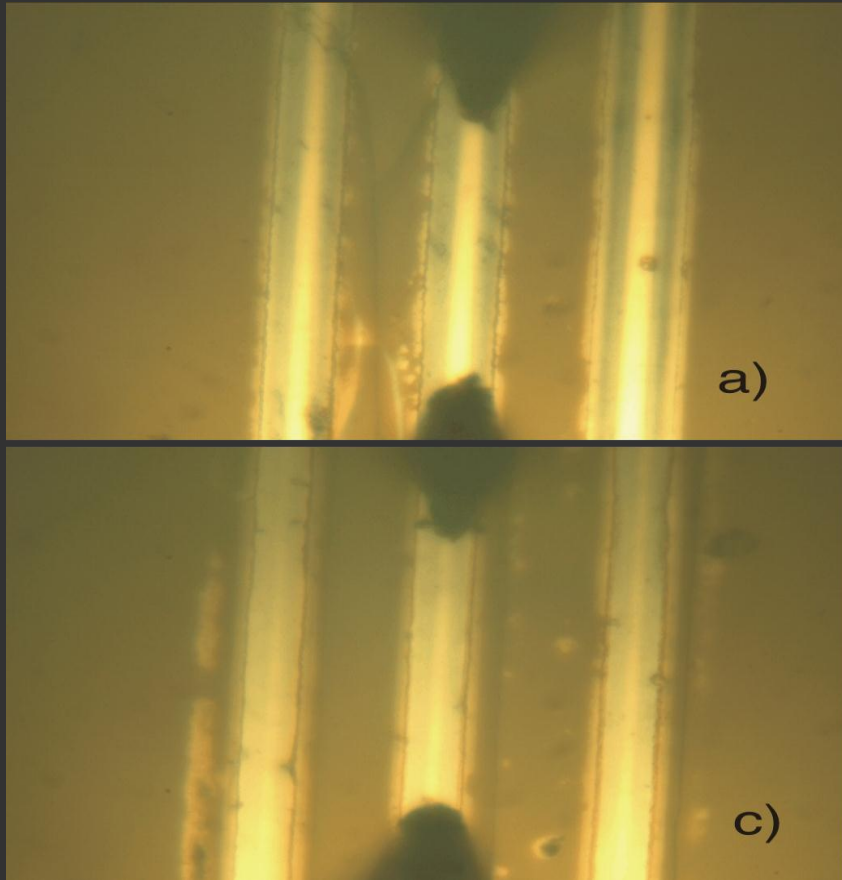
4. Experimental demonstration (SEM) of the feasibility to produce micro and nanostructured fs laser-induced metallic oxides → great significance for localized synthesis



$$E_{pp} = 4.35\text{nJ}, F_{pp} = 1.5\text{mJ/cm}^2, t=30\text{ sec}$$

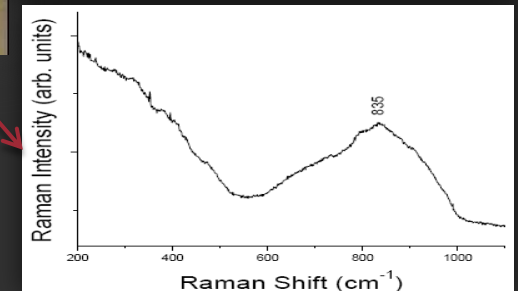
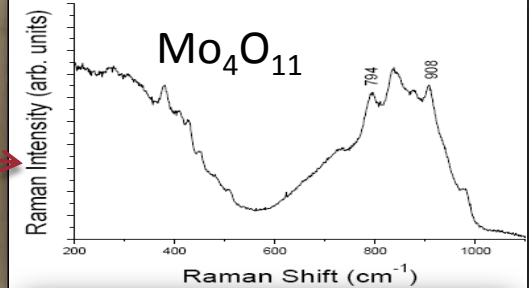
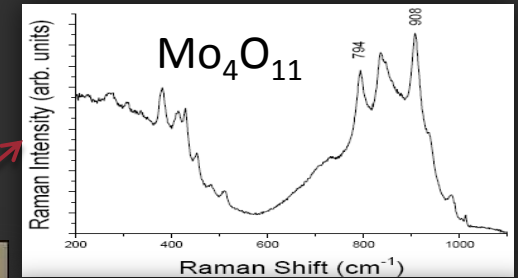
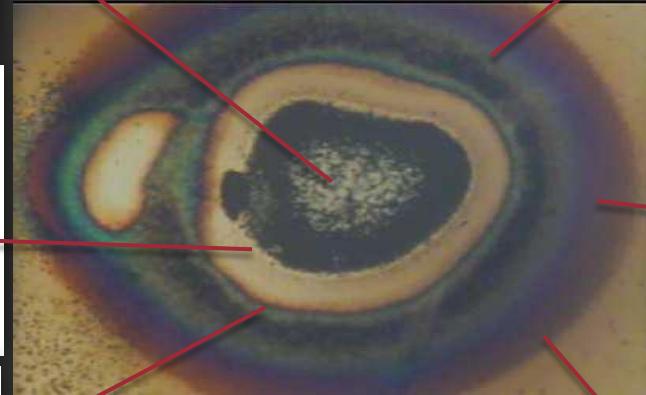
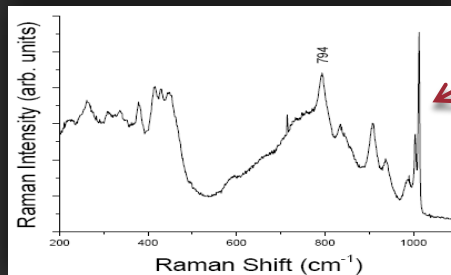
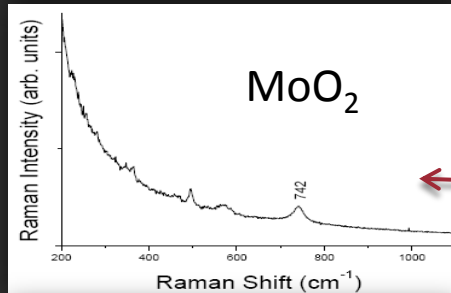
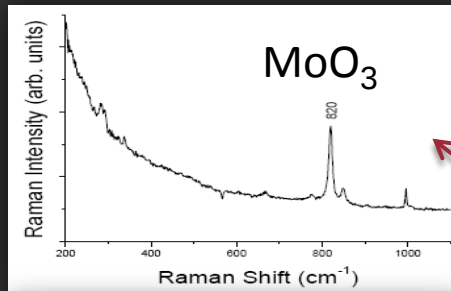


5. Determination (two-lead method) of the electrical properties of the fs laser-induced metallic oxides → could lead to a novel method to produce transparent electrodes

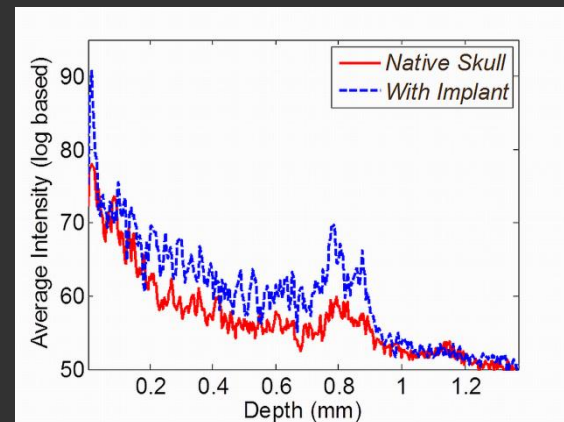
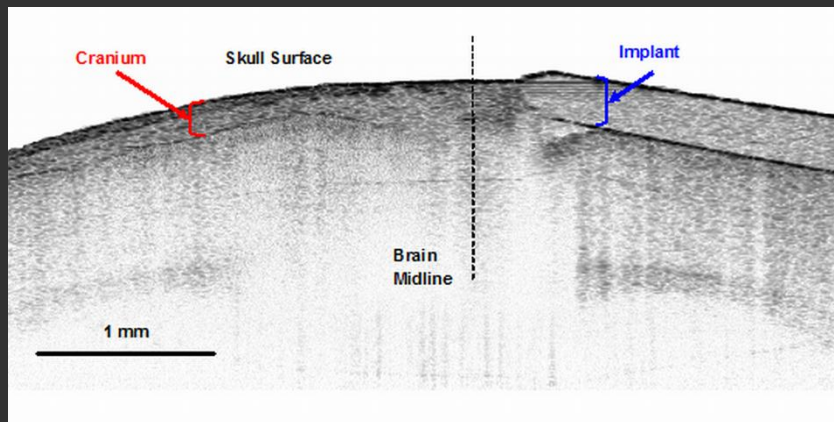
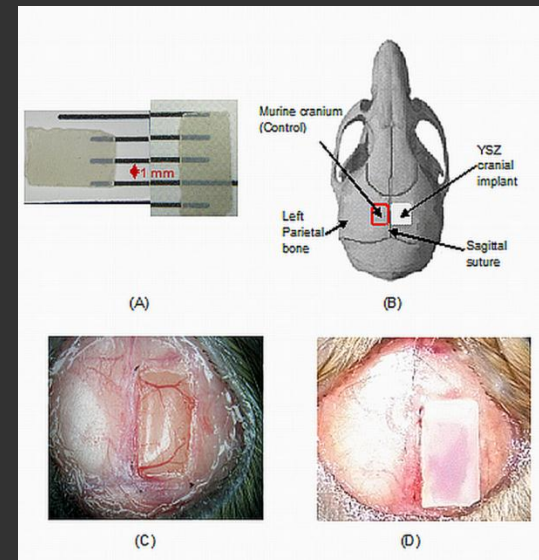
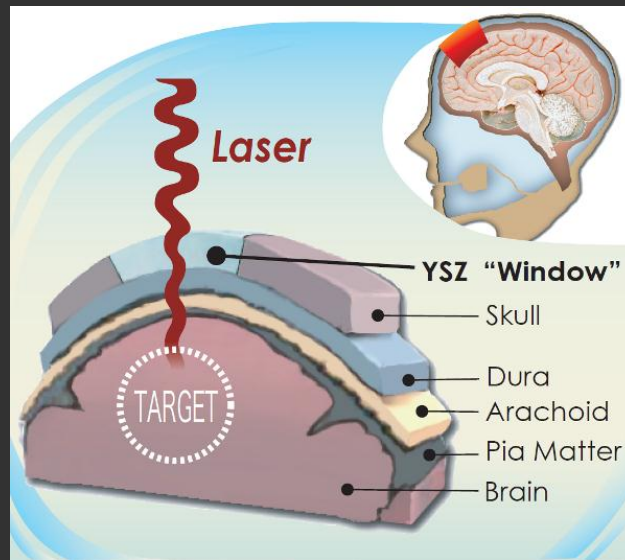


6. Determination (microRaman spectroscopy) of the formation of difficult to obtain metallic oxide phases → **novel synthesis method**

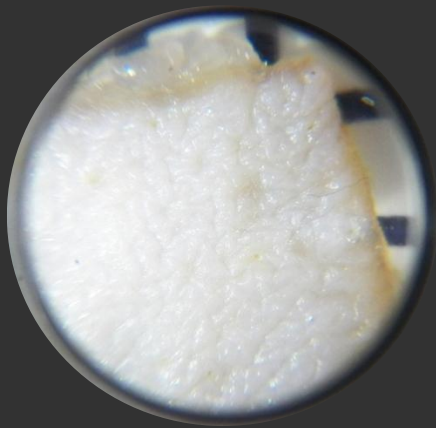
fluence per pulse of $\sim 3.5 \text{ mJ/cm}^2$ (well below the ablation threshold)
exposure time 20s



1. WINDOWS TO THE BRAIN: Proof of concept of the use of transparent YSZ as a cranial implants. Assessment based on optical coherent tomography (OCT) imaging of mouse brain → *in press Nanomedicine: Nanotechnology, Biology, and Medicine, 2013.*



2. Significant improvement of optical clearing of scalp via thermomechanical processes for localized and recurring access to the YSZ cranial implant → in progress



After 1 hour of
immersion in
37 °C glycerol



**nonreactive chemical
agents**

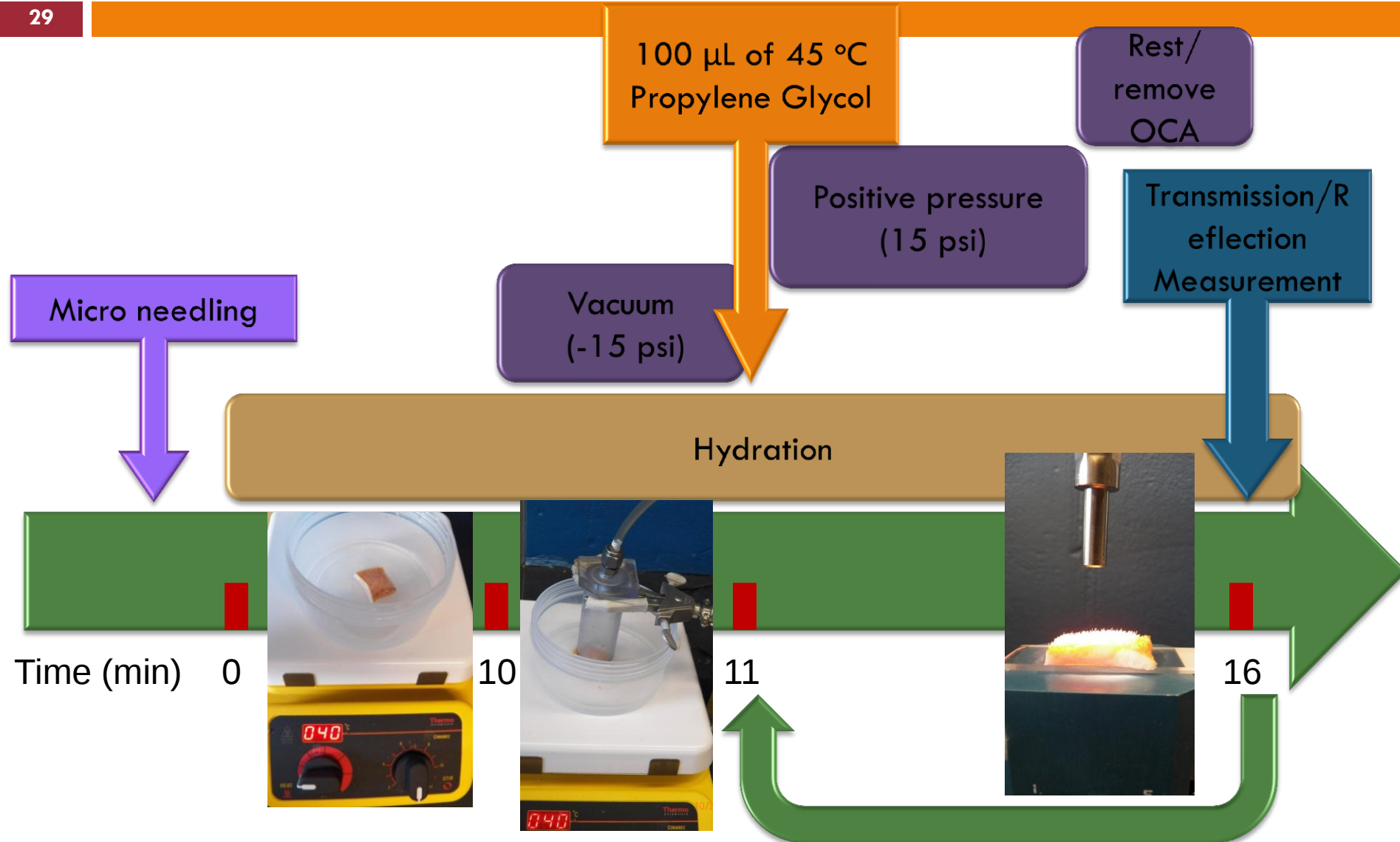
temporarily and reversibly
increase scalp
transparency



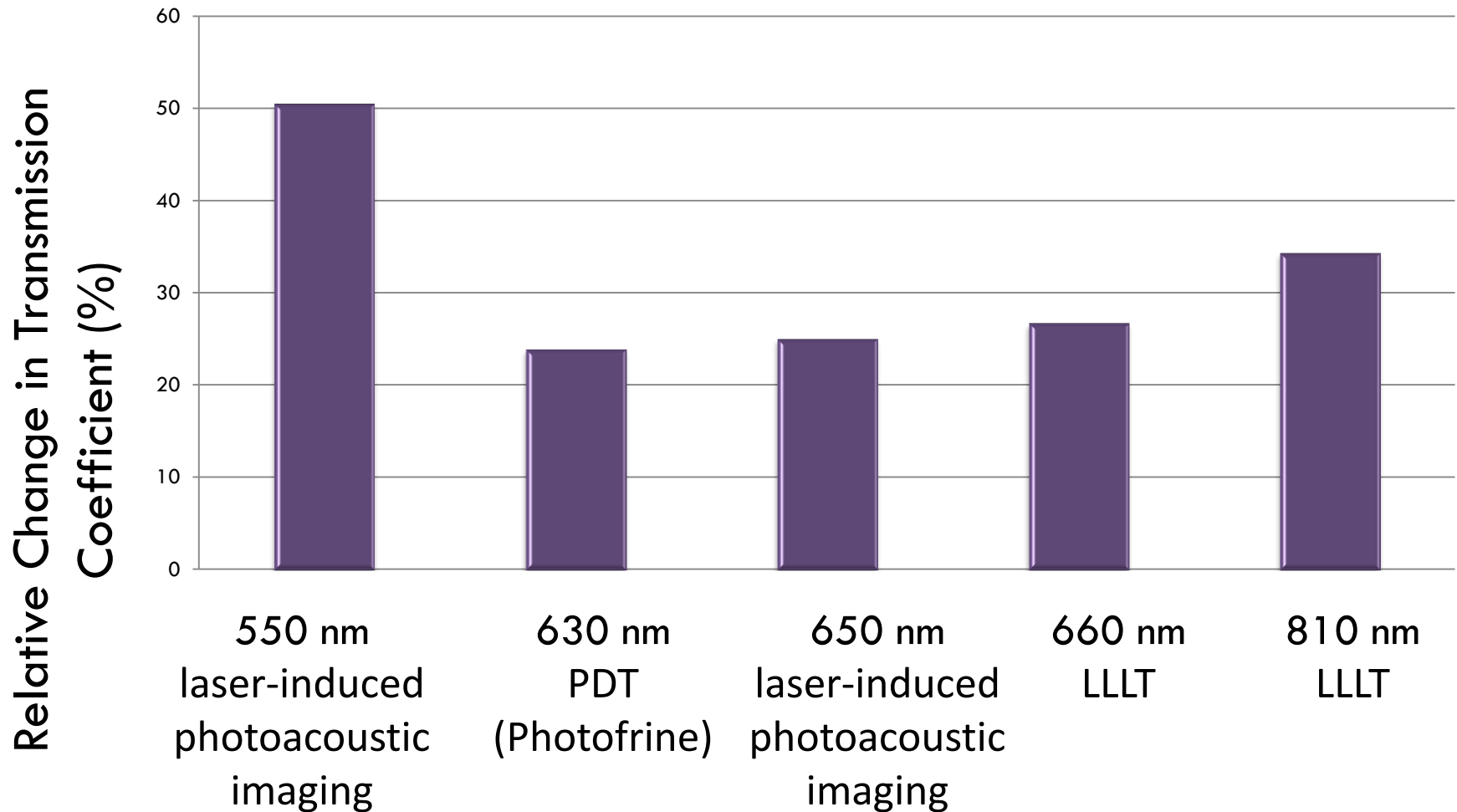
reduce the scalp optical
scattering

Drug Delivery of OCA

29



Analysis at Wavelength Applicable to Brain



3. Long term viability and biocompatibility studies of YSZ cranial windows implanted on mice skulls → ongoing in collaboration with UCSD

Significance

The prolonged inflammatory response to an implant is one of the primary causes for the failure to integrate into tissue

Assessment of inflammatory response

Leukocyte-endothelial cell interaction

Blood supply to an implant is important for reparative processes and host defense against infection.

The response of surrounding soft-tissue microcirculation to the biomaterial is of considerable significance.

Objective

Use the hamster back flap model to

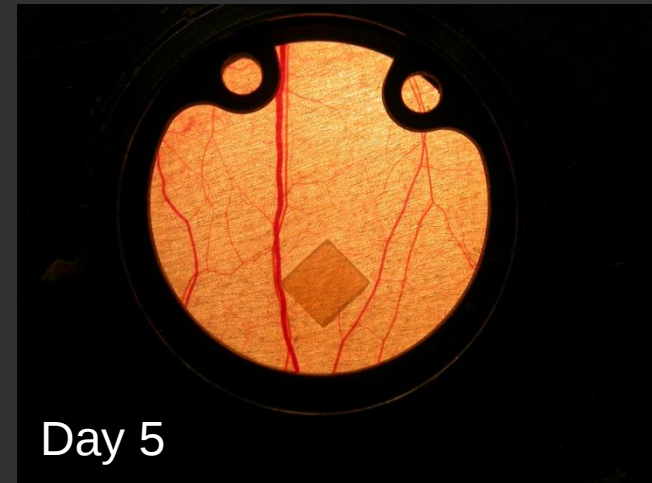
Quantitatively characterize the inflammatory reaction (or lack of) of the tissue at the microscopic level

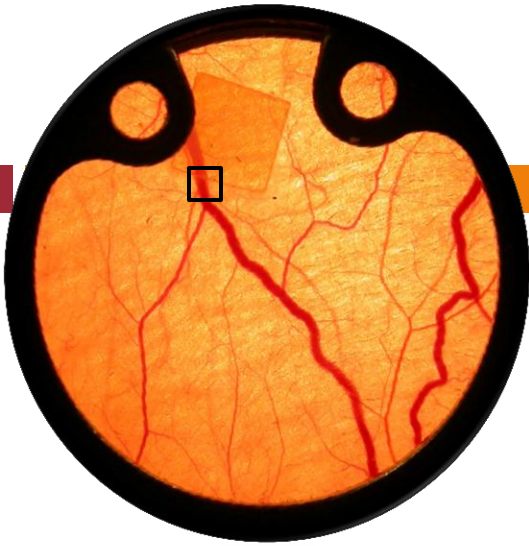
Animal Model

Male Golden Syrian hamsters of 50-70 g

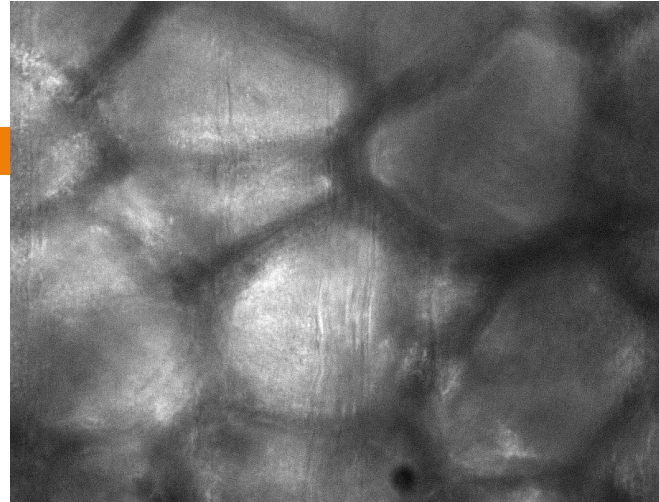
One side of the skinfold is removed until only a thin monolayer of retractor muscle and the intact subcutaneous skin of the opposing side remains.

3. Long term viability and biocompatibility studies of YSZ cranial windows implanted on mice skulls → ongoing in collaboration with UCSD

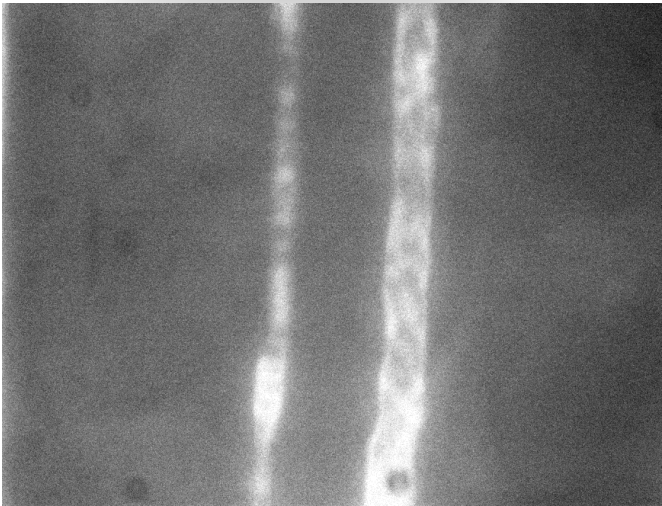




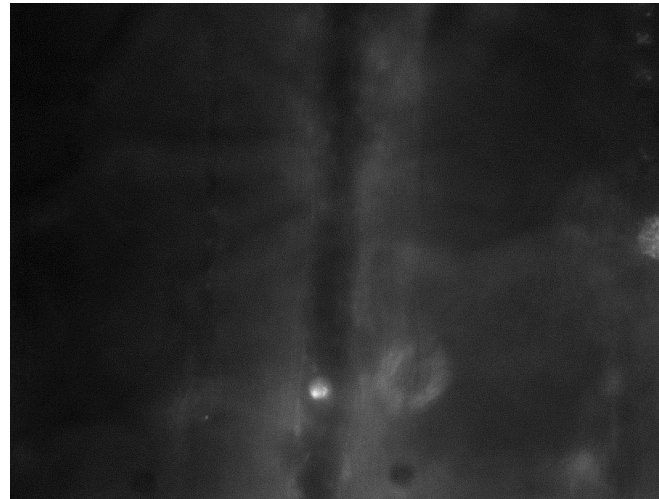
Macro image of chamber at Day 14



Light Microscopy at 20x



Macromolecules labeled with FITC
illuminated with blue light at 20x



Leukocytes labeled with Rhodamine-6G
illuminated with green light at 20x

Infrastructure

CIDEPRO Optical Tables

*Ultrashort Pulse Lasers and Materials Processing, CICESE
Advanced Materials Research , UAEMex*



Three optical tables of the following dimensions were acquired:

1. Two 4' x 6' optical tables were installed in CICESE
2. One 4' x 8' optical table was installed in UAEMex

Lambda Solutions Inc. (λ^s) microRaman System and Olympus Phase Contrast Microscope *Ultrashort Pulse Lasers and Materials Processing, CICESE*

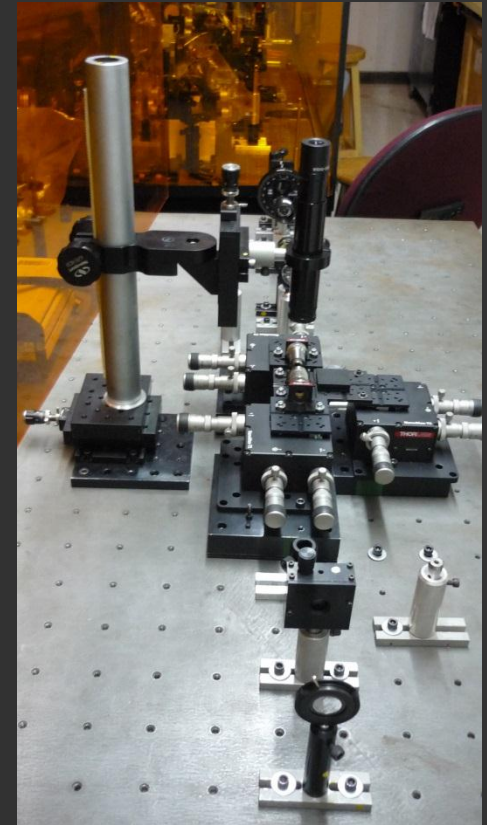
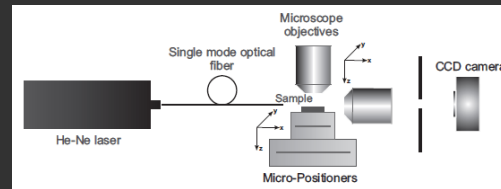
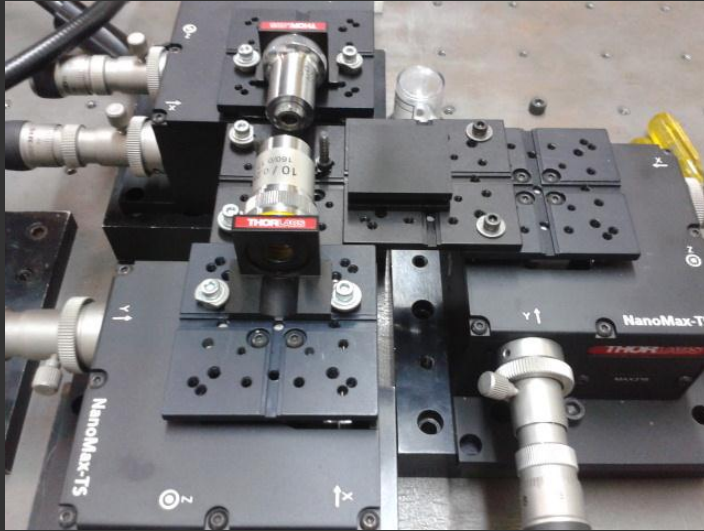


Basic microRaman system and phase contrast microscope components:

1. Raman spectrometer and Nd:YAG cw laser
2. Either multi or monomode optical fiber
3. Reflection and transmission optical microscope
4. Phase contrast microscope objectives

Waveguides Characterization Set Up

Ultrashort Pulse Lasers and Materials Processing, CICESE

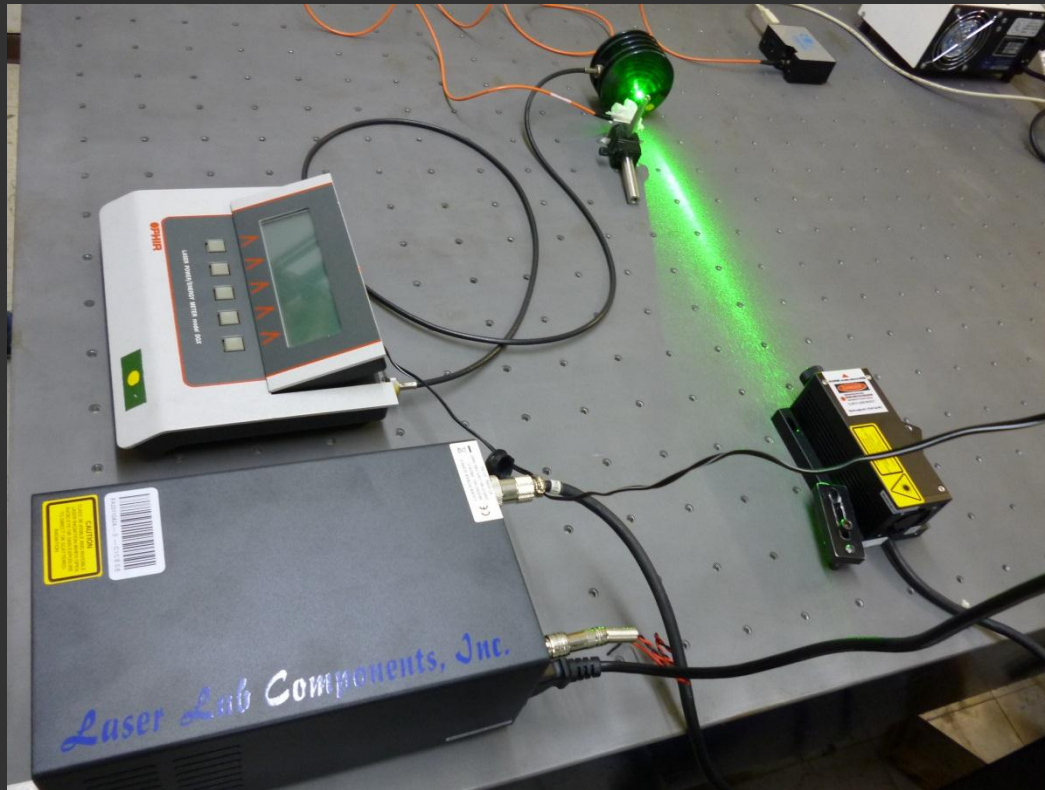


Basic waveguide characterization components:

1. Three (Thorlabs) nanopositioners
2. Input fiber and output microscope objectives, image relay optical system
3. Top view microscope and CCD camera
4. He-Ne laser; half-wave plate and polarizer

Laser Lab Components Inc. Nd:YAG Laser

Advanced Materials Research , UAEMex



A 500mW (cw) Nd:YAG laser was acquired for the purpose of:

1. Making a two line (632nm and 532nm) microRaman system

HORIBA Fluorometer (Fluorolog-3)

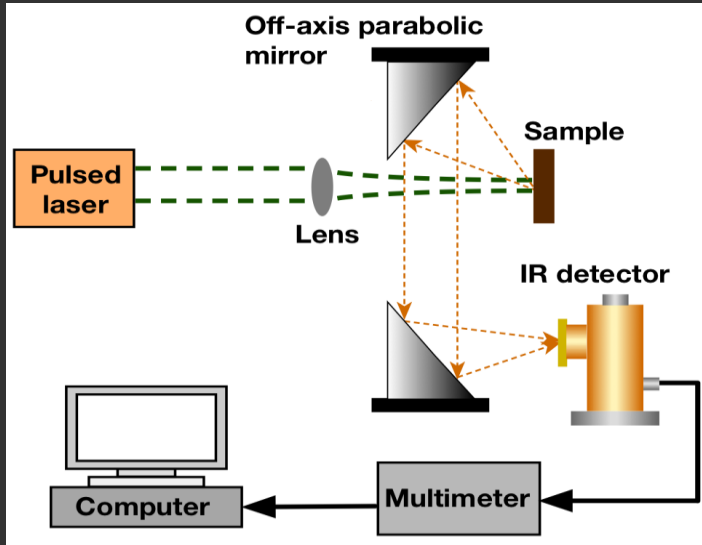
Optics Characterization Laboratory (OCL) UCR



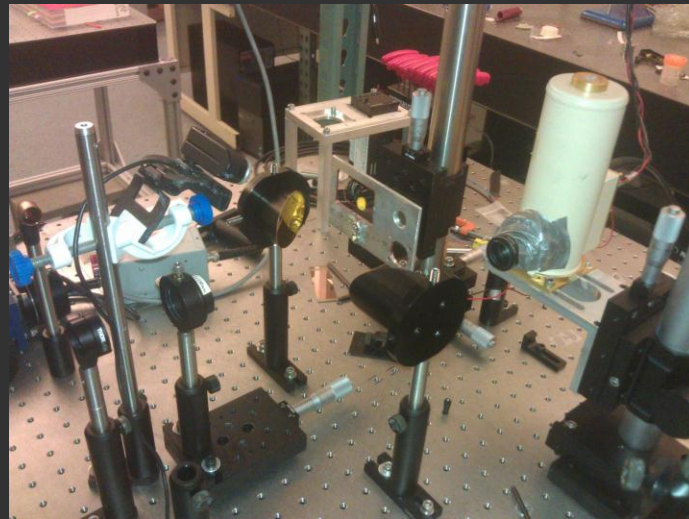
Basic spectrofluorometer components:

1. A 450 W xenon lamp
2. A single-grating excitation monochromator
3. A T-format sample compartment with excitation reference detector
4. A single-grating emission monochromator
5. An emission photomultiplier tube with photon-counting detection

Pulsed Photothermal Radiometry (PPTR) Modulated Photothermal Radiometry (MPTR) *Optics Characterization Laboratory (OCL) UCR*

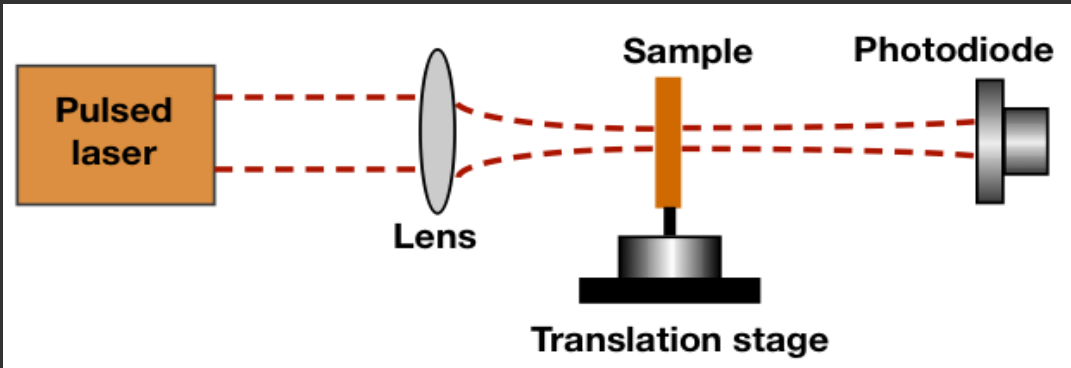


- ◆ Non-destructive and non-contact technique
- ◆ Allow to monitor absolute temperatures
- ◆ Allow to obtain thermal and optical properties



Femtosecond Laser and Z-scan

Optics Characterization Laboratory (OCL) UCR



Amplitude - Mikan

Pulse energy: $> 20\text{ nJ}$

Average power: $> 1\text{ W}$

Repetition rate: 54 MHz

Temporal pulse width: 250 fs

Laser wavelength: 1030 nm



Students and Postdocs

Directly Sponsored by Project

	Mexico (CICESE)	USA (UCR)
UG Students	L. Sanchez-Hernandez* A. Reyes-Contreras*	-
GRAD Students	G. Castillo-Vega* R. Rodriguez-Beltran* M. Cano-Lara*	50% Y. Damestani 50% E. Penilla 8.3% C. Hardin
Postdocs	I. Perez	0
Principal Investigators	Travel and conferences S. Camacho-Lopez	4% (out of 25%) G. Aguilar 4% (out of 25%) J.E. Garay
Collaborators	M. A. Camacho-Lopez	0

* Supplementary to CONACyT postgrad program

NOT Sponsored by Project

	Mexico (CICESE)	USA (UCR)
UG Students	None	4 - D. Tat; B. Melakeberhan; J. Fuerte-Gaspar; R. Ayala
GRAD Students	Y. Esqueda-Barron	1- MSc – J. Redenius* 2- PhD – K. Mensink; A. Dupuy
Postdocs	None	2 – Dr. P. Martinez Dr. D. Garcia
Principal Investigators	None	0
Collaborators	A. Esparza-Garcia	3 – M. Rao; H. Park; D. Binder (UCR) 1 – P. Cabrales (UCSD)

* Funding required to support him as PhD student

Journal Publications

1. M. Cano Lara, S. Camacho-Lopez, A. Esparza Garcia, M. A. Camacho-Lopez, "Laser-induced molybdenum oxide formation by low energy (nJ)- high repetition rate (MHz) femtosecond pulses" *Optical Materials*, 33, 1648-1653 (2011).
2. G.R. Castillo-Vega, E.H. Penilla, S. Camacho-López, G. Aguilar and J.E. Garay, "Waveguide-like structures written in transparent polycrystalline ceramics with an ultra-low fluence femtosecond laser", *Optical Materials Express*, 2 (10), pp. 1416-1424, 2012.
3. #Y. Damestani, C.L. Reynolds, J. Szu, M.S. Hsu, Y. Kodera, D.K. Binder, B.H. Park, J.E. Garay, M.P. Rao, and G.Aguilar, "Transparent nanocrystalline yttria-stabilized-zirconia calvarium prosthesis", *in press*, *Nanomedicine: Nanotechnology, Biology, and Medicine*, (2013).
4. I. Perez, M. Cano-Lara, S. Camacho-Lopez, A. Reynoso, C. Maya, M. A. Camacho-Lopez, "Fluence dependence of the electrical resistance in molybdenum oxides formed by femtosecond laser pulses" in progress.
5. Elías Penilla, P. Martinez, G. Aguilar and J.E. Garay, "Point defects of non-linear optical properties of transparent zirconia", in progress.
6. P. Martinez, E. Penilla, Santiago Camacho-Lopez, Javier E. Garay, G. Aguilar, "Mechanisms of waveguide writing in transparent zirconia" in progress.

no support from AFOSR/CONACyT

7. #G. Cook, J.E. Garay, C. Liebig and D. R. Evans, “Electrical and Optical Observations of the Coercive Poling Characteristics of Fe:KNbO₃ Single Crystals Under Different Background Gases” in progress.
8. Y. Damestani, D. Ortiz, D. Gallan-Hoffman, Y. Kodera, P. Cabrales, J. Garay, G. Aguilar, “Transparent yttria-stabilized-zirconia: In vivo analysis of biocompatibility and vascularization”, to be submitted to Journal: Biomaterials, <http://www.journals.elsevier.com/biomaterials/>
9. Y. Damestani, B. Melakeberhan, M. Rao, G. Aguilar, “Systematic study of non-invasive techniques to enhance drug delivery of optical clearing agents”, to be submitted to Lasers in Surgery and Medicine (Due Oct 2013).
10. Y. Damestani, J. Redenius, R. Ayala, J. Garay, G. Aguilar, “Determination of laser fluence rate and temperature distribution in brain with yttria stabilized zirconia cranial implant”, to be submitted to Journal of biomedical optics and SPIE conference (Due Jan 2014).
11. S. Camacho-Lopez, M. A. Camacho-Lopez, M. Cano-Lara, “laser-induced formation of α -MoO₃ using fs pulses” in progress.

no support from AFOSR/CONACyT

12. S. Camacho-Lopez, M. A. Camacho-Lopez, M. Cano-Lara, "Raman and SEM study of fs laser-induced molybdenum oxides" in progress.
13. Y. Esqueda-Barron, S. Camacho-Lopez, M. A. Camacho-Lopez, R. Rodriguez-Beltran, "Study of the formation of ZnO flower nanostructures by fs laser irradiation of Zn thin films" in progress.
14. M. A. Camacho-Lopez, S. Camacho-Lopez, A. Reyes-Contreras, "LIPSS formation in bismuth thin films by ns laser irradiation" in progress.

Thesis, dissertations, invention disclosures and patents

	Mexico (CICESE)	USA (UCR)
BS Theses	• Lidia Sanchez-Hernandez (BSc., UAEMex), “Espectroscopia microRaman aplicada al estudio de transformacion de materiales.” (2011) • Adela Reyes Contreras (BSc., UAEMex), “title; to be decided” in progress	• David Tat (BSc., Honors student UCR), “Investigation of the optical properties of Molybdenum and possible thin film applications”, in progress
MSc Theses	• Gabriel Roberto Castillo -Vega (MSc., CICESE), “Procesamiento de cerámicas con láseres pulsados” (2011) • Yasmin Esqueda Barron (MSc., CICESE), “ZnO inducido por irradiacion laser de pulsos ultracortos” (2013)	• Jon Redenius (MSc, UCR), “Characterizing Oxide Formation in Transition Metals due to Ultrashort Pulsed Laser Heating” in progress
PhD Dissertations	• Miroslava Cano-Lara (PhD., CICESE), “Óxidos de molibdeno inducidos por irradiacion laser de pulsos ultracortos” in progress • Yasmin Esqueda-Barron (PhD., CICESE), “Title to be decided” in progress	• Yasaman Damestani (PhD, UCR), “Transparent yttria stabilized zirconia cranial implant for optical therapy and imaging of brain” in progress • Kendrick Mensink (PhD, UCR), “Waveguide writing with ultralow energy and ultrashort laser pulses on YSZ polycrystalline ceramics” • Elias Penilla (PhD, UCR), “Non-Equilibrium Processing and Development of Novel Transparent Transition Metal and Rare-Earth Doped Ceramics for Photoluminescent and High-Powered Solid-State Laser Applications” in progress

1. S. Camacho-Lopez, M. A. Camacho-Lopez, “Process for obtaining metal oxides by low energy pulsed laser irradiation of metal films” US patent application (Pub No.: US2013/0171373 A1)* Also filed in Mexico (application number pending)
2. G. Aguilar, J.E. Garay, S. Camacho-Lopez, “Cranial implants for laser imaging and therapy”, USPO provisional patent application, April 23, 2013, Application# 61/815,070 .
3. S. Camacho-Lopez, G. Aguilar, J. E. Garay, “Waveguide-writing of YSZ transparent ceramics with femtosecond laser irradiation”

* There is already a US company interested in acquiring the technology.

Leveraging resources

Proposals Submitted...so far

Proposal name	Agency	Period	Amount	Status
1) "3-D laser-induced patterning of transparent ceramics"	UCMEXUS-CONACyT	07/01/10-12/31/11	\$25,000	Awarded
2) "Opto-ceramic cranial implants for brain laser imaging and therapy"	UCR	2011-2012	\$110,000	Awarded
3) "Waveguide writing with ultralow power fs-laser radiation of polycrystalline zirconia towards development of novel cranial implants "	ASLMS	2012-2013	\$70K	Not Awarded
4) " Windows to the Brain : Novel concept for providing non-invasive, chronic access to neural tissues for laser-based Mild Traumatic Brain Injury (mTBI) diagnostics & therapeutics"	DoD (DMRDP)	2012-2016	\$3.2 M	Not Awarded
5) "Windows to the Brain: Transparent Zirconia Cranial Implants for Laser and Optogenetics Therapy"	NSF	2013-2016	\$582K	Pending
6) "Transparent Cranial Implant for Laser Based Therapy and Imaging of Brain"	ASLMS	2013	\$5K	Awarded

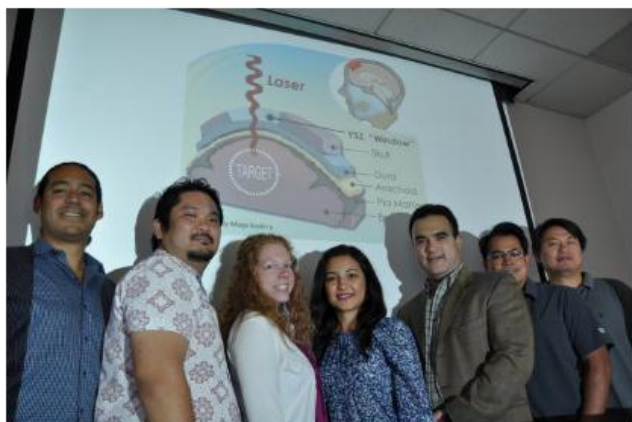


Transparent Polycrystalline Zirconia for Cranial Implants



Creating a 'Window to the Brain' University of California, Riverside researchers develop novel transparent skull implant that could provide new treatment options for disorders such as brain cancer and traumatic brain injury

By Sean Nealon On SEPTEMBER 3, 2013



Members of the research team, from left, Javier Garay, Yasuhiro Kodaera, Carissa L. Reynolds, Yasaman Damestani, Guillermo Aguilar, Masaru P. Rao and B. Hyle Park.



Transparent nanocrystalline yttria-stabilized-zirconia calvarium prosthesis

Yasaman Damestani, BS^a, Carissa L. Reynolds, BS^a, Jenny Szu, BS^b, Mike S. Hsu, MS^b,
Yasuhiro Kodaera, PhD^c, Devin K. Binder, MD, PhD^{a,b}, B. Hyle Park, PhD^a,
Javier E. Garay, PhD^{c,d}, Masaru P. Rao, PhD^{a,c,d}, Guillermo Aguilar, PhD^{a,c,*}

^aDepartment of Bioengineering, University of California, Riverside, California, USA

^bDivision of Biomedical Sciences, University of California, Riverside, California, USA

^cDepartment of Mechanical Engineering, University of California, Riverside, California, USA

^dMaterials Science and Engineering Program, University of California, Riverside, California, USA

Received 8 March 2013; accepted 12 August 2013

Abstract

Laser-based diagnostics and therapeutics show promise for many neurological disorders. However, the poor transparency of cranial bone (calvaria) limits the spatial resolution and interaction depth that can be achieved, thus constraining opportunity in this regard. Herein, we report preliminary results from efforts seeking to address this limitation through use of novel transparent cranial implants made from nanocrystalline yttria-stabilized zirconia (nc-YSZ). Using optical coherence tomography (OCT) imaging of underlying brain in an acute murine model, we show that signal strength is improved when imaging through nc-YSZ implants relative to native cranium. As such, this provides initial evidence supporting the feasibility of nc-YSZ as a transparent cranial implant material. Furthermore, it represents a crucial first step towards realization of an innovative new concept we are developing, which seeks to eventually provide a clinically-viable means for optically accessing the brain, on-demand, over large areas, and on a chronically-recurring basis, without need for repeated craniectomies. © 2013 Published by Elsevier Inc.

Key words: Optical neuroimaging; Calvarium prosthesis

Background

Laser-based techniques have shown promise for enhancing the diagnosis and treatment of many neurological disorders, including cerebral edema, stroke, and cancer, among others.^{1–3} However, the poor transparency of cranial bone to clinically-relevant laser wavelengths (i.e. $\lambda = 550$ – 1300 nm) typically necessitates use of invasive craniectomies to provide optical access to the brain. This constrains the ultimate utility of such techniques, particularly for applications where chronically-recurring access over large areas is required.

Recent studies have demonstrated potential for increasing cranial transparency through thinning.^{4,5} However, since this

diminishes protection for the brain, associated safety concerns may preclude opportunity for translation of such techniques to the clinic. Other studies have reported use of transparent glass-based implants, either in place of cranium,⁶ or as an overlay to increase the rigidity of thinned-skull preparations.⁷ However, the extremely low fracture toughness of typical glasses ($K_{IC} = 0.7$ – 0.9 MPa $\cdot$ m^{1/2}) increases potential for catastrophic failure by fracture, which will limit opportunity for use of such implants beyond the laboratory. This, therefore, motivates the search for alternate materials that will provide better potential for eventual clinical use.

While a number of synthetic materials have been evaluated for use in calvarial reconstruction, including titanium, alumina, and acrylic,⁸ none provide the requisite combination of transparency and toughness required for clinically-viable transparent cranial implants. Yttria-stabilized zirconia (YSZ) represents an attractive alternative, due to its relatively high toughness ($K_{IC} \sim 8$ MPa $\cdot$ m^{1/2}), as well as its proven biocompatibility in dental and orthopedic applications. However, YSZ is typically opaque, thus precluding its consideration thus far.

Research Support: This research was supported, in part, by the University of California, Riverside Chancellor's Strategic Research Initiative (PI: G. Aguilar).

*Corresponding author: University of California, Riverside, CA, USA.

E-mail address: gaguilar@engr.ucr.edu (G. Aguilar).

1549-9634/\$ – see front matter © 2013 Published by Elsevier Inc.
<http://dx.doi.org/10.1016/j.nano.2013.08.002>

Please cite this article as: Damestani Y., et al., Transparent nanocrystalline yttria-stabilized-zirconia calvarium prosthesis. *Nanomedicine: NBM* 2013;xx:1–4, <http://dx.doi.org/10.1016/j.nano.2013.08.002>



In the Spotlight:

- Mashable.com: 1.5min video piece
 - o <http://mashable.com/2013/09/08/brain-window-implant/>
- Which Way, LA? Show, KCRW (Los Angeles): 6min audio interview
 - o <https://soundcloud.com/kcrw/a-window-to-the-brain>
- KPBS (San Diego): Web article with 1min audio interview
 - o <http://www.kpbs.org/news/2013/sep/03/would-you-want-window-implanted-your-skull/>

In the Headlines:

- Press-Enterprise: Front page story on 9/5 (print and web)
 - o <http://www.pe.com/local-news/riverside-county/riverside/riverside-headlines-index/20130904-ucr-researchers-develop-window-to-the-brain.ece>
 - o There's also a 2min You Tube video embedded in the article
- LA Times story (web):
 - o <http://www.latimes.com/science/sciencenow/la-sci-sn-window-brain-20130903,0,6788242.story>
- BBC News (web)
 - o <http://www.bbc.co.uk/news/health-23929991>
- msnNOW (web)
 - o <http://now.msn.com/window-into-the-brain-is-now-a-reality>
- de Volkskrant (Netherlands, web)
 - o <http://www.volkskrant.nl/>
 - o article only accessible by subscription
- El Mundo (Spain, web)
 - o <http://www.elmundo.es/elmundo/2013/09/03/nanotecnologia/1378225996.html>

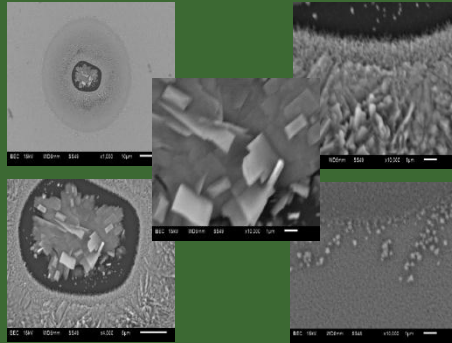
- PopularScience:
 - <http://www.popsci.com/science/article/2013-09/clear-cranial-implant-lets-doctors-see-brain>
- Smithsonian:
 - <http://blogs.smithsonianmag.com/smartnews/2013/09/a-tiny-transparent-skull-implant-could-simplify-brain-surgery/>
- ExtremeTech:
 - http://www.extremetech.com/extreme/165571-transparent-skull-implant-for-easier-cheaper-laser-based-brain-scanning#disqus_thread
- The Verge:
 - <http://www.theverge.com/2013/9/4/4694198/scientists-develop-a-literal-window-into-the-brain#comments>
- Science Daily:
 - <http://www.sciencedaily.com/releases/2013/09/130903091436.htm>
- Kurzweil:
 - <http://www.kurzweilai.net/transparent-window-to-the-brain-allows-for-laser-treatments-without-repeated-surgery>

- ❑ Biomedical implants
- ❑ Optomaterials for sensing and communications
- ❑ Metallic oxides semiconductors
- ❑ Transparent electrodes
- ❑ Plasmonic devices (sensors, light emitters)
- ❑ Chromic sensors (photochromic, gasochromic, thermochromic, etc.)
- ❑ Waveguide by laser-induced metallic implantation
- ❑ Hard tissue implants with optomechanical capabilities

Future work

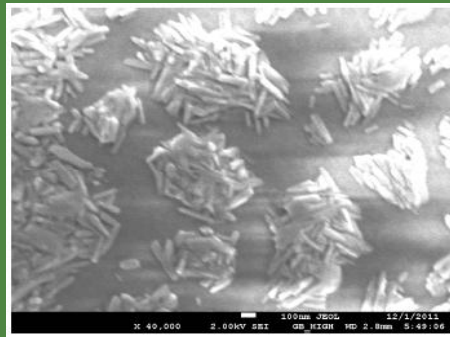
Metallic Oxides

electronic vs
thermal



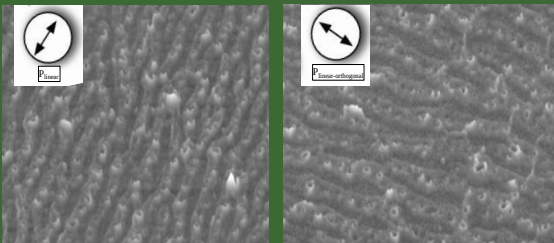
There are two processes occurring during the laser exposure: an electronic related one which must be very fast and a thermal one which is quite slow. We want to investigate the contribution of those two mechanisms to the already demonstrated novel synthesis of metallic oxides by ultrafast laser irradiation.

optical and
electric
properties



Since the ultrafast laser synthesis of metallic oxides allows obtaining nanosized crystals, it is quite relevant and very important to determine their optical and electric properties. This in view of both basic knowledge and potential applications.

plasmonic
features



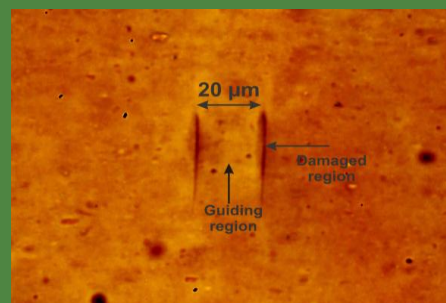
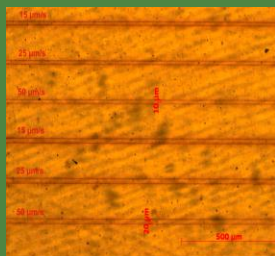
Gold and silver are getting to plateau in the field of plasmonics; therefore new materials are seek in this field. Metallic oxides are very appealing for that purpose.

active media



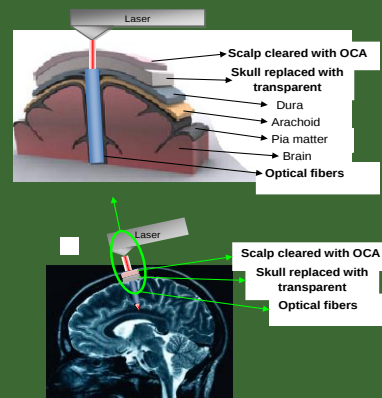
YSZ and other polycrystalline ceramics produced by our group have been shown to have strong photoluminescence emission. So that, we want to investigate this materials as active media for laser emission

multi-waveguide / multi-color lasers



Within our group we have demonstrated direct fs laser writing of the so called channel waveguides in the polycrystalline ceramics; based on this type of waveguides more complex (photonic crystal-like) structures can be written.

cranial windows



The cranial windows would allow not just to take advantage of the biocompatibility of the ceramic, but to deliver light treatments on demand by conveniently writing waveguides in the window.

Support needed/suggested for
taking our current productive
research to the next level

	MEXICO		USA	
	Quantity	Cost	Quantity	Cost
Major equipment	Diverse	\$50K	Diverse	\$50K
Materials and supplies	Diverse	\$20K	Diverse	\$20K
Postdoctoral support	2	\$40K	2	\$120K
Graduate Student support	5	-	5	\$200K
PI salary support	-	-	2	\$50K
Semester project workshop updated	3	\$5K	3	\$5k
Conference/travel expenses	2	\$6K	2	\$6k
Publishing / patent costs	2	\$20K	2	\$20K

Concluding Remarks

- ❑ Success of this collaboration has been possible due to:
 - ❑ Several, mature, productive and independent groups working together
 - ❑ Geographic proximity (UCR-CICESE)
 - ❑ Student and resource exchange
- ❑ Complementary backgrounds and research interests to explore new scientific and technological problems
 - ❑ Materials (JEG)
 - ❑ Optics (SCL)
 - ❑ Mechanical (GAM)
- ❑ Establishment of new collaborations (e.g., U. de Salamanca (CLPU), Biomedical Sciences and Bioengineering, UCR, King's College in the UK)

- Dr. Jim Fillerup, SOARD
- Dr. Charles Lee, AFOSR
- Dr. Jose Antonio de la Peña/ Dra. Leticia Torres/ Dra. Julia Tagueña, CONACyT
- Dr. Jesus Gonzalez, CIMAV
- Dr. Dean Evans, AFRL

THANKS!

¡GRACIAS!