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**Fundamental Studies of Heavy Metal Oxide Glasses for High Power Lasers: Microstructural Aspects of Er Clustering and Absorption Profile Variations Related to Photodarkening**

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Final Report

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## Final Performance Report

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**Principal Investigator:** Dr Kristina Lipinska, University of New Mexico, CHTM, Albuquerque, NM 87106, USA

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### I. Project Overview

High-power, rare-earths (REs) doped fiber lasers with a glass-based functional core are used in numerous commercial applications, such as telecommunications, as well as in those relevant to DoD missions. They require intense light for directed energy applications and for propagation over long distances within atmospheric transmission windows [1]. When considering REs-doped glasses for high-power laser applications, the phenomenon of photodarkening remains the key issue in limiting a fiber's optical performance. Photodarkening is an irradiation-induced gradual increase of a glass fiber's absorption, which reduces its light transmission capability and decreases the fiber's power output over time. It is a critical factor in limiting fiber laser operation, degrading device performance and shortening its lifetime. There are contradictory opinions about the mechanism of photodarkening and there is no clear explanation for its microscopic origin. Several explanations have been given so far that are either inspired by experimental observations or aimed at rationalizing experimental findings [2-10].

While the exact photodarkening mechanisms still remain open, it is recognized that this phenomenon may be correlated to the presence of different types of oxygen-deficiency centers (ODCs) and/or the formation of color centers (a trapped charge, i.e. an electron or a hole, which is trapped by defects within the glass matrix). However, no study has definitely identified those color centers or explained the route leading to photodarkening. One hypothesis could be that rare-earth (for example  $\text{Er}^{3+}$ ) clustering causes photodarkening in a multi-step, multi-photon absorption process, where several excited cluster ions co-operate to supply energy for capturing electrons and holes at different structural defects. The complexity of the situation is reflected by the fact that despite numerous studies, we are still unable to pinpoint what is happening in a glass fiber exposed to high power laser [8, 10-15]. It is the lack of knowledge on the relationship between photodarkening on one side, and the microstructural and chemical modifications in the glass networks on the other side, that constitutes a missing link and prevents us from understanding of the detailed structural pathways for the complex optical response leading to photodarkening.

One should note that the most effective strategy for moving towards a solution to the issues of REs clustering and glass fibers photodarkening effect cannot be unidirectional, but requires related research issues to be addressed in concert: (1) the control of local order or microstructure of host glass network, (2) the control of level of rare-earths doping and (3) the control of local structural environment of functional atoms in a glass architecture.

In this project, and in relation to photodarkening, we address the missing links connecting: on one side glass chemistry and glass network microstructure, including local structural environment around selected atoms, and on the other side rare-earths clustering effects and optical transmission losses. This is achieved by leveraging a multi-technique experimental approach.

The novelty of our project is in approaching the problem from the materials science point of view. The strategy implemented by us includes synthesis of sets of custom designed, non-esoteric model glass materials, acquisition of information about their microstructure, optical properties and study of formation of microstructural and optically-active defects. Those defects generate alterations in the architecture of glass networks and modify the glass light transmission efficiency. Specifically, we explore in detail laser irradiation-driven structural changes in our model glass systems with and without rare-earths dopants. We focus on microstructural modifications of the glass networks resulting from variable rare-earths ( $\text{Er}^{3+}$ ) concentration and from variable laser exposure conditions. The exposure of glasses to laser irradiation drives photoinduced bond-breaking and material densification, leading to an increase of the refractive index as well as to the formation of optically-active defect centers that are closely related to photodarkening phenomena.

The strategy of this project was: (i) to fabricate good optical quality model glasses, doped with heavy metal oxides, with different type of network formers, susceptible to accommodate variable levels of a luminescent dopant -  $\text{Er}^{3+}$ ; (ii) to identify the microstructure of glass networks: main building blocks, connectivity; (iii) to evaluate the correlation between variable glass chemistry and glass network structure on the one hand and the formation of defect centers and the decrease in the materials' light transmission properties; (iv) to develop an understanding of the underlying photo-chemical mechanisms of the observed light transmission losses.

The overarching motivation for this project was to extend the current understanding of the complex relationships between microstructure and chemistry of a glass network, the connectivity of glass building blocks and its macroscopic optical performance. In the long term, our findings will improve the understanding of microstructural defects and of optically-active defects in glass networks and show a pathway to mitigate photodarkening. This knowledge will lay some solid stepping stones and will push the envelope in getting us closer towards a practical solution for the problem of rare-earths concentration-related and defect-related performance limits in glasses for optical fibers.

## II. Fabrication of Materials

### Glass compositions

The glass materials synthesized for this project belong to “model” glass systems, containing heavy metal oxides and varying types of glass network formers, in addition to different levels of rare-earth doping. The choice of heavy metal oxide glasses, as opposed to conventional silicate glasses, was motivated by their better solubility for rare-earth ions, lower phonon energy, good IR transmission and higher refractive index. The glass systems selected for this project also embody the essence of good glass network formers (silica and germania) and compatible dopants (potassium, gallium), have good thermal stability and mechanical stability, and present different microstructures. And yet they are simple enough for us to search for the basic mechanisms ruling optical properties.

main network formers	secondary network former	network modifier	network modifier
<b>SiO<sub>2</sub> series</b> <b>GeO<sub>2</sub> series</b> <b>SiO<sub>2</sub>-GeO<sub>2</sub> series</b>	<b>Ga<sub>2</sub>O<sub>3</sub></b>	<b>K<sub>2</sub>O</b>	<b>Er<sub>2</sub>O<sub>3</sub>: 0 - 3mol%</b>
<ul style="list-style-type: none"> <li>• excellent glass network formers</li> <li>• good optical transparency UV – NIR</li> <li>• thermal and chemical stability</li> </ul>	<ul style="list-style-type: none"> <li>• heavy metal dopant</li> <li>• decreases lattice vibrational energy</li> <li>• expected to decrease probability of non-radiative transitions</li> </ul>	<ul style="list-style-type: none"> <li>• lowers melting point</li> <li>• allows Ga to enter in tetrahedral coordination, i.e. act as network former</li> </ul>	<ul style="list-style-type: none"> <li>• Er<sup>3+</sup>, rare-earth luminescent dopant</li> <li>• widespread use in telecom/fiber industry</li> </ul>

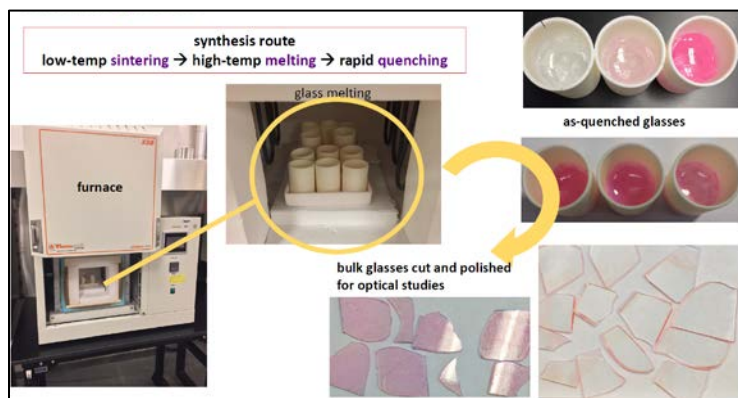
**Table 1.** Glass materials fabricated for this project: several isostructural glass systems; 14 glass compositions with and without luminescent rare-earth dopant.

The glasses were composed of isostructural, but chemically different, strong glass formers, and their microstructure was varied by adjusting the relative ratios of individual components (Table 1). The first system was comprised of silica-based glasses, the second system was comprised of germania-based glasses while the third system was comprised of mixed silica-germanate glasses. All glasses were doped with heavy-metal gallium and co-doped with a variable concentration of the luminescent dopant i.e. Er<sup>3+</sup>. The strategy was to lower the phonon energy with respect to pure SiO<sub>2</sub> glass in order to enhance erbium radiative transitions, while maintaining a non-esoteric chemistry that is compatible with silica-based optoelectronic devices (Table 1 and [16-17]).

### Glass synthesis

For glass synthesis, a mixture of initial batch components will be prepared using analytical grade reagents (99.999% purity) to avoid any spurious effects of unwanted luminescent or other contaminants, found in lower purity reagents. The batch components were thoroughly ground, mixed, sintered, re-ground and re-sintered at low temperature and afterwards melted in alumina crucible at high temperature in research grade, programmable furnace in an air atmosphere. The liquid melts were rapidly cooled to obtain glasses. The fabricated glasses were annealed at low temperature, below glass transition points, to remove internal

stresses. For optical measurements bulk glass samples were cut into platelets and optically polished (Figure 1).



**Fig. 1.** The synthesis route of glass materials: low-temperature sintering of batch components, high-temperature melting, rapid-quenching.

### III. Experimental Techniques

#### *Glass materials characterization*

The target areas for characterization of the glass materials were: microstructure of glass network, connectivity of glass building blocks, light emission properties in function of luminescent dopant concentration, local structural environment around functional components i.e. atoms, their spatial distribution and optical properties.

What?	How?	Details
<b>Before irradiation</b> microstructure and Er <sup>3+</sup> emission properties	micro-Raman spectroscopy & luminescence spectroscopy	basic structural units, network connectivity, ring structures emission: Er <sup>3+</sup>
<b>Before irradiation</b> local order in glass, coordination of Er <sup>3+</sup> and Ga <sup>3+</sup>	XAFS - synchrotron x-ray absorption fine structure spectroscopy	identification of Er and Ga, first, second neighbors, coordination
<b>After irradiation</b> changes in microstructure of glass network	fs-laser irradiation & micro-Raman spectroscopy	ring structures, glass densification
<b>After irradiation</b> changes in emission properties-controlled creation of defects	fs-laser irradiation & luminescence spectroscopy	emission: Er <sup>3+</sup> and laser-generated defects (NBOHC)
<b>During irradiation</b> <i>In situ</i> transmission loss, kinetics of defects formation	fs-laser irradiation & <i>in-situ</i> transmission loss during laser irradiation	transmission losses versus glass chemistry; density of defects, kinetics

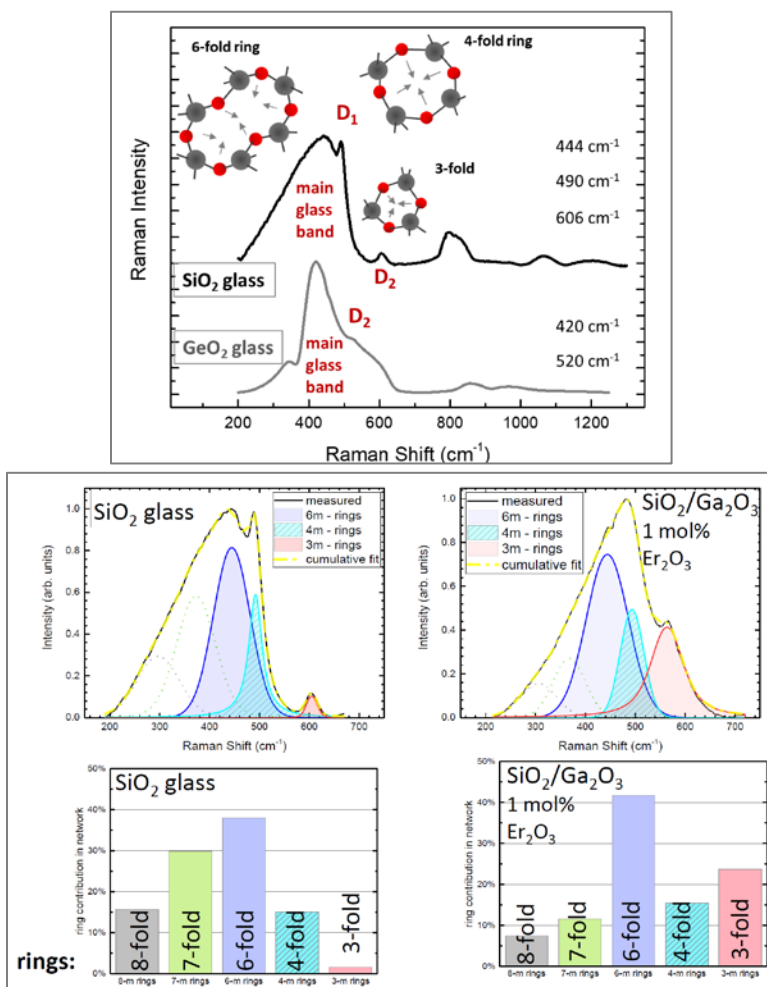
**Table 2.** A fully integrated, multi-technique approach to understanding the modification of glass networks, the local structural environment of functional glass components and laser-glass interactions leading to the formation of optically-active defect centers.

The main characterization techniques (Table 2) used were confocal micro-Raman spectroscopy, luminescence spectroscopy, transmission spectroscopy, also combined with controlled, pulsed laser irradiation using different laser sources and variable irradiation conditions and finally synchrotron x-ray absorption fine structure (XAFS) spectroscopy. Experimental details are in our publications [16-20].

## IV. Project Achievements

### A. Observation of quench-free enhanced emission in cluster-free, Er-doped heavy metal oxide glasses of our exclusive design

We successfully **demonstrated** a series of new, non-esoteric glass media (see Table 1) - of practical interest, because of their compatibility with silica – that accept high erbium concentrations and display an enhanced erbium emission, while limiting Er-Er clustering.

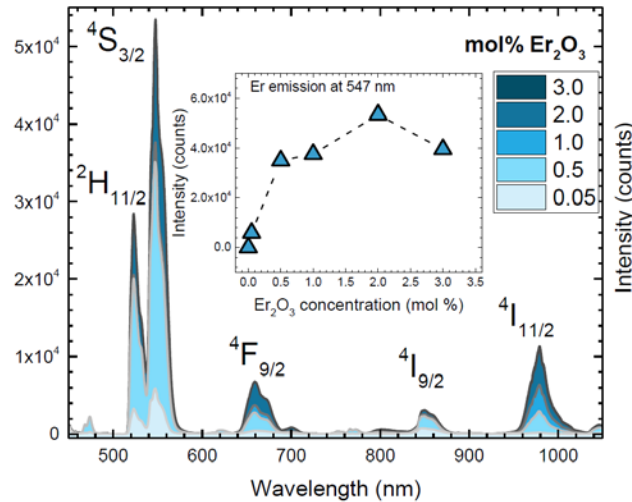


**Fig. 2.** *Top:* comparison of Raman spectra of reference SiO<sub>2</sub> and GeO<sub>2</sub> glasses. *Bottom:* Deconvolution of Raman bands showing the contribution of ring structures for a reference SiO<sub>2</sub> glass and for one of our glasses. Both for our glasses and for the reference SiO<sub>2</sub> glass, the 6-membered and larger tetrahedral rings dominate. However, our heavy-metal doped, erbium co-doped glass has a network built of fewer of the larger and more of the smaller than 6-fold rings.

We examined the effects of composition and microstructure of the glass networks on their optical properties. To understand the enhancement of emission in our glass materials we used Raman spectroscopy as a tool to develop a description of the glass' local microstructure. The deconvolution of Raman spectra illustrated how the spectral shape of the main Raman band can be used to extract information about the average ring structure (Figure 2). It is apparent that 6-membered and larger tetrahedral rings dominate for

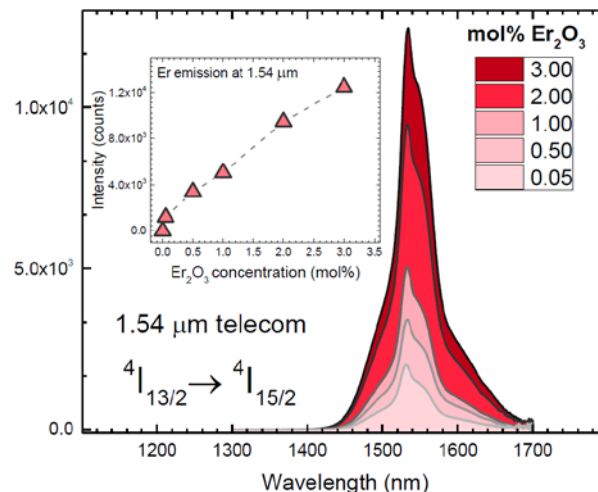


both our glasses and a reference  $\text{SiO}_2$  glass. However, our heavy-metal doped, erbium co-doped glass has a network built of fewer of the larger and more of the smaller than 6-fold rings. Both Raman spectroscopy and x-ray absorption fine structure spectroscopy [16] confirmed that gallium enters the glass network as a tetrahedral network former. In addition, the incorporation of gallium into the glass modified the energy landscape and created two distinct crystal field environments, which promoted  $\text{Er}^{3+}$  radiative transitions [16, 18].



**Fig. 3.** Visible-infrared range of Er emission as a function of concentration. In the glass compositions of our design, we did not observe any quenching of emission up to 2 mol % of  $\text{Er}_2\text{O}_3$ , which corresponds to 4 mol % of  $\text{Er}^{3+}$ .

In the visible range (Figure 3 and [16]) an examination of the strong green emission band at  $\sim 550$  nm ( $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ , Fig. 2(d)), reveals that in the '(Si)/Ga-series', emission initially slowly increases up to 2 mol% of  $\text{Er}_2\text{O}_3$ , and then drops at higher doping, indicating the onset of concentration quenching.



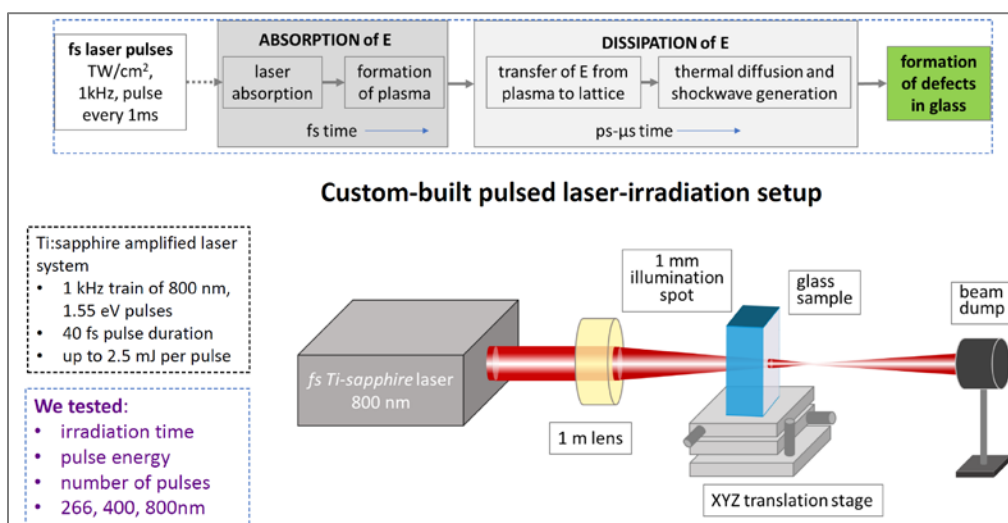
**Fig. 4.** Near-infrared, telecom Er emission at 1.5 um ( $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ ) as a function of  $\text{Er}_2\text{O}_3$  concentration. In the glass compositions of our design, we did not observe any quenching of the 1.54  $\mu\text{m}$  emission up to 3 mol % of  $\text{Er}_2\text{O}_3$ , which corresponds to 6 mol % of  $\text{Er}^{3+}$ .

In the NIR range (Figure 4) the levels of  $\text{Er}_2\text{O}_3$  doping without emission quenching are better than those reported for other oxide glasses, such as aluminosilicate, phosphate or chalcogenide glasses. At the  $\sim 1.5$   $\mu\text{m}$  telecom emission there is no sign of luminescence quenching up to 3 mol% of  $\text{Er}_2\text{O}_3$  (Fig. 4 and [16]). This is a noteworthy outcome and since the close-to-linear trend of increasing intensity does not show signs of tapering off, it could imply that higher  $\text{Er}_2\text{O}_3$  doping could be accepted.

Our results point the way to designing host glass matrices that limit interactions between neighboring rare-earth ions (Er-Er interactions) and thus minimize loss of excitation by energy migration and maximize light output. Detailed knowledge of the relationship between the glass network structure and chemistry, as well as full understanding of the microstructural and optical roles of all components provides a path forward to develop higher performance glass-based optical devices, such as lasers and amplifiers.

### B. Ultrafast laser-generated structural modifications in networks of isostructural but chemically different and Er-doped glass materials

The interaction between glass materials and femtosecond (fs) laser pulses can result in a variety of effects, including changes in: (i) local composition, (ii) valence states of certain ions, (iii) optical properties, as well as (iv) nucleation of nanoparticles and crystallization [21-23]. Understanding and controlling the processes governing such structural alterations in glasses is important for the fabrication of photonic structures. The most common substrate investigated frequently is pure amorphous silica, with focus on writing of optical waveguides [24-28].

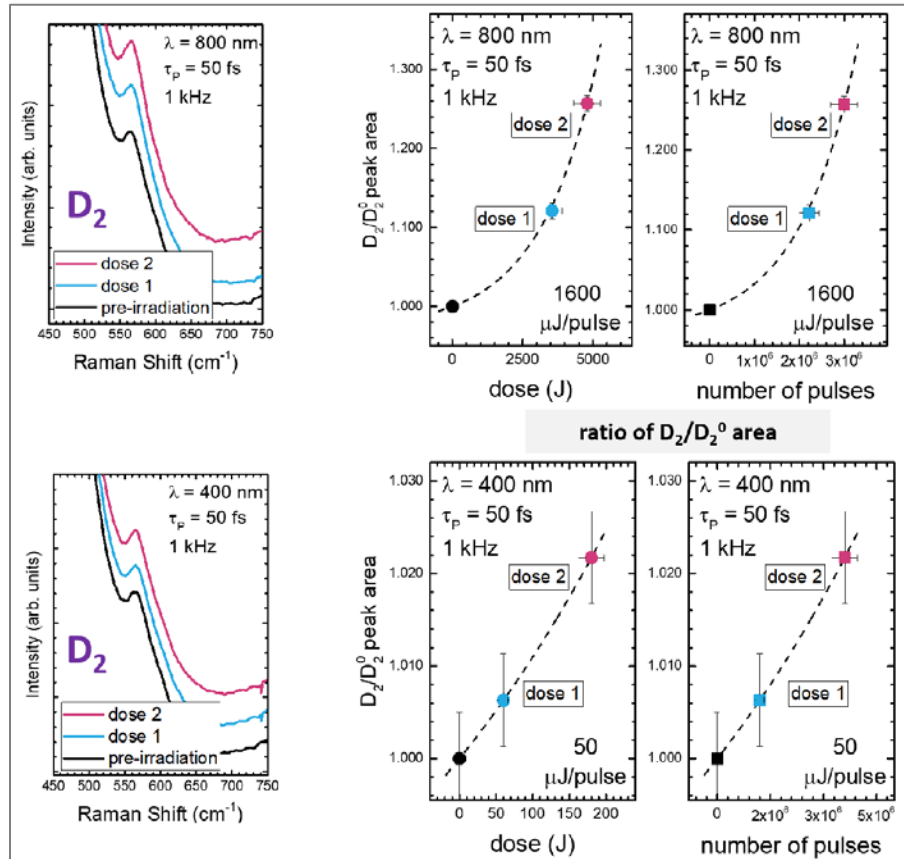


**Fig. 5.** Custom-built set-up for pulsed laser irradiation used for the controlled generation of defects in our glasses. Top inset shows the steps in the process of fs-laser irradiation leading to the formation of microstructural defects in the glass network.

A consistent picture of fs-laser induced alterations, the mechanisms linked to the creation of microstructural defects and of defect-assisted densification in different glass networks still remains elusive. When a glass medium is additionally doped with luminescent rare-earths ions (REs), fs-laser processing can be used to fabricate high-gain optical devices, such as waveguide lasers and waveguide amplifiers [29-32]. The majority of studies that report on monitoring of fs-laser created defects in glasses have focused only on undoped glasses, mostly silicate or phosphate compositions [24-30]. In fact, when a glass is doped with  $\text{Er}^{3+}$ ,

the fundamental study of optically active defects becomes very challenging. This is because the strong emission bands of  $\text{Er}^{3+}$ , spanning from visible to infrared, dominate over the emission signatures (luminescence), which are used to monitor the formation of fs-laser created defects [17].

We investigated the effects of femtosecond, multi-pulse laser exposure on the structural changes in a series of our  $\text{Er}^{3+}$ -doped glasses. We analyzed microstructural alterations in the glass network and we monitored the formation of defect centers resulting from variable laser exposure conditions (Figure 5 and [17]).

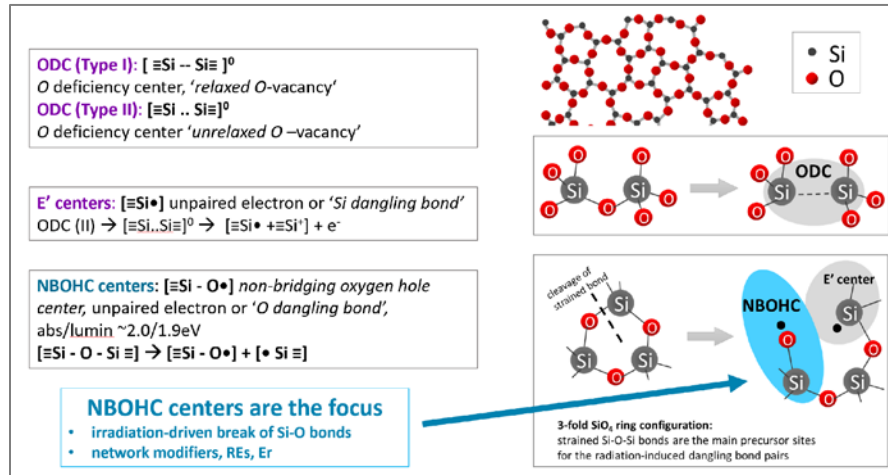


**Fig. 6.** Densification of glass microstructure probed by Raman. Comparison of Raman spectra of pre- and post-irradiated glasses. Different irradiation doses at 400 nm versus 800 nm, that control the laser energy delivered to the sample. For both 400 and 800 nm irradiation, glass densification depends on the photon dose used.  $D_2$  bands mark the contribution of the smallest 3-fold tetrahedral rings.

First, we induced and subsequently probed, using Raman spectroscopy, the subtle differences in the glass network architecture, which are generated by different laser wavelengths and at different doses. (Figure 6). Next, using luminescence spectroscopy, we monitored the fs-laser driven formation of optically-active defects in the glass network. Finally, we demonstrated how to decouple the luminescence signals of laser-induced optically-active defects from the much stronger and usually dominating emission of  $\text{Er}^{3+}$  (Figure 7, Figure 8 and [17]).

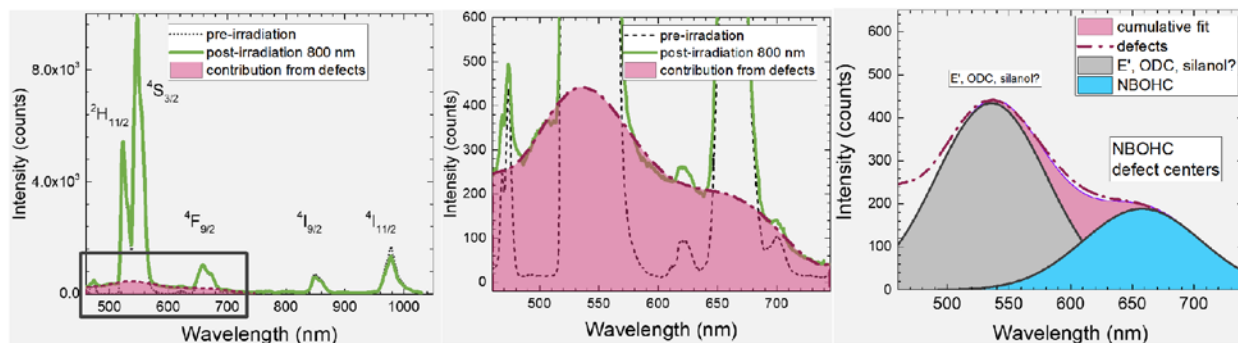
The results of Raman studies can be summarized into a few key findings (Figure 6). Femtosecond laser exposure of  $\text{Er}^{3+}$ -doped and heavy-metal co-doped oxide glass, leads to various degrees of microstructural reorganization in the network. Specifically, in the short-to-medium range order, such exposure generates

an increasing number of small, i.e. 3- and 4-fold tetrahedral rings in the backbone of the irradiated volume of the glass. The formation of such low-dimensional, strained rings occurs at the expense of 6-fold and larger rings, increases connectivity of the network and leads to the creation of a more compacted network, meaning glass densification.



**Fig. 7.** Most common types of defects in glasses.

Irradiation can generate different types of defects in glass by breaking of bonds in the network. We focus here on the search for optically active defects that have a spectral signature in the visible range of emission and on type of defects called non-bridging oxygen hole centers (NBOHC, Figure 7)) they are important for the fabrication of optical devices written in glass [17].



**Fig. 8.** Luminescence spectra of glasses before and after 800 nm fs-laser irradiation, at the highest dose (1kHz, 40 ns, 50 mJ/pulse) [17]. Left: full luminescence spectrum dominated by the typical Er emission. Center: zoom on the region of interest where we observe the emission from MBOHC defects. Right: a Gaussian deconvolution of the irradiation-generated background, showing the contribution from NBOHCs as well from unknown defects. The outcome of irradiation at 800nm is: (i) bond breaking in glass network and (ii) formation of Non-Bridging-Oxygen-Hole-Centers.

Luminescence spectroscopy allowed us to monitor the formation of optically active defects (Figure 7) in the irradiated volume of the  $\text{Er}^{3+}$ -doped glass (Figure 8)

**We demonstrated** how to decouple the very weak luminescence signals of laser-generated optically-active defects from the dominating emission of  $\text{Er}^{3+}$ . We elucidated the relationship between the initial and the irradiation-modified glass microstructure, including bond breaking, the formation of optically active defects and defect-assisted densification build-up in the glass network [17].

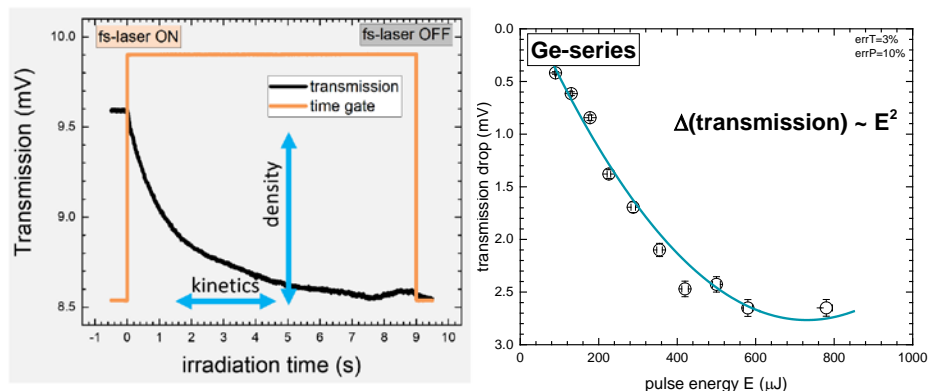
Femtosecond laser exposure ultimately brings a gradual, defect-driven glass network densification within the laser-irradiated volume. This study extends our understanding of fs-laser irradiation-driven structural modifications and demonstrates defect monitoring in  $\text{Er}^{3+}$ -doped oxide glasses.

To the best of our knowledge, no study has reported the detection of luminescence from defect centers in glasses, when an  $\text{Er}^{3+}$  dopant is also present. In fact, strong emission bands of typical  $\text{Er}^{3+}$  radiative transitions can overwhelm the weak intensity luminescence signals from irradiation-created defect centers, when those signals occur in the same spectral range [31, 33-34]. In this work we are able to successfully decouple the very weak luminescence of laser-generated defects from the dominating luminescence of  $\text{Er}^{3+}$ .

### C. Kinetics of defect formation: transmission losses during fs-irradiation

We studied the irradiation-driven losses in transmission signal in various glasses during fs-laser irradiation. The goal was to quantify the kinetics of formation of defects, specifically: the defect saturation time, the relative rate of defects formation and the density of defects for different glass matrices.

We built a custom optical set-up for measuring *in situ* and in real time, the kinetics of formation of defects during fs-laser irradiation. To generate defects in glass we used a fs laser at 800 nm delivering a 1 kHz train of pulses of 2.5 mJ energy/pulse. To monitor transmission losses through a glass as a function of irradiation time we used a 100 kHz, 430 nm photodiode [19].



**Fig. 9.** *Left:* A typical signal of transmission loss versus fs laser exposure time. Arrows indicate how quantification of time (kinetics) and of density of defects generated by the irradiation process can be extracted. *Right:* Transmission loss as a function of energy for one of our glasses.[19]

We performed single point transmission measurements during 800 nm, fs-laser irradiation, for different irradiation doses, different pulse energies and different glasses. Figure 9 shows a typical signal of transmission loss versus fs laser exposure time. Transmission loss is a measure of the number of defects created by fs laser-irradiation. We found that for all glasses the transmission signal loss occurs at a very fast time scale (a few seconds). The kinetics of creation of defects is characterized by 3 stages: fast decrease of transmission, followed by slower decrease and finally a plateau [19].

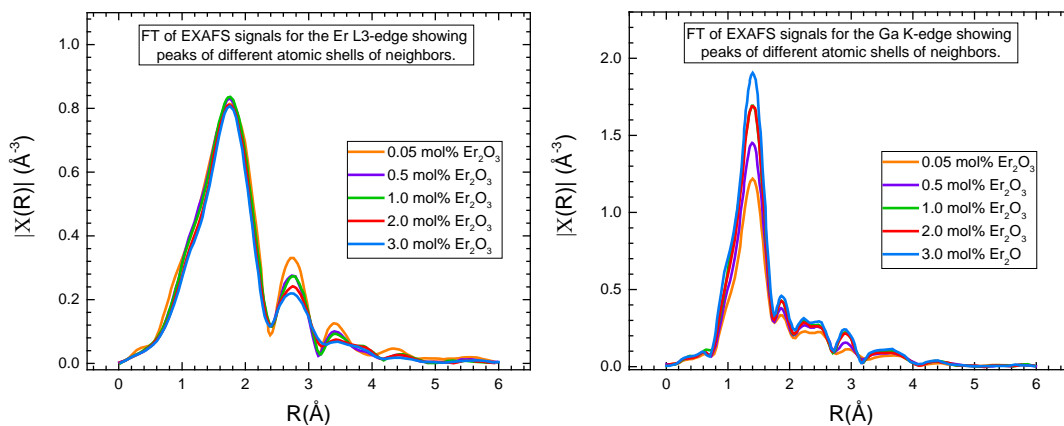
The magnitude of transmission drop is a function of laser pulse energy for all glasses. For our Si-based and Ge-based glass systems we found that the transmission loss scales only as  $E^2$ , as shown in Figure 9. We identified in literature one comparable study of commercial boro-silicate glass. In that study it was found that in the boro-silicate glass the transmission drop scales as  $E^{14.6}$ , hence is extremely sensitive to laser pulse energy. **We demonstrated** that, remarkably, our glasses are much less sensitive to pulse energy, meaning they can handle much higher laser powers, which is an advantage for practical applications [19].

#### D. Microscopic model of $\text{Er}^{3+}$ environment in heavy-metal silica glasses by XAFS spectroscopy: network former mixing effects

We investigated a series of erbium-doped and gallium-co-doped silica-based glasses using synchrotron x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopies [18, 20]. We used these two techniques to explore the effect of dopants on the medium range order of the glass network. Specifically, the objective was to understand the effect of gallium on the local environment of erbium in the glass network which, in turn, will affect the emission properties of  $\text{Er}^{3+}$ . Experiments were carried out at the facilities of the MRCAT beamline [35-36] at the Advanced Photon Source of Argonne National Laboratory (Chicago, IL).

Regardless of the presence or absence of long-range order in a material, the spectral shape in the element-selective XANES, provides a picture of the electronic properties (i.e. oxidation state) and of the local geometry (i.e. coordination chemistry) of the element studied.

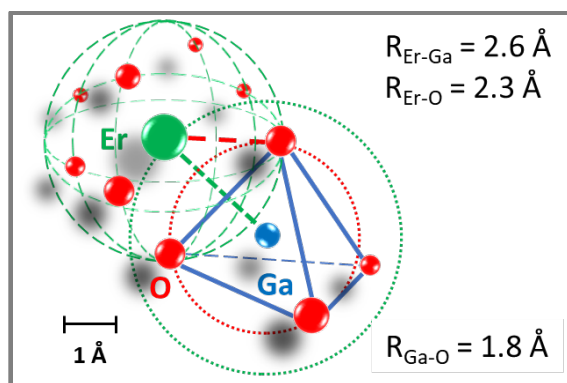
The element-selective EXAFS spectroscopy is highly sensitive to the short-range order in a material. A detailed analysis of EXAFS data, based on the multiple scattering formalism, allows to describe the local structural order around the selected atom i.e. erbium and gallium atoms in our glasses.



**Fig. 10.** Left: Er edge XAFS results. Right: Ga edge XAFS results. Details are in [18, 20].

Figure 10 shows a summary of XAFS results, for one of our glasses. Figure 11 shows a sketch representative of the local environment of  $\text{Er}^{3+}$  and  $\text{Ga}^{3+}$  that is based on a quantitative analysis of the scattering paths and occupancies of EXAFS data. At all erbium concentrations EXAFS data show only Er-O, Ga-O and Ga-O-[Er/Ga] interactions, with no detectable contribution of direct Er-Er or Er-Si or Ga-Si correlations up to  $\sim 4$  Å, that is up to two nearest neighbor coordination shells [18, 20].





**Fig. 11.** Model of the short-range order in our erbium-doped and gallium-co-doped silica-based glass. The local environment of Er and Ga is based on quantitative analysis of XAFS results.

In our glasses the solubility of erbium is markedly increased and in EXAFS we detect the formation of Ga-O-[Er/Ga] rich regions, which are similar to the Er-Al complexes proposed by Lægsgaard [37], or the solvation-shell model by Arai [38]. It appears that  $\text{Ga}^{3+}$  plays a role similar to  $\text{Al}^{3+}$  in our glasses: in order to enter a tetrahedral coordination with oxygens ( $\text{GaO}_4$ ), Ga is being charge-compensated by  $\text{Er}^{3+}$ . In fact, EXAFS confirms that Ga and Er are located in proximity. In the second shell of Ga, the fractional occupancy of Er is  $\sim 0.4$ . In other words, there is 1 Er per  $\sim 2.5$   $\text{GaO}_4$  tetrahedra. We suggest that in our glasses 1  $\text{Er}^{3+}$  can charge-compensate 2.5  $\text{Ga}^{3+}$ . This process of charge compensation allows the Er ions to fit better within an otherwise ‘inhospitable’ silica glass network. In Figure 4 (presented in section A) there is no decrease of luminescence intensity with increasing  $\text{Er}^{3+}$  concentration, i.e. no quenching up to 6 mol% of  $\text{Er}^{3+}$ . This favorable outcome is well explained by our EXAFS results: the proximity of Er to where Ga is found, as well as the formation of Ga-O-[Er/Ga] rich domains within the  $\text{SiO}_4$  tetrahedral network, create a more energetically favorable environment for  $\text{Er}^{3+}$  ions [18, 20].

**We demonstrated**, using EXAFS, that  $\text{Er}^{3+}$  prefers  $\text{Ga}^{3+}$ - rich domains. Our XANES findings and presence of isosbestic points show that the incorporation of Ga into the glass matrix results in a modification of the energy environment of Er atoms i.e. gallium likely increases the diversity of erbium energy sites. Put together these results point to the idea that gallium’s role within the glass network is to counteract the clustering of  $\text{Er}^{3+}$ , and to prevent luminescence concentration quenching by decreasing the probability of detrimental non-radiative Er - Er energy transfer processes.

## V. What Are Our Accomplishments?

- Designed and synthesized several isostructural, non-esoteric glasses, variably doped with  $\text{Er}^{3+}$
- Quantified the glass network microstructures, local environments (synchrotron EXAFS spectroscopy) around target atoms
- Achieved quench-free emission, from  $\text{Er}^{3+}$ -doped, cluster-free glasses of our invention in NIR and in visible spectral ranges
- Assessed how pulsed-laser irradiation affects the glass network and creates optically-active defect centers and generates glass (network) densification
- Appraised how variable wavelengths, pulsed-laser irradiation affects the glass network and creates defects i.e. defect centers related closely to photodarkening effect observed in glass cores of optical fibers
- Quantified how pulsed-laser irradiation affects the glass light transmission properties and quantified the density of those defects and more importantly the kinetics of defect formation, all in custom-made glass materials

## VI. Published papers and papers in preparation

K. Lipinska, F. Cavallo, J-L Ayitou, C. Segre: Quench-free enhanced emission in cluster free Er-doped heavy metal oxide glasses, *Optical Mat. Express* 9 (3) 2019

K. Lipinska, L. Emmert, F. Cavallo, J-C. Diels: Ultrafast laser-generated structural modifications in an Er-doped heavy metal oxide glass, *Optical Mat. Express* 9 (5) 2019

K. Lipinska, C. Segre: Microscopic model of  $\text{Er}^{3+}$  environment in heavy-metal silica glasses: network former mixing effects, to be submitted to *J. Appl. Phys.*

K. Lipinska, L. Emmert: Kinetics of defect formation in fs-laser irradiation in heavy-metal glasses, in preparation

## VII. Presentations

K. Lipinska, “Fundamental Studies of Heavy Metal Oxide Glasses for High Power Lasers”, 2017 Program Review of Aerospace Materials for Extreme Environments, May 15-19, 2017, KAFB, NM

K. Lipinska, “Fundamental studies of Er-doped heavy metal oxide glasses: glass networks, generation of defects and optical properties related to photodarkening.”, 2018 Program Review of Aerospace Materials for Extreme Environments, May 14-18, 2018, Niceville, FL.

K. Lipinska, “Study of Er-doped glasses: microstructure, optical properties and laser-generated defects related to photodarkening”, 2019 Joint AFOSR & NSF Program Review: Quantitative Representation of Microstructure and Materials for Extreme Environments. May 20-24, 2019, Alexandria, VA

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20. K. Lipinska, "Study of Er-doped glasses: microstructure, optical properties and laser-generated defects related to photodarkening", 2019 Joint AFOSR & NSF Program Review: Quantitative Representation of Microstructure and Materials for Extreme Environments. May 20-24, 2019, Alexandria, VA
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