## International Summer School on Rare-Earth-Doped Optical Materials: Synthesis, Characterization, and Applications to Lasers

### Krakow, Poland, 27 August – 1 September 2023

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### **Lecturers and Lectures**



Matthias Jäger Leibniz-Institut für Photonische Technologien Jena, Germany

#### "Strategies for the spectral extension of fiber lasers" (90 min.)

Silica fiber lasers have been tremendously important for telecommunications at wavelengths near  $1.5\mu m$  (erbium) as well as for laser materials processing near  $1\mu m$  (ytterbium) and to a lesser extent near  $2\mu m$  (thulium, holmium). Laser emission outside these 3 spectral windows requires laser host material properties which are not compatible with standard silica fiber technology and require a shift to new materials and compositions. The necessary material requirements will be reviewed and several new material approaches will be introduced, including nanoparticle doping, fibers drawn using the molten core method, and non-silica glass fibers (e.g. fluoride and chalcogenide fibers).



Christian Kränkel Leibniz-Institut für Kristallzüchtung Berlin, Germany

#### a) "Fluoride crystals as host materials for visible lasers" (45 min.)

Fluoride crystals provide excellent properties as gain materials visible lasers. Their high band-gap energies prevent two-photon absorption into the conduction band and their low phonon energies permit non-radiative multi-phonon decay of the excited levels. Moreover, they provide low crystal field strengths, which avoids excited state absorption into 4f5d energy levels. However, their growth in high optical quality is challenging: The starting materials and the growth atmosphere must be free of oxides and hydroxides. In particular doped with the rare-earth doping ions Pr<sup>3+</sup> and Tb<sup>3+</sup>, fluorides enable outstanding laser performance in the visible. In my lecture, I will explain the properties of fluorides and the difficulties in their synthesis and introduce the latest developments in the field of visible lasers based on fluoride host materials.

#### b) "Rare-earth doped fluoride crystals for solid-state laser cooling" (45 min.)

Cooling of optically active solids can be obtained by irradiation of light with a wavelength longer than the average wavelength of the emitted photons. Such situation is enabled by anti-Stokes processes,

in which the energy of a lattice phonon is transferred to the emitted photon. In this way, phonons are destroyed and thermal energy is removed. To efficiently drive this process, any non-radiative recombination of the excited state and energy transfer to impurities must be avoided. Their low phonon energies make high purity fluorides excellent candidates for solid-state laser cooling. In my lecture I will briefly introduce the concept of solid-state laser cooling, explain the underlying theory as well as commonly used characterization techniques and the required experimental conditions before I review the current progress in this field.



Markus Pollnau University of Surrey Guildford, United Kingdom

## "Thermal equilibrium and relation between Boltzmann, Fermi-Dirac, and Bose-Einstein distributions"

Quasi as the aperitif to our Summer School, this lecture questions common knowledge, namely that the Boltzmann distribution is a classical approximation of the quantum-mechanical Fermi-Dirac (FD) and Bose-Einstein (BE) distributions. We derive a general differential equation of thermal equilibrium. Integration yields the Boltzmann distribution. We establish quantum principles ruling the population numbers of (i) fermions by utilizing Pauli's exclusion principle and (ii) bosons by utilizing Einstein's rate-equation approach to Planck's law of blackbody radiation. Inserting these quantum principles into the Boltzmann distribution or exploiting them as boundary conditions when integrating the differential equation of thermal equilibrium yields the FD or the BE distribution. It suggests that the FD and BE distributions are special cases of the general Boltzmann distribution; fermions and bosons simultaneously obey their own and the general Boltzmann distribution.

#### a) "Rare-earth-doped channel-waveguide amplifiers and lasers" (45 min.)

In this lecture, we will discuss rare-earth-doped channel-waveguide amplifiers and lasers based on a family of monoclinic crystalline materials, potassium double tungstates. By liquid-phase epitaxy we have grown thin layers co-doped with Gd, Lu, and Y to simultaneously achieve lattice matching and high refractive-index contrast with the Y-containing substrate, as well as high doping concentrations of active rare-earth ions such as Yb or Tm. We have demonstrated a small-signal gain per unit length of ~1000 dB/cm in Yb, which is two orders of magnitude higher than previously reported in the literature for any rare-earth-doped material and comparable with semiconductor optical amplifiers, as well as lasers with slope efficiencies of 80% in Tm, reaching the absolute theoretical limit for the involved transitions.

#### b) "Fundamental Laser linewidth and rare-earth-doped narrow-linewidth lasers" (45 min.)

This lecture will address spectral properties of lasers. We will derive the fundamental laser linewidth. This derivation demonstrates that the laser is an amplifier of spontaneous emission and that the gain narrows the linewidth of the passive resonator to the laser linewidth. In a continuous-wave laser, spontaneous and stimulated emission together compensate the losses, hence the gain is smaller than the losses, leading to a finite laser linewidth. The historic Schawlow-Townes equation is a four-fold approximation of this fundamental laser linewidth. We will then discuss experimental methods to obtain single-longitudinal-mode lasing and present an example of a narrow-linewidth laser, an Yb-doped aluminum-oxide distributed-feedback channel-waveguide laser on a silicon chip.



Heike Ebendorff-Heidepriem University of Adelaide Adelaide, Australia

#### a) "Rare-earth ions as indicators for local structure" (45 min.)

The absorption and fluorescence properties of certain RE transitions are sensitive to the local environment around the RE ions. For polyvalent rare earth ions such as Ce3+/4+, Tb3+/4+ and Eu2+/3+, the intense spin-allowed f-d transitions of the lower valent allow investigation of the redox behaviour of these RE ions in different glasses and under different fabrication conditions, which has applications for sensing of ionising radiation. The so-called hypersensitive f-f transitions, e.g. the green transition of Er3+ at 520-540nm, allow to distinguish whether the RE ions are in a glassy or crystalline environment. This has been used to quantitatively study the dissolution of RE doped nanocrystals in glass, which has implications for the development of nanocrystal-doped glasses and fibres for laser applications.

#### b) "Rare-earth ions for temperature measurement" (45 min.)

The fluorescence properties of certain RE transitions are sensitive to the temperature, which makes RE doped materials attractive for temperature sensing. This lecture focusses on the use of the green transition of Er3+ at 520-540nm in tellurite glass. The low phonon energy of tellurite glass allows excitation of the green fluorescence in the infrared through upconversion energy transfer, which prevents autofluorescence and hence increases the temperature sensitivity. The lecture presents two examples for temperature sensing; (i) in-vivo temperature sensing using tellurite coated silica fibre and (ii) temperature mapping with high spatial resolution and fast speed for monitoring fast temperature changes on the micron-scale.



Maurizio Ferrari Instituto di Fotonica e Nanotecnologie Università di Trento Trento, Italy

#### a) "Photonic glass ceramics: advances and perspectives" (45 min.)

The development of efficient luminescent systems, such as microcavities, solid state lasers, integrated optical amplifiers, optical sensors is the main topic in glass photonics. The building blocks of these systems are glass ceramics activated by rare-earth ions, because they exhibit specific morphologic, structural and spectroscopic properties. Among various materials that could be used as nanocrystals to be imbedded in a silica matrix, tin dioxide and hafnium dioxide present some interesting peculiarities, e.g., the presence of SnO<sub>2</sub> or HfO<sub>2</sub> nanocrystals allows an increase in both solubility and emission of rare-earth ions. Here, we focus on rare-earth-doped photonic glass-ceramics mainly fabricated by the sol-gel route.

#### b) "Flexible photonics: an exciting new research field" (45 min.)

Flexible photonics is a hot technological and scientific area with a broad spectrum of immediate applications. As already done in electronics, passive and active photonic devices demand integration on flexible substrates for a broad spectrum of applications ranging from optical interconnection to sensors for civil infrastructure and environments, to coherent and incoherent light sources and functionalized coatings for integration on biological tissue. The aim of this lecture is to highlight the development of flexible photonics. The historical steps of this new research area and a summary of the materials and fabrication techniques used will be discussed. Finally, some scientific and technological achievements in this field will be presented.



Alessandra Toncelli Università di Pisa Pisa, Italy

#### "Rare-earth-doped nanoparticles" (45 min.)

The photoluminescence properties of rare earth ions incorporated into bulk crystals or optical fibers have fascinated researchers for decades. The incorporation of these ions into nanometer-sized materials opens the possibility of completely different applications, especially in the biomedical field. Indeed, rare-earth-doped nanoparticles possess many advantages when compared, for example, with the more common quantum dots, such as large Stokes shift, sharp emission lines, long lifetimes, anti-Stokes emission, high chemical and photochemical stability, low toxicity and reduced photobleaching. For these reasons, they have already been proposed for displays, sensors, solar cells, electroluminescent devices, and biomedical imaging. In this talk, I will review some of the most interesting applications of rare-earth-doped nanoparticles, especially focusing on two peculiar applications: fingerprint visualization and luminescence thermometry.

#### "MID-infrared transitions of rare-earth ions" (45 min.)

The interest in developing new sources for the mid-infrared (MIR) region is increasing for the wide range of scientific and technological applications possible in this region. In fact, MIR is called the "fingerprint region" for the large number of roto-vibrational absorption features molecules show in this range. MIR spectroscopy can then be extremely useful, for example, in trace gas sensing, medical applications, information technology, food quality control, security controls, etc. Among the various proposed materials, lanthanide-doped crystals with their intriguing emission properties are promising emitters in this region, but obtaining an efficient MIR emission is not easy. In this lecture I will explain tips and tricks for obtaining mid-infrared emission from rare earth ions and I will review some of the best results obtained so far.



Rafael Valiente Università di Cantabria Santander, Spain

#### "Photoluminescence of lanthanide ions: beyond the atomic behavior" (90 min.)

Lanthanide ions exhibit unique luminescence properties that make them valuable for a range of applications, including optoelectronics, bioimaging, sensing, and lasers. While their spectroscopic behavior has traditionally been simplified to be atomic in nature and slightly influenced by the local environment, the experimental evidence reveals a more complex picture. This lecture will be focused on the origins of the lanthanide ions' spectroscopic properties, covering topics such as spectroscopic notation, the mechanisms underlying electronic transitions in free ions, and the selection rules that apply via group theory. Additionally, the lecture will explore how embedding lanthanide ions in a solid (such as a crystal or glass) affects their electronic states, including the role of the crystal field and the configurational coordinate model. Throughout the lecture, the lanthanide ions' optical properties will be compared with those of transition metal ions, providing a comprehensive overview of this area of research.



Maria J. Pascual Ceramics and Glass Institute (ICV-CSIC) Madrid, Spain

#### "Optical glass-ceramics" (90 min.)

Glass-ceramics (GCs) are constituted by nanometer-to-micron-sized crystals embedded in a glass matrix; usually, their structural or functional elements (clusters, crystallites or molecules) have dimensions in the 1 to 100 nm range. As the name says, GCs must be considered an intermediate material between inorganic glasses and ceramics; in most cases the crystallinity is between 30 and 50%. GCs share many properties with both glasses and ceramics, offering low defects, extra hardness, high thermal shock resistance (typical of ceramics) together with the ease of fabrication and moulding (typical of glasses). The embedded crystalline phase, however, can enhance the existing properties of the matrix glass or lead to entirely new properties. GCs are produced by controlled crystallization of certain glasses, generally induced by nucleating additives; they may result opaque or transparent. Rare earth doped transparent GCs are now gaining a competitive advantage with respect to amorphous glasses and, sometimes, to crystals too. The aim of these lessons is to introduce the basic characteristics of transparent glass-ceramics, with particular attention to the relationship between structure and transparency and to the mechanism of crystallization, which may also be induced by selective laser treatments. Their applications to the development of guided-wave structures including optical fibers are also described.



Robert Müller Leibniz-Institut für Photonische Technologien Jena, Germany



Katrin Wondraczek Leibniz-Institut für Photonische Technologien Jena, Germany

# "Laser active, silica based fiber materials by gas phase deposition technologies and powder based fabrication techniques" (90 min.)

Fiber lasers are of increasing importance in biomedical applications and industry. They are mainly based on silica fibers doped with rare earth elements for the lasing, and co-doping elements for adjustment of further optical properties. The lecture will present different methods for making optical fiber core materials and preforms. Special focus will be given to gas phase deposition technologies (such as modified chemical vapor deposition) and powder based fabrication techniques (e.g. precipitation and sol-gel approach combined with sintering). Challenges in achievable dopant compositions, dopant distributions and dopant levels will be addressed. Also the effect of fiber core material synthesis on resulting fiber performance will be touched.



Juliane Posseckardt Fraunhofer-Institut für Keramische Technologien und Systeme IKTS Dresden, Germany

#### "Micro- and nanoanalytics in material science" (60 min.)

Within the framework of the EU project "Nano-Crystals in Fiber Lasers", our group is responsible for the micro- and nanoanalytics in preforms as well as in readily prepared fibers. In the group "Microelectronic Materials and Nanoanalytics" at the Fraunhofer Institute for Ceramic Technologies and Systems (IKTS) we offer analytics ranging from scanning electron microscopy, via transmission electron microscopy, to X-ray microscopy. All of them can be combined with different in-situ tools, such as heaters, bender and indenter. In my lecture, I will introduce the different analysis methods and how they have been applied within the scope of this project.



#### Slawomir Sujecki

Wroclaw University of Science and Technology Wroclaw, Poland

#### "Mid Infrared Fibre Lasers" (90 min.)

Mid infrared (MIR) fibre lasers are subject to very intense research. The most successful path to achieve MIR lasing from fibres turned out so far to be via the use of low phonon energy glasses and lanthanide ion doping. Therefore, the first part of this lecture will cover the theoretical fundamentals of luminescence emitted by lanthanide ions doped into a low phonon energy glass. Particular focus will be given to fluoride and chalcogenide glasses. In the second part of the lecture the theoretical fundamentals of fibre lasers will be covered. Both practical aspects related to laboratory realisation of fibre lasers and theoretical modelling will be discussed. The presented theory will be backed up by examples of practical MIR fibre lasers realised in the photonics laboratory at Wroclaw University of Science and Technology.



Marcin Kochanowicz AGH University of Science and Technology Krakow, Poland

#### "Rare earth-doped soft optical fibers" (90 min.)

In this lecture, we will discuss the considerations of technology and optical properties of rare-earthdoped multicomponent (e.g., tellurite, germanate, antimonate, fluoride) optical fibers for the operation at visible (VIS), near-infrared (NIR), and mid-infrared (MIR) wavelengths. The manufacturing techniques of soft fibers (crucible, rod-in-tube, powder-in-tube) will be presented. Next, different fiber geometries (double-clad, shaped cladding, multicore, helical core, structured core, RE-double/triplydoped) will be analysed. Finally, applications and challenges for the realization of high-efficiency soft optical fibers in broadband sources and fiber-laser applications will be discussed.



Hartmut Liebetrau LASOS Lasertechnik GmbH Jena, Germany

#### "Lasers for life sciences" (30 min.)

Lasers are a versatile tool used in a multitude of applications within the Life Sciences - from fluorescence imaging over spectroscopic analysis to surgical applications. A large variety of lasers are used in life sciences: cw- and pulsed lasers; solid-state and gas-lasers; low- and high-power lasers. The talk will give an overview of lasers used for selected applications, such as microscopy, spectroscopy, and flow cytometry. Building principles and technical aspects are highlighted.



Jan Mrázek Institute of Photonics and Electronics Czech Academy of Sciences Prague, Czech Republic

# "Nanoparticle-doping of fibers. From birth control to aging and how to breed super-doped fiber" (90 min.)

The luminescence properties of rare earth-doped active glass strongly depend on the chemical and structural properties of the host matrix. The implementation of rare earth-doped nanoparticles into the fiber core can improve the luminescence properties allowing to increase the power and efficiency of fiber laser. The lecture will provide a comprehensive overview of strategies for preparing nanoparticle-doped optical fibers and the basic relationships between nanostructure and optical properties. The widely used direct nanoparticle deposition method will be compared with bottom-up preparation of nanoparticle-doped fibers. The stability of the nanoparticles in selected glass system and the basic processed occurring during the preparation of the fibers, including the synthesis, processing and post-treatment, will be compared with the conventional solution doping method and bulk glass technology.



Magdalena Lesniak AGH University of Science and Technology Krakow, Poland



Dominik Dorosz AGH University of Science and Technology Krakow, Poland

#### "Optical glasses for photonics - methods, properties, rare-earth doping" (90 min.)

Continuous progress in photonics requires the development of new glasses with luminescent properties in a broad spectral range from ultraviolet to mid-infrared. Projecting such optical materials requires substantial knowledge about glass formation systems and their pure manufacturing processes. Both will be presented in this lecture, as well as their optical and spectroscopic properties based on FTIR and Raman analysis. The relationship between the glass structural models and their optical properties will also be discussed briefly. An introduction to the most important types of glasses used for lanthanide doping will be presented. Silicate, non-silicate, and non-oxide glasses, considered the most important glasses in recent developments, will be presented in the context of applications in active optical fibres.