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DT-CRYS
Double Tungstate Crystals:
synthesis, characterization and applications

Specific Targeted Research
PRIORITY 3: Nanotechnologies and nano-sciences, knowledge-based multifunctional materials and new production processes and devices

Final Activity Report

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Project coordinator organization name:	Forschungsverbund Berlin e.V./ Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie
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Publishable executive summary

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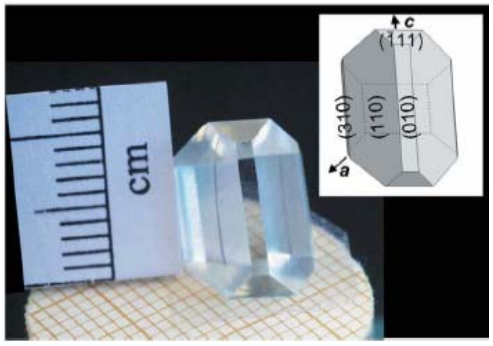
Double tungstate (DT) compounds with the general formula $AT(WO_4)_2$ (shortly ATW), where A and T are monovalent and trivalent cations, respectively, can be grown as single crystals in different crystallographic phases. The activity of the DT-CRYS project covered the monoclinic *C*2/*c* and tetragonal *I*-4 phases, including their growth, doping with Ln^{3+}-ions, structural, optical, spectroscopic, magnetic, and thermo-mechanical characterization, their processing in the form of bulk crystal elements, epitaxial layers, composite structures and nanopowders, their micro- and nano-structuring, and their various applications as photonics devices.

The measurement of the melting points and polymorphic transition temperatures of most of the monoclinic potassium DTs, KREW (RE: rare earth) with RE=Y, Gd, Dy, Ho, Er, Tm, Yb, and Lu, indicated that they exhibit polymorphic transition just below their melting point. Hence, they can be grown only from high temperature solutions. Once an appropriate solvent, $K_2W_2O_7$, was chosen, the solubility curves of the above crystals were recorded and important physical properties of the growth solutions, such as density, surface tension and viscosity were investigated. Optically inert monoclinic DT hosts (KYW, KGdW, and KLuW) were then synthesized by the top-seeded solution growth (TSSG) method, with and without pulling, and their morphology was analyzed. Core-free monoclinic crystals of KYW and KLuW with increased size (up to 200 g) were produced once the growth technology was optimized. In the family of the tetragonal DTs, the congruent melting of NaBiW, NaYW, NaLaW, and NaGdW allowed growing them by the Czochralski method. However, NaTmW, NaYbW and NaLuW do not melt congruently. Therefore, such stoichiometric compounds (e.g. NaLuW) or crystals with high Yb or Tm doping were grown by the TSSG method using Na_2WO_4 and $Na_2W_2O_7$ fluxes.

The various Ln-doped (activated) DT crystals, grown with high crystalline quality, were fully spectroscopically characterized, and employed as bulk laser materials: These include Yb-doped KYW, KGdW, KLuW, NaYW, NaLaW, NaGdW, and NaLuW for the 1 µm spectral region, co-doped monoclinic Er,Yb:KYW and Er,Yb:KLuW for the eye-safe region near 1.5 µm, and Tm-doped monoclinic KGdW and KLuW, and tetragonal NaYW, NaLaW, NaGdW and NaLuW for the 2 µm region. Some additional stoichiometric monoclinic DTs, KSmW, KDyW, KErW, KHoW, KTmW, KYbW, and RbNdW were also synthesized for magnetic and optical studies.

The structural characterization of the grown DTs, performed by single crystal and powder X-ray diffraction, aimed at refinement of the unit cell parameters and accurate identification of the symmetry of the tetragonal DT crystals, essential for understanding the inhomogeneous spectral broadening mechanisms when such hosts are doped with optically active Ln^{3+} ions. The latter gave first evidence for a non-centrosymmetric space group with two non-equivalent lattice sites that can be occupied by the dopant ions.

The evolution of unit cell parameters with doping was investigated in order to evaluate the lattice mismatch - a key parameter for subsequent epitaxial layer growth. Raman spectroscopy was used to identify the main phonon modes for stimulated Raman scattering (SRS). The anisotropic optical and thermo-mechanical properties studied include the transparency window, the refractive index ellipsoid and the dispersion, the linear thermal expansion tensor, the thermal conductivity tensor and the hardness. Finally, suitable cutting and polishing techniques were developed for fabrication of high optical quality laser elements with different geometry.



*Crystal of $KLu(WO_4)_2$ with monoclinic symmetry, grown in the **b** direction by the top-seeded solution growth (TSSG) slow-cooling method without pulling.*

Inset: morphological scheme.

This pure potassium lutetium double tungstate crystal was grown using $K_2W_2O_7$ as a solvent with a flux composition 11.5 mol % solute / 88.5 mol % solvent. Undoped crystals like this one were used for characterization of the physical properties and as substrates for subsequent epitaxial growth.

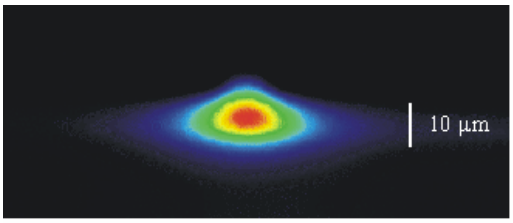
The spectroscopic characterization of the different dopant-host combinations included determination of the energy sublevels from low-temperature absorption and fluorescence measurements, absorption cross sections, emission cross sections of the lasing channels, identification of the two non-equivalent sites in the tetragonal DT compounds, calculation of the intrinsic quantum efficiency and gain cross sections in quasi-three-level laser systems, as well as measurements of lifetimes of the emitting states eliminating reabsorption effects.

The monoclinic DT crystals belong to the class of the magneto-elastics with interrelation between magnetic and elastic ordering. A systematic and complex [thermodynamic (specific heat, thermal expansion), spectroscopic (optical, EPR), magnetic (magnetization, susceptibility, magnetostriction), X-ray and neutron scattering] investigation of interactions between ions, spins and lattice, especially the elastic and magnetic interactions, has been performed. Suitable phase transitions in such crystals were also considered and analyzed.

Nano-crystalline DTs were fabricated using two methods differing in the choice of reagents and the thermal treatment. The fabrication costs of such materials are considerably lower than of their bulk counterparts. Nanocrystals of KYW and Yb:KYW were synthesized using a Complex Sol-Gel Process, which involved a maximum annealing temperature of 550°C. Their purity was improved by the introduction of a self-ignition step. The second technique, a modification of the Pechini method, was implemented to KGdW and KYbW with a maximum annealing temperature of 700°C. Precise control of the pH level in the precursor solution improved here the chelation process and limited the metal precipitation. Highly homogeneous nanopowders were produced by both methods, with crystalline sizes between 10 and 250 nm. The doped and undoped powders were studied by thermal analysis and thermogravimetry in order to determine their purity. The crystal phase and size of the nanocomposites were studied by X-ray diffraction, Raman spectroscopy, scanning and transmision electron microscopy. Electron spin resonance of the Yb:KYW powders confirmed that the Yb ions occupy the Y crystal lattice positions. Absorption and emission spectroscopy allowed identifying the Stark split Yb-levels in KYbW powders.

The growth of thin doped layers was undertaken by liquid phase epitaxy, using two different types of solvents, but at a later stage the lower temperature chloride solution was abandoned in favour of the oxide solvent which has a number of advantages. The epitaxial films were doped with different Ln-ion concentrations, up to 50 at. % substitution of Lu by Yb. The solution kinetics for such epitaxial growth was studied. Different types (KYW and KLuW), orientation, and sizes of the substrates were tested and the growth rate was analyzed. The micromorphology of the epitaxial surfaces, studied by optical and atomic force microscopy, revealed that the growth is layer-by-layer and the process is governed mainly by diffusion. The grown films were characterized by X-ray diffraction for the orientation, and X-ray fluorescence or electron probe microanalysis for the thickness and the composition variation. The produced planar waveguides showed excellent waveguiding properties evidenced by the guided fluorescence observed after excitation. In some cases the films were overgrown with undoped layers, resulting in buried waveguide structures. Optical investigation of the grown layers involved different coupling schemes at several wavelengths, as well as optical loss measurements (propagation losses as low as 0.08 dB/cm measured). Micro-structuring of the

fabricated layers was studied by reactive ion etching, light-ion implantation, femtosecond laser writing, and focused ion beam etching, to obtain channel waveguides, Y-splitters and Bragg gratings. The production of micro-structured channels using reactive ion etching of the activated epitaxial layers allowed demonstrating successfully channel waveguide emission. Losses in the range of 0.5 dB/cm at 1550 nm were measured for them by optical low-coherence reflectometry.



Experimentally recorded rib-waveguide beam profile at 965 nm, etched in a 1.7 at. % Yb-doped KYW layer grown on KYW substrate.

The confinement in such waveguides was considerably improved by increasing the refractive index step through co-doping the film with the optically "inert" Gd and Lu ions.

In order to obtain more freedom for engineering the waveguiding properties and improve the lattice mismatch, both for the monoclinic and tetragonal DTs, co-doping (of the film or the substrate) with additional, passive Ln-ons was investigated. Finally, the epitaxial growth was extended (by pulling the crystal) to segmented growth for fabrication of larger composite (doped + undoped part) structures based on Yb:KYW and KYW. An alternative technique for production of such composites, diffusion bonding, was also successfully demonstrated for Yb:KYW/KYW composites. Both were realized for the first time with monoclinic crystals as the DTs.

The laser performance was successfully studied for a number of Ln^{3+}-doped DT compounds including novel bulk crystals (a total of 14 dopant-host combinations demonstrated for the first time) and composite structures. Different types of laser setups (oscillators and amplifiers) and temporal regimes (continuous-wave, nanosecond, picosecond, femtosecond) including tunable operation were investigated in the 1.0 μm (Yb), 1.5 μm (Er,Yb) and 2 μm (Tm) spectral regions.

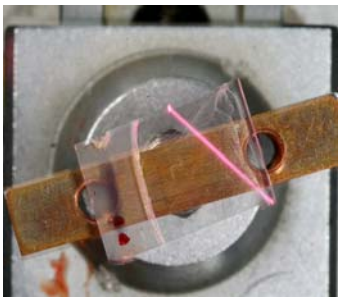
As a result of theoretical modelling of the power scalability of Yb-doped DT lasers, high-power continuous-wave laser operation was achieved by diode pumping the monoclinic Yb:KGdW and Yb:KLuW. Output powers as high as 12.4 W and slope efficiency of 74% with respect to the incident pump power were obtained with simple two-mirror cavities. The thermal lensing effect was studied in the same materials using athermal crystal cuts. Narrow-band, tunable operation from 997 to 1050 nm was achieved with reflective volume Bragg grating in a Yb:KYW laser. Very promising results were obtained also with the disordered Yb-doped tetragonal DTs: Slope efficiency of 77% with respect to the absorbed pump power and extended tunability from 1014 to 1079 nm were achieved by pumping Yb:NaGdW with a Ti:sapphire laser, while diode-pumping led to output powers as high as 1.45 W.

Pioneering work was performed introducing composite laser structures based on monoclinic DTs feasible for use in thin disk laser designs, and in general for face-cooled laser concepts, microchip and waveguide lasers. After successful initial experiments with epitaxially grown Yb:KYW/KYW and Yb:KLuW/KLuW, more than 600 mW output power near 1030 nm were obtained with diffusion bonded Yb:KYW/KYW composites and a slope efficiency as high as 80% with respect to the absorbed pump power was achieved for segmented grown composites.

The high quality of the Yb-doped epitaxial layers allowed demonstrating for the first time waveguide lasing based on monoclinic DTs. Laser operation in the continuous-wave regime was achieved with 6-mm long and 17 μm thin Yb:KYW waveguides with both, surface and buried planar structure. An output power of 290 mW near 1024 nm was obtained in the fundamental mode and the slope efficiency exceeded 80%.

Improvement of the design of femtosecond mode-locked Yb:KYW and Yb:KGdW oscillators allowed achieving average powers of the order of 3 W for <300 fs pulse durations at a repetition rate of 100 MHz in the 1 μm spectral region. Pulse duration of 250 fs was achieved also with oscillators operating at relatively low (20 MHz) repetition rates which provide output energies as high as 100 nJ. With tight folding and packaging of the resonator whilst keeping low misalignment sensitivity a commercial fs-Yb:KYW oscillator of this type with a resonator length of 7.5 m and a size of $460\times200\times80$ mm^3 was developed. The challenging sub-100 fs region was

impressively entered using Yb-doped monoclinic KYW and KLuW (including epitaxial, segmented grown and diffusion bonded structures) as well as tetragolal NaGdW, NaLuW and NaYW hosts in lasers operating at a repetition rate of about 95 MHz: Pulses as short as 81 fs, 62 fs, and 53 fs were obtained with bulk Yb:KLuW, diffusion bonded Yb:KYW/KYW and bulk Yb:NaYW, respectively. The last result represents the shortest pulse duration achieved with an Yb-laser and underlines the potential of the disordered DTs for diode-pumped sub-50 fs pulse generation. Regenerative amplification using Yb:KYW, to increase the pulse energy, produced an average power of >2 W at repetition rates of 100-500 kHz or a pulse energy of 10 μJ at 100 kHz (1 mJ at 1 kHz) at sub-400 fs pulse durations. Completed prototype systems of this type fulfill the requirement of compact design having a size of only 780×340×180 mm^3.



Photograph of the Tm:KYW waveguide placed on a Cu-plate in the lasing state. The reddish fluorescence indicates the pump channel.

The 35-μm thick Tm:KYW waveguide exhibits reddish fluorescence originating from upconversion fluorescence from the $^1G_4$ and possibly $^1D_2$ levels and the visible dislocations of the sample stem from the bottom side of the substrate which is not polished. This 1 at. % Tm-doped sample lased between 1960 and 1970 nm with a threshold of 244 mW when pumped by a Ti:sapphire laser at 801.6 nm.

As a result of theoretical and experimental investigations of the excitation transfer dynamics between Er and Yb, the optimum doping concentrations were found and finally lasing near 1.5 μm was established for the first time with Er,Yb:KYW and Er,Yb:KLuW. Pumping by a diode laser at 980 nm, the quasi-continuous-wave lasers produced peak output power up to 150 mW.

The Tm-lasers developed for the 2 μm spectral range operated continuous-wave, both with Ti:sapphire laser pumping where tuning was also studied, and with diode pumping near 800 nm. Tm:KLuW was the most successful laser based on monoclinic DT with tunability from 1800 to 1987 nm on the 1 W output level, and reaching 4 W output (69% slope efficiency) under diode pumping. Lasing was demonstrated also with epitaxial Tm:KLuW/KLuW (low threshold, tunable operation with a slope efficiency as high as 64%) and Tm:KYW/KYW using longitudinal and waveguide pump geometry, respectively. Furthermore, successful Tm-laser operation was achieved with the disordered tetragonal DT hosts which offer larger gain bandwidths. With Tm:NaGdW, e.g., the tunability extended from 1813 to 2025 nm which corresponds to ≈17 THz.

As a main element of their multifunctionality, the nonlinear properties of the DT materials were exploited for wavelength conversion of the laser output, either extracavity or intracavity, in the same crystal, using SRS. SRS was studied with undoped KYW pumped at 532 nm by 3 ns pulses and placed in a cavity to amplify the generated Raman radiation. Raman lines originating from two phonons were observed. Measurements of undoped disordered DTs showed that at least NaLaW and NaYW, with their broader Raman bandwidths, offer substantial SRS gain for relatively short (~2 ps) pulses. A Raman laser based on Yb:KLuW was realized to demonstrate laser effect and nonlinear conversion in the same crystal. When passively Q-switched, the laser produced fundamental radiation near 1030 nm and the first Stokes radiation near 1140 nm. The maximum pulse energy of the fundamental and Raman radiation at a repetition rate of 28 kHz was 32.4 and 14.4 μJ, respectively. The corresponding pulse durations were 1.41 and 0.71 ns. In terms of energy and peak power these results are higher by more than one order of magnitude in comparison to previous work with Yb:KYW or Yb:KGdW.

The potential for optical cooling by fluorescence was investigated with Yb:KLuW and Tm:KLuW samples and cooling by demagnetisation was observed in RbDyW.

The project DT-CRYS had very active dissemination policy resulting in 110 papers in peer-reviewed journals (81 of them already published) and more than 120 presentations at different international conferences. All these and a lot of additional information can be found in the website www.dt-crys.net, which will be maintained and possibly updated also in the near future.