Project: **QUANTUM CONVERSION PROCESSES OF EXCITATION IN PHOTON SOURCES OF PROSPECT FOR SUSTAINABLE ENERGY PRODUCTION**
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RESULTS IN 2012-2014

The activities covered specific tasks of the stages planified within this period as well as preparatory work for the next stages.

1. **Selection of laser active and sensitizer ions and of host materials**.

The selection was based on data existing in literature and on preliminary investigation of spectroscopic properties of several systems:

- Laser active ions: Nd^{3+} and Yb^{3+};
- Sensitizer ions based on f-f transitions (Nd^{3+} for Yb^{3+}), on d-d transitions (Cr^{3+} for Nd^{3+}) or on d-f transitions (Ce^{3+} for Nd^{3+}) for simple or complex (Ce-Cr-Nd, Cr-Nd-Yb) sensitiztion schemes;
- Host materials: simple (YAG) or complex (GSGG, YSAG) disordered garnets, simple sesquioxides, intrinsic or accidentally disordered garnets (CLNGG family), mixed systems;
- The spectroscopic properties of Sm^{3+} were investigated in order to assess its potential to suppress the amplification of spontaneous of Nd^{3+} or Yb^{3+} in some of these systems.

2. **Preparation of ceramic samples**.

Undoped or doped translucent ceramics of garnet structure (YAG, $Y_3Sc_xAl_{5-x}O_{12}$) and sesquioxides (Y_2O_3, Lu_2O_3, Sc_2O_3) with well developed grains of fairly uniform distribution of sizes have been produced by the technique of solid-state reaction. The process involves homogeneous mixing of raw materials, spray drying granulation, thermal synthesis, preliminary isostatic compression compacting, and sintering. XRD confirmed the garnet or sesquioxide single-phase of these ceramics. Several other ceramics (YAG, GSGG, CLNGG, CLNTGG) were obtained in a cooperation with World Lab. Co., Nagoya, Japan.

3. **Spectroscopic properties of potential doping ions.**

3.1. Laser active ions.

A. Composition and temperature effects in Nd^{3+} spectra of disordered garnets of scandium and aluminium

New spectroscopic data were obtained from low temperature investigation of mixed translucent ceramic garnets $Y_3Sc_xAl_{5-x}O_{12}$ (x=0-2) doped with Nd^{3+}, important systems for ultrashort (fs) laser pulses or emission at two wavelengths. Thus, from 10 K absorption and emission spectra of Nd^{3+} in disordered $Y_3Sc_xAl_{5-x}O_{12}$ garnets were analysed:

- The composition effects, manifested by line shifts and lineshape (and widths) changes, associated with structural effects induced by larger Sc^{3+} ions replacing Al^{3+} in octahedral sites;
- The energy levels schemes of Nd^{3+} in various compositions (for x=1 a “quasicenter” model was used) in terms of nephelauxetic and crystal field effects in mixed garnets;
- Multicenter structure (*reported for the first time on this system*), and the connection of spectral characteristics and local structure;
- Temperature effects on Nd^{3+} emission and its influence on emission and laser generation.

B. Spectroscopic properties of Nd^{3+} in GSGG.

It was found that in this material accidental degeneracy of two absorption transitions would increase considerably the absorption efficiency and thermal stability of the direct pumping into the emitting level. Advantages of diode laser pumping in this transition were demonstrated for continuous-wave and active or passive Q-switched laser emission.

C. Spectroscopic investigation of Nd^{3+} and Yb^{3+} in intrinsic disordered CLNGG crystals and ceramics.

It was found that in such systems the necessity of electric charge compensation at substitution of the host cation by trivalent rare earth ions imposes modification of the host material function on doping concentration. This would modify the composition of the cationic coordination spheres around the

doping ion, leading to composition-dependent multicenter structure of the optical spectra and to considerable inhomogeneous broadening of the absorption and emission bands. Such emission bands can be utilized for ultrashort laser emission by mode-locking, as demonstrated recently by other research groups.

3.2. Spectroscopic investigation of sensitizer ions

A. Investigation of the optical spectra of Cr^{3+} in YAG ceramics evidenced the negligible intensity of the parasitic perturbed centers specific to the melt-grown crystals and the similarity of the spectroscopic properties of the main doping center and of their temperature dependence in ceramics and crystals.

B. Multicenter structure in visible emission of Ce^{3+} in YAG ceramic

The investigation of the 5d→4f Ce^{3+} emission and kinetics in YAG transparent ceramics under excitation with visible sources revealed different Ce^{3+} centers. Under short pulsed excitation with 532 nm (probably by a two photon process), complex temperature dependent spectra and decays were detected, associated with perturbed Ce^{3+} centers. The spectral characteristics in the 5d→4f Ce^{3+} emission of these perturbed Ce^{3+} centers were analysed in terms of the effects of the structural changes induced by Ce^{3+} doping on the interaction with defects, such as residual antisites Y_{Al}^{3+} in ceramics.

C. Spectroscopic properties of potential ASE suppressers.

Investigation of spectroscopic characteristics of Sm^{3+} in YAG confirmed the prospect of this system for suppressing the ASE of Nd:YAG and its utility for side-pumped lasers with clad-core monolithic composite laser rods. Our investigation enabled a correlation of the Nd^{3+} emission properties with the Sm^{3+} absorption in YAG and Y_2O_3 at different temperatures. It was experimentally shown that the lines involved in ASE suppression show strong differences in these matrices and individually-selective temperature dependent shifts. It was thus found that in case of Nd^{3+}, Sm^{3+} can act as suppressor of ASE in YAG at 300 K, but not at low temperatures, whereas in Y_2O_3 this ability manfests both at 300K and cryogenic temperatures. It was also found that Sm^{3+} cannot supress ASE of Yb^{3+} in YAG, but this would be possible in Y_2O_3, regardless of temperature. The spectroscopic investigation of Sm^{3+} in YAG and sesquioxides suggests that this ion could be useful for reduction of solarization in case of broad-band pumped lasers.

4. **Sensitization of infrared emission under visible - near IR and broad-band (blue, violet, ultraviolet) excitation.**

4.1. Investigation of sensitization of Nd^{3+} emission by Cr^{3+}

By using a large variety of (Nd_xCr_y):YAG ceramic samples, the main characteristics of the sensitized process were revealed and allowed the selection of the optimal dopants concentrations within the restrictions imposed by parasitic processes inside the system of active ions. Thus:

- The characteristics of the concentration-dependent selfquenching emisson of Nd^{3+} in YAG function on pump intensity have been investigated, based on the competition between the upconversion and down-conversion energy transfer processes. It was found that these processes would limit the useful Nd concentration;
- The temperature, in the range 10 to 300 K, influences strongly the characteristics of Cr^{3+} emission (spectra, dynamics), it has much less effects on Nd^{3+} in single doped material;
- The emission dynamics investigation over larger Cr^{3+} or Nd^{3+} concentration ranges (that can be obtained in ceramics), much superior to those used by other authors, evidenced that the Cr^{3+} to Nd^{3+} energy transfer proceeds both by direct transfer by electric dipole-dipole and superexchange interactions and by migration-assisted processes, thus it depends on both Cr and Nd concentrations. The transfer microparameters and the transfer efficiency, function of concentrations and temperature were evaluated. At the temperatures and Cr and Nd concentrations covered by this study the global de-excitation of Cr^{3+} remains slower than the intrinsic de-excitation of Nd^{3+};

- The characteristics of the energy transfer indicate that that much higher doping concentrations than used earlier in the solar-pumped (Cr,Nd):YAG lasers would be necessary to optimize the sensitization process and the efficiency of these lasers.

4.2. Sensitization of Yb^{3+} emission in (Nd, Yb): CLNGG

High-resolution spectroscopic investigation of compositionally disordered calcium niobium gallium lithium garnets - CLNGG doped with Nd^{3+} or Yb^{3+} and modeling enabled the correlation of the broadening effects of the lines with the actual composition of the material, which are similar in laser crystals and ceramics. These studies have suggested that such systems with intrinsic disorder could be appropriate for improvenment of sensitization of Yb^{3+} emission by energy transfer from Nd^{3+} in (Nd, Yb) codoped ceramics, due to larger overlap of Nd^{3+} emission and Yb^{3+} absorption than in ordered garnets, such as YAG. Sensitization effects were examined in infrared emission under excitation in Nd^{3+} absorption bands of different codoped samples: CLNGG: (1%Nd, 1%Yb), (2.5% Nd si 5% Yb) and emission kinetics. For large concentrations, the Nd→Yb energy transfer, accelerated by migration on donors, leads to a global efficiency of energy transfer close to ~100%, i.e. larger than the 93% transfer efficiency at the same Yb^{3+} concentration in YAG.

Our studies have shown that for Yb:CLNGG, the emission band width show potential for generation of pulses in the range of 50 fs, demonstrated experimentally recently by other research groups. Our recent investigation evidences also that the Yb^{3+} emission linewidth in a solid solution of CLNGG with CLTGG (niobium replaced by tantalum) is with ~ 20% larger than for CLNGG and one could estimate the possibility of laser pulses of ~ 40 fs.

VALORIFICATION OF RESULTS

I. PAPERS IN ISI JOURNALS

1. V. Lupei, A. Lupei, C. Gheorghe, L. Gheorghe, A. Achim, A. Ikesue, "Crystal field disorder effects in the optical spectra of Nd^{3+} and Yb^{3+}-doped CLNGG laser crystals and ceramics", J. Appl. Phys. **112**, 063110 (2012).
2. V. Lupei, "Pump intensity dependence of emission quantum efficiency in Nd-doped materials", Rom. Rept. Phys. **64**, 1291-1306 (2012)
3. A. Lupei, C.Tiseanu, C.Gheorghe, F.Voicu, "Optical Spectroscopy of Sm^{3+} in C_2 and C_{3i} sites in Y_2O_3", Appl. Phys. B. **108**, 909-918 (2012)
4. A. Lupei , V. Lupei, C. Gheorghe, Thermal shifts of Sm^{3+} lines in YAG and cubic sesquioxide ceramics, Optical Materials Express, **3** (10), 1641-1646 (2013) DOI:10.1364/OME.3.001641
5. A. Lupei, V. Lupei, C. Gheorghe, "Electronic structure of Sm^{3+} ions in YAG and cubic sesquioxide ceramics", Optical Materials **36 (2),** 419-424 (2013) , DOI 10.1016/j.optmat.2013.10.004
6. C. Gheorghe, A. Lupei, F. M. Voicu, C. Tiseanu, Emission properties and site occupation of Sm^{3+} ion doped Lu_2O_3 translucent ceramics, J. Alloys and Comp. **588**,388-393 (2014)
7. V Lupei, N Pavel and A Lupei**,** Improved laser efficiency by direct diode laser pumping of the radiation-resistant Nd:gadolinium–scandium–gallium garnet, Laser Physics, **24,** 4, 045801 (2014)
8 A. Lupei, V. Lupei, C. Gheorghe, S. Hau, A. Ikesue, Multicenters in Ce^{3+} visible emission of YAG ceramics, Optical Materials, **37** (2014) 727–733, DOI: 10.1016/j.optmat.2014.09.001
9. Lupei, A. Lupei, "Nd:YAG at its 50th anniversary:still to learn", to be published (J. of Luminescence)

II. COMMUNICATIONS IN INTERNATIONAL CONFERENCES

1. V. Lupei, A. Lupei, C. Gheorghe, L. Gheorghe, A. Achim, A. Ikesue, "Nd^{3+} and Yb^{3+} In disordered garnet crystals and ceramics", ICFE8, 26-31 Aug.2012, Udine, Italy - OPT 26P.
2. A. Lupei, C. Tiseanu, C. Gheorghe, F. Voicu, "Spectroscopic analysis of Sm^{3+} in C_2 and C_{3i} sites of Y_2O_3", ICFE8, Aug. 26-31, 2012, Udine (Italy), OPT 23P.
3. A.Lupei, C. Tiseanu, C. Gheorghe, "Electronic structure and energy transfer processes of Sm^{3+} in sesquioxides", ICOM 2012, 3-6 sept, 2012, Belgrad, Serbia, 144
4. C. Gheorghe, A.Lupei, F. Voicu, C. Tiseanu, "Sm^{3+} emission from different sites in Lu_2O_3 ceramics", 3rd International Conference on Rare Earth Materials (REMAT) Advances in Synthesis, Studies and Applications, Wroclaw, Poland, 26-28 April 2013

5. F. Voicu, A.Lupei, C. Gheorghe, C. Catalin, M. Dumitru, Sm doped YAG and sesquioxides transparent ceramics, " International Conference "Modern Laser Applications" Third Edition, INDLAS 2013, 20-24 May 2013, Bran, Romania, O11
6. V. Lupei, Selfquenching of Emission and Heat Generation in Nd Lasers Revisited, Poster AM4A.13 Advanced Solid-State Lasers, 27 oct. - 01 nov. 2013, Paris, Franta
7. V. Lupei, A. Lupei, C. Gheorghe, A Ikesue, Sensitization processes of Nd^{3+} and Yb^{3+} doped YAG ceramics for broadband pumped lasers, 9th Laser Ceramics Symposium (LCS), Dec. 2-6, 2013, Daejeon, Korea
8. A. Lupei, V. Lupei, C. Gheorghe, A. Ikesue, F. Voicu, Thermal effects on Sm^{3+}doped ceramic laser materials for ASE suppression, Poster AM4A.02 Advanced Solid-State Lasers, 27 oct. - 01 nov. 2013, Paris, Franta, Poster AM4A.02
9. V. Lupei, A. Lupei, C. Gheorghe, A. Ikesue, F. Voicu, Suppression of Nd and Yb ASE by Sm absorption in ceramics, 9th Laser Ceramics Symposium (LCS), Dec. 2-6, 2013, Daejeon, Korea
10. V. Lupei, A. Lupei, "Nd:YAG at its 50^{th} anniversary: still to learn", „17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter (ICL2014)" Invited lecture I 31
11. A. Lupei, V. Lupei, C. Gheorghe, S. Hau, A. Ikesue, 17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter (ICL2014), "Perturbed centers in visible emission of Ce^{3+}:YAG ceramic," Poster P 25.

III. UNPUBLISHED RESULTS

A large volume of new results will be the subject of further publication; several manuscripts are now in various stages of completion.

IV. OTHER IMPLICATIONS

The approach, method of investigation and the obtained results were useful in consolidation of the conclusions and identification of the general trends of this field of research, exposed in the recent (June 2013) book **"Ceramic Lasers"** by A. Ikesue (the inventor of transparent ceramic laser materials), Y. L. Yang and V. Lupei, Cambridge Univ. Press.