SYNTHESIS AND CHARACTERIZATION OF $La_3Ga_{5.5}Ta_{0.5}O_{14}$ DOPED WITH HOLMIUM AND YTTERBIUM*

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Ceramic langatate ($La_3Ga_{5.5}Ta_{0.5}O_{14}$) doped with holmium and ytterbium (1 at% and 3 at%, respectively) – LGT:Yb:Ho – was synthesized by solid-state reaction. The phase purity of LGT:Yb:Ho was analyzed by X ray diffraction. The sample was characterized by optical spectroscopy (absorption and luminescence). Green ($^5S_2$+$^5F_4 \rightarrow {}^5I_8$) and red ($^5F_5 \rightarrow {}^5I_8$) upconversion luminescence was obtained for the first time in ceramic LGT:Yb:Ho.

Key words: upconversion luminescence, Ho^{3+}, LGT.

1. INTRODUCTION

The aim of this paper is the investigation of the upconversion processes in langatate ceramics doped with Ho^{3+} and Yb^{3+}.

The crystals from the langasite family: langasite ($La_3Ga_5SiO_{14}$–LGS), langanite ($La_3Ga_{5.5}Nb_{0.5}O_{14}$–LGN) and langatate ($La_3Ga_{5.5}Ta_{0.5}O_{14}$–LGT) – generic LGX – are uniaxial partially disordered crystals, two different ions occupying the same crystallographic position.

The structure of these crystals is given by the formula $A_3BC_3D_2O_{14}$ where A represents the dodecahedral positions (distorted Thompson cubes), B – octahedral positions and C, D – tetrahedral positions. La^{3+} occupies the position A and can be substituted by the rare earth ions. The local symmetry at this site is C_2 [1]. In LGS Ga^{3+} and Si^{4+} share with equal probability the D position while in LGN and LGT Ga^{3+} and Nb^{5+} (Ta^{5+}) substitute the octahedral (B) position [2].

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There are only few papers concerning the growth of crystals from the langasite family doped with a single species of ions: Er^{3+} [3–6], Tm^{3+} [7–9], Ho^{3+} [10–11]. The green upconversion emission in LGT single crystal doped with low concentrations of Ho^{3+} and Yb^{3+} was observed recently [12]. In this paper, a LGT ceramic sample doped with higher concentrations of Holmium and Ytterbium was synthesized by solid-state reaction. The results of the spectroscopic investigations are compared with those obtained on single crystal [12].

2. EXPERIMENTAL

The $La_3Ga_{5.5}Ta_{0.5}O_{14}$ ceramic samples doped with holmium and ytterbium (1 at.% and 3 at.%, respectively) was synthesized by solid-state reaction.

Stoichiometric quantities of high purity oxides (La_2O_3, Ga_2O_3, Ta_2O_5, Ho_2O_3, Yb_2O_3) were mixed in an agate mortar, pressed with a hydraulic press at 2.5 MPa and then annealed in air at 1350ºC for 35 h. As a result of the thermal treatment, a solid ceramic sample was obtained. The sample was cut, dry polished and washed in an ultrasonic bath to remove the abrasive particles.

The phase purity of LGT:Yb:Ho was analyzed by X ray diffraction. The sample was characterized by optical spectroscopy (absorption and luminescence).

The absorption spectra were recorded using a tungsten-halogen lamp; the light beam was modulated using a mechanical chopper (Stanford Research Systems SR540) and analyzed using a Horiba Jobin-Yvon (1000M Series II) for the UV-vis and a Jarrell-Ash monochromator for IR. The detectors used were an EMI S-20 photomultiplier for UV-vis and a thermo-electrically cooled InGaAs for IR. The signal was processed by a lock-in amplifier (Stanford Research Systems SR830) connected to a PC.

The luminescence of the LGT:Yb:Ho solid sample was excited in blue (at 488 nm), with the Argon laser (Melles Griot, 35LAP431-230) and in IR, at 973 nm, with the laser diode DioMod980/30/400. The measurement chain was similar to that used for absorption measurements. All measurements were performed at room temperature.

Both absorption and luminescence spectra are averaged on the two polarization directions due to the polycrystalline structure of the ceramic sample.

3. RESULTS AND DISCUSSION

The diffraction lines shown in Fig. 1 belong to the langatate phase (card PDF-00-047-0532). Besides these diffraction lines, very-low-intensity extra diffraction lines, denoted with (*) and (o), which could be attributed, respectively, to $LaGaO_3$ (card PDF-01-072-8227) and to β-Ga_2O_3 (card PDF-00-041-1103) are observed.

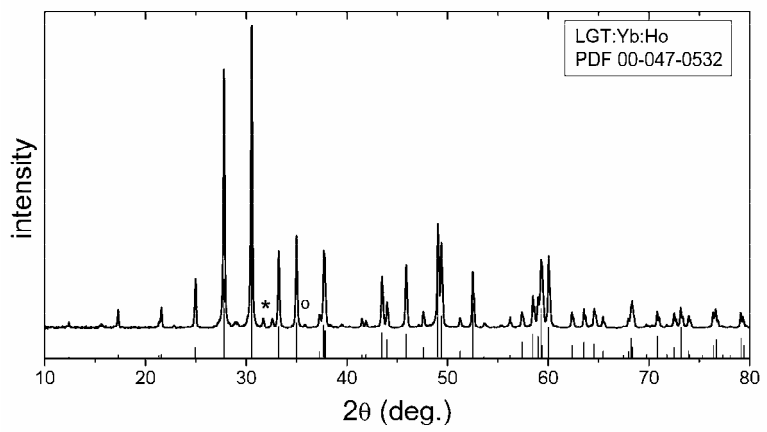

Fig. 1 – XRD pattern of LGT:Yb:Ho. The diffraction lines belong to the LGT phase (card PDF-00-047-0532); besides these diffraction lines, very low intensity 'extra' diffraction lines, denoted with (*) and (o), which could be attributed, respectively, to $LaGaO_3$ (card PDF-01-072-8227) and to β-Ga_2O_3 (card PDF-00-041-1103) are observed.

Experimental data acquired during this study will be discussed with reference to the energy level scheme for Ho^{3+} and Yb^{3+} ions depicted in Fig. 2.

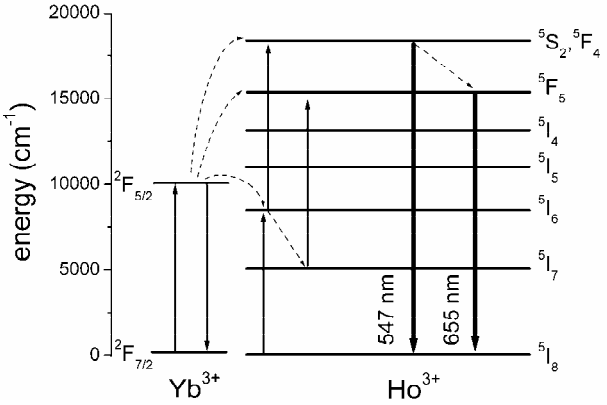

Fig. 2 – Energy level scheme of Ho^{3+} and Yb^{3+}. Upward arrows represent two-photon upconversion processes; downward arrows represent luminescence processes; downward dashed arrows are for multiphonon processes.

The absorption spectra of the LGT:Yb:Ho sample measured in the UV–vis and in IR domains are shown in Figs. 3 and 4. The observed bands in the UV-vis absorption spectrum of LGT:Yb:Ho are due to the $^5I_8 \rightarrow (^5G_1, {}^3H_5)$, $^3H_6$, $^5I_8 \rightarrow {}^3K_7$, $^5I_8 \rightarrow {}^5G_4$, $^5I_8 \rightarrow {}^5G_5$, $^5I_8 \rightarrow (^5G_6, {}^5F_1)$, $^5I_8 \rightarrow {}^5F_2$, $^5I_8 \rightarrow {}^5F_3$, $^5I_8 \rightarrow {}^5S_2, {}^5F_4$ and $^5I_8 \rightarrow {}^5F_5$ transitions. In the range of 800–1300 nm, the observed bands are due to the $^5I_8 \rightarrow {}^5I_5$ and $^5I_8 \rightarrow {}^5I_6$ transitions of Ho^{3+} and $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+}.

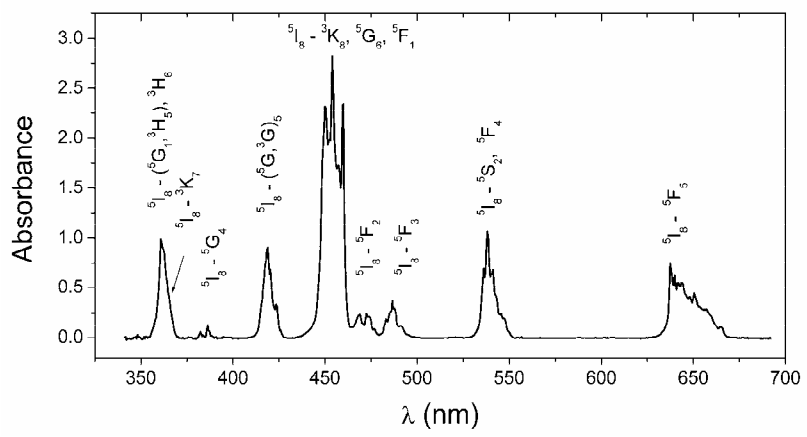

Fig. 3 – Absorption spectrum in the UV–vis domain of the LGT:Yb:Ho.

The absorption spectrum in the UV-vis spectral range (Fig. 3) is similar to that obtained on the single-crystalline sample used in Ref. [12]. In the IR, the absorption spectrum of Yb^{3+} (Fig. 4) presents line intensity ratios very different from those obtained in the single crystal sample.

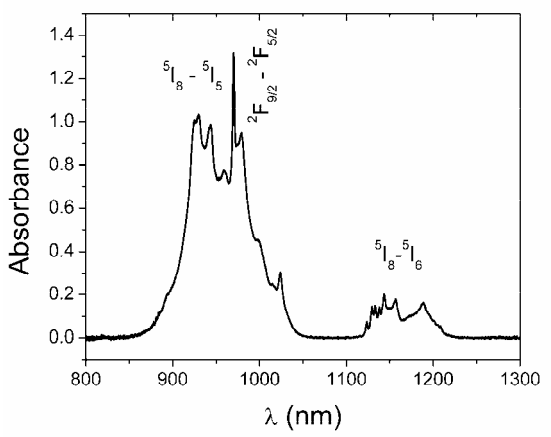

Fig. 4 – Absorption spectrum in the IR domain of the LGT:Yb:Ho.

In Fig. 5 is given the luminescence spectrum (excited at 488 nm with the argon laser, absorption transition $^5I_8 \rightarrow {}^5F_3$) in the wavelength range 700–1600 nm. Due to the experimental limitations (the sensitivity domain of the InGaAs detector is limited to ~1600 nm), we cannot observe the $^5I_7 \rightarrow {}^5I_8$ transition (at ~ 2000 nm). In their common spectral range, the spectrum obtained on the ceramic sample and the directly-pumped spectrum reported in Ref. [12] are similar.

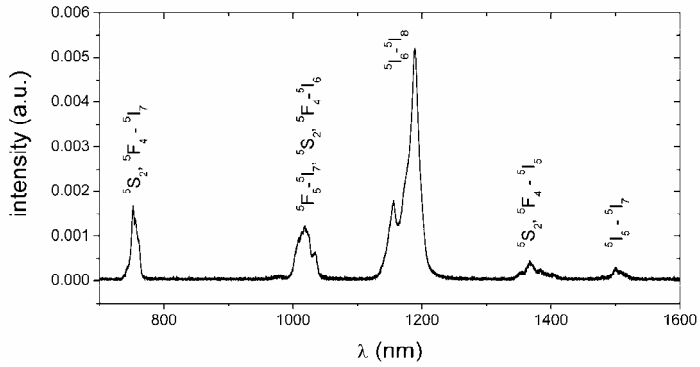

Fig. 5 – Luminescence spectrum in IR (700-1600 nm) domains of LGT:Yb:Ho excited at 488 nm. The luminescence transitions are indicated in the figure.

In Fig. 6, is given the spectrum of up-converted emission containing the green $^5S_2$, $^5F_4 \rightarrow {}^5I_8$ band and the red $^5F_5 \rightarrow {}^5I_8$ band. Two-photon energy transfer processes are involved in these emission processes. In the first step, an excitation from the $^2F_{5/2}$ level of Yb^{3+} is transferred on the $^5I_6$ level of Ho^{3+}: [$^2F_{5/2}$ (Yb^{3+}), $^5I_8$ (Ho^{3+})] $\rightarrow$ [$^2F_{7/2}$ (Yb^{3+}), $^5I_6$ (Ho^{3+})]; in the second step, the ($^5S_2$, $^5F_4$) level is populated *via* the $^5I_6$ intermediate level: [$^2F_{5/2}$ (Yb^{3+}), $^5I_6$ (Ho^{3+})] $\rightarrow$ [$^2F_{7/2}$ (Yb^{3+}), $^5S_2$, $^5F_4$ (Ho^{3+})]. The $^5F_5$ level is populated by the multiphonon transition from ($^5S_2$, $^5F_4$) and by $Yb^{3+} \rightarrow Ho^{3+}$ processes: [$^2F_{5/2}$ (Yb^{3+}), $^5I_8$ (Ho^{3+})] $\rightarrow$ [$^2F_{7/2}$ (Yb^{3+}), $^5I_6$ (Ho^{3+})] followed by multiphonon transition $^5I_6 \rightarrow {}^5I_7$ and by [$^2F_{5/2}$ (Yb^{3+}), $^5I_7$ (Ho^{3+})] $\rightarrow$ [$^2F_{7/2}$ (Yb^{3+}), $^5F_5$ (Ho^{3+})].

The dependence of the upconversion luminescence intensity on the incident pump power (log–log plot) is presented in Fig. 7. The slope in the log–log plot of the luminescence originating on ($^5F_4$, $^5S_2$) (green luminescence) is 1.80 and from $^5F_5$ (red luminescence) is 1.75, confirming the population of ($^5F_4$, $^5S_2$) and $^5F_5$ levels by two-photon processes (see Fig. 2).

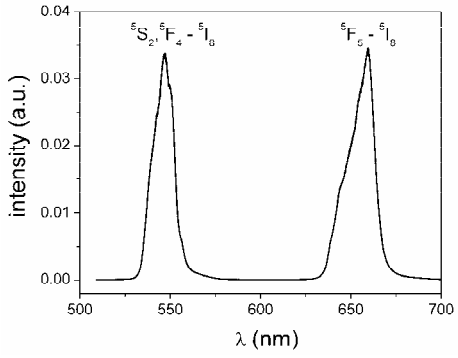

Fig. 6 – Upconversion luminescence spectrum of LGT:Yb:Ho excited at 973 nm.

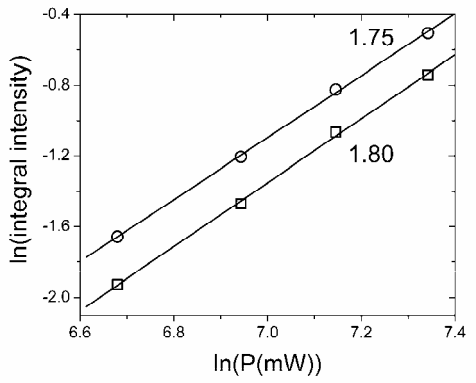

Fig. 7 – Log–log plot of the luminescence intensity *versus* IR pump intensity (P in mW) for the LGT:Yb:Ho ceramic sample. Squares: green luminescence; circles: red luminescence.

4. CONCLUSIONS

Preliminary data concerning synthesis and characterization of ceramic LGT:Yb:Ho was presented. LGT:Yb:Ho with good phase purity was obtained by solid-state reaction in air.

Under the excitation of the 973 nm laser, LGT:Yb:Ho ceramic sample emitted green and red light. The slopes in the double logarithmic plot of the green luminescence (corresponding to the transition ($^5S_2$, $^5F_4$) → $^5I_8$ of Ho^{3+} ion) and of the red luminescence ($^5F_5 \rightarrow {}^5I_8$) confirm the presence of two-photon processes.

The study of the spectroscopic properties of rare-earth-doped LGT can be performed on ceramic samples with much lower costs than the similar investigations performed on single crystals.

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REFERENCES

1. B.V. Mill, A.V. Butashin, G.G. Khodzhabagyan, E.L. Belokoneva, N.V. Belov, *Модифицированные редкоземельные галлаты со структурой $Ca_3Ga_2Ge_4O_{14}$*, Sov. Phys. Dokl. **27**, 434–437 (1982), (Dokl. Akad. Nauk SSSR **264**, 1385–1389) (in Russian).
2. S. Georgescu, O. Toma, A.M. Chinie, L. Gheorghe, A. Achim, A.S. Stefan, *Spectroscopic characteristics of langasite ($La_3Ga_5SiO_{14}$) and langatate ($La_3Ga_{5.5}Ta_{0.5}O_{14}$) crystals doped with Eu^{3+}*, Opt. Mater. **30**, 1007–1012 (2008)
3. W. Ryba-Romanowski, G. Dominiak-Dzik, P. Solarz, M. Berkowski, *Optical study of erbium-doped $La_3Ga_{5.5}Ta_{0.5}O_{14}$ single crystal,* Molec. Phys. **101**, 1067-1072 (2003).
4. Z.M. Wang, D.R. Yuan, X.Z. Shi, X.F. Cheng, D. Xu, M. Lv, L.H. Pan, S. Y. Guo, *Crystal growth and spectroscopic properties of Er: $La_3Ga_5SiO_{14}$ single crystals*, J. Crystal Growth, **257**, 141-145 (2003).

5. V.I. Burkov, O.A. Lysenko, B.V. Mill, *Absorption and Circular Dichroism Spectra of $La_3Ga_5SiO_{14}$ Crystals Doped with Pr^{3+}, Ho^{3+}, and Er^{3+} Ions*, Crystallography Reports, **55**, 983-989 (2010).
6. Z.M. Wang, Y.C. Liu, Y.S. Yin, D.R. Yuan, *Spectroscopic properties of $La_3Ga_5SiO_{14}$: Er^{3+} (1%) crystals*, Cryst. Res. Technol. **41**, 1142-1147 (2006).
7. Y.S. Kim, K. H. Auh, *Tm-doped Langasite ($La_3Ga_5SiO_{14}$) crystals grown by the Czochralski method for optical applications,* Mater. Lett., **57**, 28-31 (2002).
8. Z. Wang, Y. Yin, D. Yuan, *Crystal growth and optical properties of Tm: $La_3Ga_5SiO_{14}$ single crystals*, Appl. Phys. A – Materials Science & Processing, **85**, 437-440 (2006).
9. S. Georgescu, A.M. Voiculescu, C. Matei, A. Stefan, O. Toma, R. Birjega, *Upconversion luminescence in langatate ceramics doped with Tm^{3+} and Yb^{3+},* J. Lumin., **154**, 74-79 (2014).
10. A.A. Kaminskii, B.V. Mill, A.V. Butashin, K. Kurbanov, P.A. Polyakova, *Spectroscopy of disordered $La_3Ga_5SiO_{14}$ single- crystals doped with Pr^{3+}, Ho^{3+}, and Er^{3+} ions*, Phys. Stat. Solidi A **120**, 253-266 (1990).
11. Z.M. Wang, D.R. Yuan, Y.S. Yin, G. Su, *Crystal growth and spectroscopic properties of Ho: $La_3Ga_5SiO_{14}$ single crystals,* Opt. Mater., **29**, 663-666 (2007).
12. R. Lisiecki, W. Ryba-Romanowski, L. Macalik, J. Komar, M. Berkowski, *Optical study of $La_3Ga_{5.5}Ta_{0.5}O_{14}$ single crystal co-doped with Ho^{3+} and Yb^{3+}*, Appl. Phys. B, **116**, 183-194 (2014).