Transparent glass-ceramics with Yb$^{3+}$,Ho$^{3+}$:YNbO$_4$ nanocrystals for green phosphors

A Volokitina$^1$, P Loiko$^{1,*}$, O Dymshits$^2$, M Tsenter$^2$, S Zapalova$^2$, K Bogdanov$^1$, A Baranov$^1$ and A Zhilin$^2$

$^1$ITMO University, Kronverkskiy pr., 49, 197101 St. Petersburg, Russia
$^2$NITIOM S.I. Vavilov State Optical Institute, 36 Babushkina St., 192171 St. Petersburg, Russia

Abstract. We report on synthesis, structure, Raman and optical spectroscopy of transparent glass-ceramics (GCs) containing nanocrystals of rare-earth orthoniobates, Yb$^{3+}$,Ho$^{3+}$:YNbO$_4$ and β-quartz solid solution. Under the near-IR excitation, the GCs exhibit intense upconversion luminescence which color properties can be tuned by the heat-treatment regime due to the structural changes in the orthoniobate nanocrystals. The developed GCs are promising as thermal shock resistant green phosphors.

1. Introduction

Materials containing couples of Yb$^{3+}$ ion and other RE$^{3+}$ ion are attractive for the development of upconversion phosphors [1]. In the particular case of RE$^{3+}$ = Er$^{3+}$, Tm$^{3+}$ or Ho$^{3+}$, this is supported by direct and efficient energy-transfer (ET) process Yb$^{3+}$ → RE$^{3+}$ facilitated by the resonance in energy of the excited states of the considered ions. Transparent glass-ceramics (GCs) containing nanosized crystals and an amorphous residual phase are promising matrices for (Yb$^{3+}$,RE$^{3+}$) codoping [2-4]. With a proper selection of the composition of the initial glass and the regime of the secondary heat-treatment leading to crystallization, one can ensure predominant entering of the active ions in the nanocrystalline phase [5]. This opens the possibility of tuning of emission color according to structural transformations of these nanocrystals [6].

Rare-earth orthoniobates, RENbO$_4$ (where RE = La, Y, Gd, and Lu are the host-forming “passive” ions), doped with the active ions as specified above, are promising luminescence materials [7-10]. A clear example of such a material is fergusonite, YNbO$_4$, belonging to the class of ABO$_4$-type oxides, and exhibiting two main modifications, namely the tetragonal ( scheelite-like) and monoclinic ones [11,12]. Rare-earth orthoniobates possess low phonon frequencies (for oxide matrices), $\hbar\nu_{ph}$$\sim$800 cm$^{-1}$, they offer high available doping concentrations with a weak quenching of luminescence, long emission lifetimes, strong interionic interactions, high refractive index ($n \sim 2.1$) and relatively broad bandgap of $\sim$4.3 eV.

GCs containing the nanocrystals of rare-earth orthoniobates, RENbO$_4$, have been recognized as efficient luminescent materials [13,14]. To date, GCs containing Yb$^{3+}$, Er$^{3+}$:YNbO$_4$ and Yb$^{3+}$, Eu$^{3+}$: YNbO$_4$ nanocrystals have been prepared showing intense green and red upconversion luminescence (UCL) under the near-IR excitation by InGaAs laser diodes, respectively. In the present work, we have
developed and studied GCs based on the nanocrystals of Yb$^{3+}$:Ho$^{3+}$:YNbO$_4$ and β-quartz solid solution, for the first time, to the best of our knowledge.

2. Synthesis and structure

The initial glass with the composition of 18 Li$_2$O – 27 Al$_2$O$_3$ – 55 SiO$_2$ (mol%) [13] doped with the rare-earth oxides, 2.2 Y$_2$O$_3$, 0.5 Yb$_2$O$_3$, 0.5 Ho$_2$O$_3$, and niobium oxide, 3.2 Nb$_2$O$_5$ (mol%) was prepared by the melt-quenching technique. Batch to produce 300 g of glass was melted in a quartz ceramic crucible in a laboratory electric furnace at 1580 °C for 4 h with stirring, then the glass melt was bubbled by oxygen for 0.5 h to remove the OH-groups from the melt. The melt was poured onto a metal plate and the as-cast glass was annealed at 620 °C. The initial glass was transparent and had a yellow coloration. The calculated concentration of the RE$^{3+}$ active ions in the initial glass was $N_{Yb} = N_{Ho} = 1.97 \times 10^{20}$ cm$^{-3}$ (measured glass density, $\rho = 2.76$ g/cm$^3$). To produce transparent GCs, the initial glass was heat-treated at temperatures ranging from $T = 720$ to 1000 °C for 6–24 h in air.

![XRD patterns and Raman spectra](image)

**Figure 1(a, b).** (a) XRD patterns and (b) Raman spectra [combined data for $\lambda_{exc} = 514$ nm (<600 cm$^{-1}$) and 488 nm (>600 cm$^{-1}$)] of the initial glass and GCs containing Yb$^{3+}$:Ho$^{3+}$:YNbO$_4$ nanocrystals. The numbers denote the heat-treatment regime, °C / hours.

The structure of GCs was studied with X-ray diffraction (XRD) and Raman spectroscopy, figure 1. The initial glass is X-ray amorphous. Crystals of RENbO$_4$ with a disordered fluorite-type cubic structure (T$^\text{I}$) (sp. gr. $Fm\bar{3}m$) evolve in the glass heat-treated at 720 °C for 6 h, see figure 1(a). The prolongation of this heat-treatment for 24 h leads to crystallization of tetragonal phase with orthorhombic distortion (T) RENbO$_4$ (sp. gr. $Im\bar{a}2$); traces of β-quartz solid solution (ss) appear as well. For T-phase, the RE$^{3+}$ cations occupy the $S_1$ symmetry site with an VIII-fold O$^2-$coordination. After heat-treatments at 800–1000 °C, the GCs contain two crystalline phases, RENbO$_4$, and β-quartz ss. High thermal shock resistance of GCs is ensured by crystallization of the latter phase. Monoclinic (M) RENbO$_4$ crystals (fergusonite-type structure, sp. gr. $I2/a$) appear additionally to the distorted tetragonal ones after heat-treatment at 1000 °C. For M-phase, the RE$^{3+}$ cations occupy the $C_2$ symmetry site also with an VIII-fold O$^2-$coordination. The large RE$^{3+}$-RE$^{3+}$ distances for the RENbO$_4$ crystals and the closeness of ionic radii of Y$^{3+}$ (1.019 Å), Yb$^{3+}$ (0.985 Å) and Ho$^{3+}$ (1.015 Å) [15] determine the possibility for the active ions to enter easily into the YNbO$_4$ lattice where they are expected to replace the Y$^{3+}$ "passive" ones.

Raman spectra of the initial glass and GCs are shown in figure 1(b). Raman spectra of the initial glass contains two broad bands centered at ~472 cm$^{-1}$ and 860 cm$^{-1}$. Heat-treatment at 720 °C / 6 h induces the modification of the spectrum due to precipitation of RENbO$_4$ nanocrystals with a disordered fluorite-type cubic structure. After the heat-treatment at 720 °C / 24 h, the Raman spectra show enhanced 801 cm$^{-1}$ band and some other signs of the T-RENbO$_4$ crystals, namely several low-frequency bands at 121-344 cm$^{-1}$ [16]. The increase of the heat-treatment temperature to 800 °C leads to the appearance of two bands at 482 cm$^{-1}$ and at 1086 cm$^{-1}$ indicative for β-quartz ss [17]. Finally,
the heat-treatment at 1000 °C results in the appearance of several bands at 238, 426, 442, 690 and 802 cm\(^{-1}\) representing precipitation of M-RENbO\(_4\) crystals [18].

3. Optical spectroscopy

The absorption spectra of the initial glass and GCs containing absorption bands of the Yb\(^{3+}\) and Ho\(^{3+}\) ions are shown in Figure 2. The spectra vary accordingly to the structural transformations of the GCs. This proves that the active ions, Ho\(^{3+}\) and Yb\(^{3+}\), are embedded in the YNbO\(_4\) nanocrystals.

As for Yb\(^{3+}\) ions, the broad absorption band spanning from 850 nm to 1050 nm is due to the \(^{2}\text{F}_{7/2} \rightarrow ^{2}\text{F}_{5/2}\) transition, and it can be used for their excitation with the InGaAs laser diodes. For the initial glass, the maximum absorption cross-section of Yb\(^{3+}\) ions is \(\sigma_{abs} = \alpha_{abs}/N_{Yb} = 2.1 \times 10^{-20}\) cm\(^2\) at 977.1 nm (zero-phonon line, ZPL). For GCs obtained by heat-treatment at 1000 °C, the position of the ZPL shifts to 974.5 nm, accompanied by the rise of absorption at shorter wavelengths, so that the maximum \(\sigma_{abs} = 1.29 \times 10^{-20}\) cm\(^2\) at 953.2 nm. For Ho\(^{3+}\) ions, the maximum \(\sigma_{abs} = 0.43 \times 10^{-20}\) cm\(^2\) at 1947 nm (for the initial glass) and it increases to \(0.60 \times 10^{-20}\) cm\(^2\) at 1936 nm (for GCs obtained by heat-treatment at 1000 °C).

![Figure 2(a, b). Absorption spectra of the initial glass and GCs containing Yb\(^{3+}\), Ho\(^{3+}\):YNbO\(_4\) nanocrystals (a) in the visible and (b) in the near-IR. The numbers denote the heat-treatment regime, °C / hours. Each spectrum is shifted on 0.5 cm\(^{-1}\) (a) or 0.2 cm\(^{-1}\) (b) for the convenience of observation.](image)

![Figure 3(a, b). (a) Scheme of the energy-levels of Yb\(^{3+}\) and Ho\(^{3+}\) ions with the relevant processes: GSA and ESA – ground- and excited-state absorption, respectively, NR – non-radiative relaxation, UCL – upconversion luminescence, ET – energy-transfer. (b) Upconversion luminescence spectra for the initial glass and GCs containing Yb\(^{3+}\), Ho\(^{3+}\):YNbO\(_4\) nanocrystals, \(\lambda_{exc} = 960\) nm (the spectra are normalized to unity).](image)

Under the excitation by a commercial InGaAs laser diode emitting at ~962 nm (to the \(^{2}\text{F}_{5/2}\) state of the Yb\(^{3+}\) ion), intense visible emission is detected from the initial glass and GCs, see figure 3(b). It is
related to the upconversion in the (Yb$^{3+}$, Ho$^{3+}$) ion couple, see figure 3(a). This process includes ground-state absorption (GSA) by Yb$^{3+}$ ions, energy-transfer (ET) $2F_{22}(Yb^{3+}) \rightarrow 5I_6(Ho^{3+})$, excited-state absorption (ESA) from the $5I_6$ and $5I_7$ intermediate states, and emission from the higher-lying $5F_5$ and $5S_2+5F_4$ excited-states of Ho$^{3+}$. A remarkable feature of the GCs is the redistribution of intensity between the green (535-555 nm, the $5S_2+5F_4 \rightarrow 5I_6$ transition) and red (635-670 nm, the $5F_5 \rightarrow 5I_6$ transition) upconversion luminescence (UCL) with the heat-treatment thus leading to the tunability of color properties.

The color coordinates (Commission internationale de l’eclairage, CIE 1931) for UCL of the initial glass are $x = 0.534$, $y = 0.441$ (dominant wavelength, $\lambda_d = 584$ nm, color purity, $p = 93\%$, orange-yellow color) and for the GCs prepared by the heat-treatment at 1000 °C, they are $x = 0.317$, $y = 0.648$ ($\lambda_d = 553$ nm, $p = 99\%$, green color).

4. Conclusion
Transparent thermal shock resistant glass-ceramics containing (Yb$^{3+}$, Ho$^{3+}$) ion couple entering the fluorite-type, distorted tetragonal and monoclinic yttrium orthoniobate nanocrystals, YNbO$_4$, are synthesized for the first time, to the best of our knowledge. The possibility to excite intense color-tunable (orange-green) upconversion luminescence is demonstrated with the synthesized GCs. Such materials are of interest for green phosphors. Further work will focus on the determination of the efficiency of the Yb$^{3+}$ → Ho$^{3+}$ ET.

Acknowledgments
This work was partly supported by the RFBR (Grant 16-03-01130). P.L. acknowledges financial support from the Government of the Russian Federation (Grant 074-U01) through ITMO Post-Doctoral Fellowship scheme.

References
[1] Auzel F 2004 Chem. Rev. 104 139
[2] Wang Y and Ohwaki J 1993 Appl. Phys. Lett. 63 3268
[3] Biswas A, Maciel G S, Friend C S and Prasad P N 2003 J. Non-Cryst. Solids 316 393
[4] Dymshits O S, Loiko P A, Skoptsov N A, Malyarevich A M, Yumashev K V, Zhilin A A, Alekseeva I P, Tsenter M Ya and Bogdanov K 2015 J. Non-Cryst. Solids 409 54
[5] de Pablos-Martin A, Patzig C, Höche T, Durán A and Pascual M J 2013 Cryst. Eng. Comm. 15 6979
[6] Lu J, Ma E, Chen D, Yu Y and Wang Y 2006 J. Phys. Chem. B 110 20843
[7] Nazarov M, Kim Y J, Lee E Y, Min K I, Jeong M S, Lee S W and Noh D Y 2010 J. Appl. Phys. 107 103104.
[8] Liu X, Lü Y, Chen C, Luo S, Zeng Y, Zhang X, Shang M, Li C and Lin J 2014 J. Phys. Chem. C 118 27516
[9] Li K, Zhang Y, Li X, Shang M, Lian H and Lin J 2015 Phys. Chem. Chem. Phys. 17 4283
[10] Liu Y, Tang X, Yan L, Li K, Liu X, Shang M, Li C and Lin J 2013 J. Phys. Chem. C 117 21972
[11] Blasse G and Bril A 1970 J. Lumin. 3 109
[12] Mather S A and Davies P K 1995 J. Amer. Ceram. Soc. 78 2737
[13] Dymshits O S, Alekseeva I P, Zhilin A A, Tsenter M Ya, Loiko P A, Skoptsov N A, Malyarevich A M, Yumashev K V, Mateos X and Baranov A V 2015 J. Lumin. 160 337
[14] Loiko P A, Dymshits O S, Alekseeva I P, Zhilin A A, Tsenter M Ya, Vilejshikova E V, Bogdanov K V, Mateos X and Yumashev K V 2016 J. Lumin. 179 64
[15] Shannon R D 1976 Acta Cryst. A32 751
[16] Blasse G 1972 J. Solid State Chem. 7 169
[17] Chuvaeva T I, Dymshits O S, Petrov V I, Tsenter M Ya, Shaskin A V, Zhilin A A and Golybkov V V 2001 J. Non-Cryst. Solids 282 306
[18] Yashima M, Lee J-H, Kakihana M and Yoshimura M 1997 J. Phys. Chem. Solids 58 1593