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Er-doped and Er, Yb co-doped oxyfluoride glasses and glass–ceramics, structural and optical properties

Radosław Lisiecki [a,*], Elżbieta Augustyn [b], Witold Ryba-Romanowski [a], Michał Żelechower [b]

[a] Institute of Low Temperature and Structure Research Polish Academy of Sciences, Wrocław 50-422, Poland
[b] Department of Material Science, Silesian University of Technology, Katowice 40-019, Poland

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ABSTRACT

The selected glasses and glass–ceramics pertinent to following chemical composition in mol%:48%SiO_2–11%Al_2O_3–7%Na_2O–10%CaO–10%PbO–11%PbF_2–3%ErF_3 and 48%SiO_2–11%Al_2O_3–7%Na_2O–10%CaO–10%PbO–10%PbF_2–1%ErF_3–3%YbF_3 have been manufactured from high purity components (Aldrich) at 1450 °C in normal atmosphere. Glass optical fibers were successfully drawn. Subsequently they were subject to the heat-treatment at 700 °C in various time periods. The preceding differential thermal analysis (DTA) studies allowed estimating both the fiber drawing temperature and the controlled crystallization temperature of glass fibers. It has been observed that the controlled heat-treatment of oxyfluoride glass fibers results in the creation of $Pb_5Al_3F_{19}$, $Er_4F_2O_{11}Si_3$ and $Er_3FO_{10}Si_3$ crystalline phases. The identified phases were characterized by X-ray powder diffraction (XRD) and confirmed by selected area electron diffraction (SAED). The fibers consist of mixed amorphous–crystalline microstructure with nanocrystals of size even below 10 nm distributed in the glassy host. Their morphology was investigated applying high-resolution transmission electron microscopy. Optical properties and excited state relaxation dynamics of optically active ions (Er^{3+}, Yb^{3+}) in glass and glass–ceramics have been studied. Based on absorption spectra the Judd–Ofelt analysis was carried out. The main attention was directed to NIR luminescence at. 1.6 μm related to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er^{3+} and less effective emission associated with $^4I_{11/2} \rightarrow {}^4I_{15/2}$ Er^{3+} and $^2F_{5/2} \rightarrow {}^2F_{7/2}$ Yb^{3+} transitions. The dissimilar spectroscopic properties have been revealed for glasses and glass–ceramic samples, respectively. The reduction of emission linewidth at 1.6 and 1.0 μm combined with substantial increase of $^4I_{13/2}$ lifetimes of erbium in glass–ceramics appear to be evidences that Er^{3+} ions are accommodated in crystalline phases. The structural and optical characteristics of oxyfluoride glass–ceramic fibers indicate that these optical systems may be considered as promising materials for Er-doped optical amplifiers operating within third telecommunication window.
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1. Introduction

Wide interest in materials doped with rare-earth ions seems to be a consequence of their potential application, for instance as optical fiber amplifiers. In particular, materials doped with Er^{3+} can be used for signal amplification at the wavelength of 1.55 μm corresponding to the telecommunication window (the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition). The extensive development of fiber-optic technology for high-effective Erbium-doped fiber amplifiers (EDFA) becomes increasingly attractive. In addition Er^{3+} and Yb^{3+} co-doping in oxyfluoride glasses enables to increase the absorption cross-section at 980 nm band, hence they can be optically pumped by commercial diodes [1,2]. One of the promising candidates for optical amplifiers is the oxyfluoride transparent glass–ceramics in the form of optical fibers. Oxyfluoride transparent glass–ceramics combine some features of glasses (easier shaping or lower than single crystals cost of fabrication) and some advantages of rare-earth doped single crystals (narrow absorption/emission lines and longer lifetimes of luminescent levels). In relation to that the material seems to be promising candidate for efficient fiber amplifiers. Moreover, the manufacturing as well as structural and optical examination of the oxyfluoride glass–ceramic fibers doped with rare-earth ions seems to be a serious challenge.

Many studies were dedicated to the oxyfluoride glasses and glass–ceramics in the ternary systems: SiO_2–PbO–PbF_2 [3–5], SiO_2–CdF_2–PbF_2 [6–8], GeO_2–PbO–PbF_2 [9–11], however in the papers mentioned above only the bulk (or thin film) form of glass–ceramics materials were considered but not fibers.

The intention of this work is to get a more close insight into microstructure of the glass–ceramic fibers with Er/Yb rich fluoride or oxyfluoride nano-crystals distributed in the oxyfluoride glassy host and assess the potential of these composite materials for application in optoelectronics.

* Corresponding author. Tel.: +48 71 343 50 21; fax: +48 71 344 10 29.
E-mail address: R.Lisiecki@int.pan.wroc.pl (R. Lisiecki).

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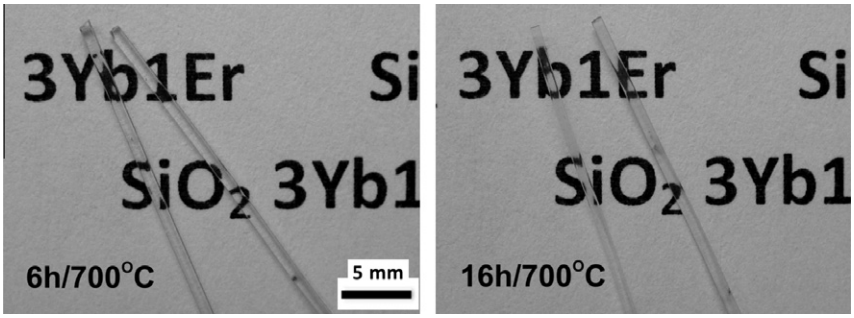

Fig. 1. Er /Yb co-doped transparent glass–ceramics fibers heat treated for 6 and 16 h at 700^{0}C.

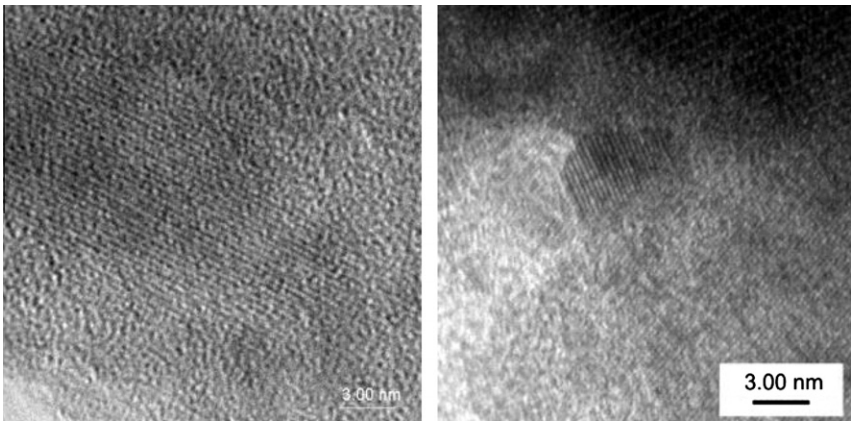

Fig. 2. High-resolution TEM images of Er doped and Er/Yb co-doped glass–ceramics fiber structure. Ordered and disordered areas of several nanometers size are clearly visible.

2. Experimental

The high quality fluoride and oxide substrates (99,99% purity) were used to fabricate the precursor glasses with following composition 48%SiO_2–11%Al_2O_3–7%Na_2O–10%CaO–10%PbO–11% PbF_2–3%ErF_3, 48%SiO_2–11%Al_2O_3–7%Na_2O–10%CaO–10%PbO–10% PbF_2–3%YbF_3–1%ErF_3 and 48%SiO_2–11%Al_2O_3–7%Na_2O–10%CaO–10%PbO–13%PbF_2–1%ErF_3 (mol%). Starting materials were mixed and subsequently put in a covered corundum crucible. The mixture was melted at 1450 °C for 2 h in normal atmosphere. The liquid material was poured into preheated copper mould to obtain a rapid quenching. The fibers were drawn (720–740 °C; drawing rate 5–40 cm/s) from the preform (rod) employing the mini-tower (vertical resistant furnace with mobile head) and subsequently they were heat-treated (700 °C) to achieve controlled precipitation of crystalline phases. The preceding differential thermal analysis (DTA) allowed to determine both the fiber drawing temperature (between the glass transition temperature T_g = 614 °C and the crystallization onset temperature T_X = 769 °C) and the controlled crystallization temperature of glass fibers (above T_g but below the softening point). The DTA measurements were performed using a NETZSCH differential scanning calorimeter DSC 404/3/F with 10 K/min heating rate. The crystal structure of the grown nanocrystals has been determined by X-ray diffraction (XRD- X-Pert Philips diffractometer, curved graphite monochromator, Cu Kα radiation at 40 kV and 30 mA) and confirmed by SAED. The morphological properties were measured with transmission electron microscope (HRTEM JEOL JEM-3010 equipped with the GATAN CCD slow-scan camera, at an accelerating voltage of 300 kV). The emission spectra were excited by an argon ion laser and Apollo Instruments diode lasers at 980 nm. The luminescence was dispersed by an Optron DongWoo monochromator with 750 mm focal length and detected by a Hamamatsu R-955 photomultiplier or InGaAs detector depending on the spectral range. Selective excitation from the Continuum Surelite optical parametric oscillator (OPO) pumped with the third harmonic of Nd:YAG was employed to record the luminescence decay curves. The duration of the laser pulses was 4 ns. The resulting transients were acquired with a cooled InSb Janson J10D detector or a Hamamatsu R-928 photomuliplier coupled with a Tektronix model TDS 3052 digital oscilloscope.

3. Results and discussion

3.1. Structural and morphological characterization

The transparent oxyfluoride glass–ceramic thick fibers provided for structure examination were obtained by controlled heat-treatment of glass fibers (6 h and 16 h at 700 °C). The shapes of the fibers are displayed in Fig. 1. The high-resolution transmission electron microscope images of erbium doped and erbium–ytterbium co-doped glass–ceramic fibers presented in Fig. 2 comprise both the crystalline and the amorphous areas of various sizes (several nanometers). The identification of the nano-crystals structure (Er/Yb co-doped samples) was carried out upon the sample fibers heated for longer period (50 h). Based upon the X-ray pattern shown in Fig. 3, the following phases: $Er_4F_2O_{11}Si_3$ (triclinic; ICSD 51510), $Pb_5Al_3F_{19}$ (triclinic; ICSD 91325) and $Er_3FO_{10}Si_3$ (monoclinic; ICSD 92512) were identified. The latter two phases have been mentioned by other authors in [12,13] respectively. In order to confirm the XRD identification of crystalline phases in glass–ceramic fiber, a high-resolution transmission electron microscopy combined with selected area electron diffraction

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