Spectral properties of novel transparent glass-ceramics based on Fe$^{2+}$:ZnAl$_2$O$_4$ nanocrystals

K Eremeev$^{1,2,*}$, O Dymshits$^{2,**}$, I Alekseeva$^3$, A Khubetsov$^2$, S Zapalova$^2$, M Tsenter$^2$, L Basyrova$^3$, P Loiko$^4$, A Zhilin$^2$ and V Popkov$^5$

$^1$ Saint-Petersburg State Institute of Technology, 26 Moscovsky Pr., 190013 St. Petersburg, Russia
$^2$ S.I. Vavilov State Optical Institute, 36 Babushkina St., 192171 St. Petersburg, Russia
$^3$ ITMO University, 49 Kronverkskiy Pr., 197101 Saint-Petersburg, Russia
$^4$ Centre de Recherche sur les Ions, les Matériaux et la Photonique (CIMAP), UMR 6252 CEA-CNRS-ENSICAEN, Université de Caen Normandie, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex 4, France
$^5$ Ioffe Institute, 26 Politekhnicheskaya St., 194021 St Petersburg, Russia

*E-mail: kirilleremeev42@gmail.com; **e-mail: vodym1959@gmail.com

Abstract. Transparent glass-ceramics of the zinc aluminum silicate system nucleated by TiO$_2$ and doped with FeO were developed by melt-quenching at 1580 °C with subsequent secondary heat-treatments at 720 – 1050 °C. The glass-ceramics based on nanosized gahnite crystals were characterized by X-ray diffraction, Raman and optical spectroscopy. The glass-ceramics exhibit a broad (1.5-2.5 μm) absorption due to the $^5$E $\rightarrow$ $^5$T$_2$ ($^5$D) transition of Fe$^{2+}$ ions in T$_d$ sites in gahnite crystals. They are promising as saturable absorbers of the short-wave IR lasers.

1. Introduction

Optical materials doped by Fe$^{2+}$ ions in tetrahedral site symmetry positions and thus demonstrating intense absorption in the spectral range of 2-3 μm are promising for the development of active elements and passive Q-switches of lasers in the mid-IR spectral range. One of the such materials is magnesium aluminate spinel optical ceramics [1]. Transparent glass-ceramics (GCs) based on nanosized spinel crystals have advantages over single crystals and optical ceramics due to the flexibility and convenience of manufacturing by a glass melting technology, a variety of nanocrystal compositions, structures and sizes controlled by the heat-treatment schedule of the same initial glass. Previously, we developed transparent GCs in the zinc-aluminum silicate (ZAS) system containing nanosized gahnite (ZnAl$_2$O$_4$) crystals doped with cobalt Co$^{2+}$ ions [2,3] and promising as passive Q-switches of Er lasers of the 1.5-μm eye-safe spectral region [4]. Their high transparency and high laser damage threshold were demonstrated [4,5]. We are not aware of any study of GCs based on gahnite nanocrystals doped with Fe$^{2+}$ ions. The aim of this work is the development of novel transparent GCs of the ZAS system based on nanosized gahnite crystals doped with Fe$^{2+}$ ions, and study of the relationship between their spectroscopic properties, the phase composition and structure.
2. Experimental

2.1. Glass synthesis and preparation of glass-ceramics
The glass with a composition of 25 ZnO, 25 Al₂O₃, 50 SiO₂ (mol %) nucleated by 9 mol% TiO₂ and
doped with 0.6 mol% FeO was melted at 1580 °C with stirring and annealed at 680 °C. The batch
weight was 400 g. To promote the growth of spinel nanocrystals, the glass was subjected to secondary
two-stage heat-treatment at 750 to 1050 °C with a holding time of 6 h (the first, nucleation stage heat-
treatment was at 720 °C for 6 h).

2.2. Characterization of glass-ceramics
The sequence of phase transformations was determined by the differential scanning calorimetry (DSC)
method. For the DSC study, bulk samples of about 20 mg in weight were used. A simultaneous
thermal analyzer NETZSCH STA 449 F3 Jupiter with a dynamic flow atmosphere of Ar was
employed. The temperature range was RT - 1250°C, and the heating rate was 10°C/min. The samples
were the initial glass and the glass heat-treated at the nucleation stage of 720°C for 6 h. Densities were
determined by the hydrostatic weighing method in the toluene. XRD patterns of powdered samples
were recorded by a Shimadzu XRD-6000 diffractometer with Cu Kα radiation and a Ni filter. The
parameters of the unit cell (a=b=c) of gahnite nanocrystals were determined using the Rietveld
refinement in the MAUD program. The mean crystal sizes were estimated from broadening of the X-
ray diffraction peak at 2θ ≈ 65.0° according to the Scherrer equation:

\[ D_{\text{XRD}} = \frac{K\lambda}{\Delta(2\theta) \cos\theta} \]  

where \( \lambda \) is the wavelength of the X-ray radiation (1.5406 Å), \( \theta \) is the diffraction angle, \( \Delta(2\theta) \) is the
width of the peak at half of its maximum and \( K \) is the constant assumed to be 1. The error for the
crystal size estimation was ~5%. The relative gahnite fraction was estimated by the intensity of the
ghanite peak with 2θ = 36.6°. All the spectroscopic studies were performed at room temperature (RT,
20 °C). The Raman spectra were measured with the Renishaw inVia confocal Raman microscope
using a Leica ×50 objective and an edge filter. The excitation wavelength \( \lambda_{\text{exc}} \) was 514 nm (Ar⁺ ion
laser). The absorption spectra of the initial glass and GCs were recorded with a Shimadzu 3600
spectrophotometer in the spectral range 250 - 3300 nm with a resolution of 1 nm. We used plane-
parallel polished plates with a thickness of 1 mm. Absorption coefficient \( \alpha \) was calculated taking into
account reflection losses.

3. Results and discussion

3.1 Differential Scanning Calorimetry (DSC) studies
Figure 1 presents the results of the DSC study of the initial glass and glass heat-treated at the
nucleation stage. Nucleation pronouncedly affects the kinetics of all processes occurring during
heating: the glass transition temperature \( T_g \) decreases by ~10 °C; the temperature of gahnite
crystallization decreases by ~30 °C; there is also the difference in high-temperature parts of the DSC
curves associated with rutile (TiO₂) and cristobalite (SiO₂) crystallization.

3.2 Powder X-ray Diffraction (XRD) analysis
The initial glass (Figure 2) shows an amorphous halo with a maximum at 2θ = 25.5° and no sign of
any crystalline phase. The traces of gahnite crystals are seen on the XRD pattern of the glass heat-
treated at 720°C for 6 h: there are three of its strongest peaks with maxima at 2θ = 31.2°, 36.6° and 65.5°.
After two-stage heat-treatments, all gahnite peaks appear on the XRD patterns; and it remains the sole
crystalline phase in GCs prepared by heat-treatments in the range of 750 – 950 °C. With increasing the
heat-treatment temperature, the position of the amorphous halo shifts from 2θ = 25.5° toward 22°, its
position in silica glass, which indicates the enrichment of the residual glass with silica caused by the
formation of gahnite and zinc aluminotitanate (ZAT) amorphous phase [2,3,6]. The nucleating agent,
TiO₂, crystallizes in the form of rutile starting from the heat-treatment at 1000 °C.
Figure 1. DSC curves of the initial glass and glass heat-treated at 720°C for 6 h. $T_g$ stands for glass transition temperature, $T_{on}$ stands for the onset crystallization temperature.

The gahnite crystallinity fraction increases with increasing the heat-treatment temperature (Figure 3), first gradually (for temperatures of the second stage varying from 750 to 950 °C), then sharply (for temperatures of 1000 °C and 1050 °C). Previously, we demonstrated the development of three-phase immiscibility in the structure of the base glass under study [2,3,6]: during heat-treatment at the nucleation stage, amorphous ZAT regions and low-silicate regions enriched with zinc aluminate are formed. Gahnite crystallizes from these low-silicate areas enriched with zinc aluminate. When rutile is crystallized from amorphous ZAT regions, an additional source of gahnite crystallization appears, and a noticeable increase in the degree of crystallization can be observed. So, this sharp increase in intensity may be due to the additional gahnite crystallization from the zinc aluminotitanate amorphous phase after the removal of titanium dioxide from its composition as a result of the crystallization of rutile (Figure 3).

Figure 2. XRD patterns of initial and heat-treated glasses

Figure 3. The intensity of the ZnAl$_2$O$_4$ peak with (311) hkl and average crystallite size of ZnAl$_2$O$_4$ as functions of the heat-treatment temperature of the initial glass. The heat-treatment at the nucleation stage is 720 °C for 6 h. The lines are the guide for the eye.
As the temperature of heat-treatment increases, the size of gahnite crystals gradually increases from 7 to 19 nm. The parameter of the gahnite unit cell changes with increasing the heat-treatment temperature in a complex manner (Figure 4) and has a value from 8.082 Å (750 °C) to 8.094 Å (1050 °C). The maximum value of \( a = 8.105 \) Å was observed after heat-treatment at 900 °C. These changes reflect a complex variation in the composition and structure of the crystals with heat-treatment temperature. Rutile crystallized during the heat-treatment at 1000 °C have a size of 24 nm and unit cell parameters \( a = 4.6102 \) Å, \( c = 2.9571 \) Å. After increasing the temperature to 1050 °C, the rutile size increases to ~28 nm; the parameters slightly change, i.e., \( a = 4.5922 \) Å, \( c = 2.9574 \) Å.

Figure 4. Unit cell parameter \( a \) as a function of the heat-treatment temperature of the initial glass. The heat-treatment at the nucleation stage is 720 °C for 6 h.

3.3 Density analysis
The density of the initial glass is 3.0126 g·cm\(^{-3}\), a significant increase in density is observed after the nucleation (\( \rho = 3.0952 \) g·cm\(^{-3}\)) and low-temperature crystallization heat-treatment at 750 °C (\( \rho = 3.1879 \) g·cm\(^{-3}\)) (Figure 5). Then the density decreases slightly, reaching a minimum value of 3.1642 g·cm\(^{-3}\) for the GCs prepared at 950 °C, and then increases again to a value of 3.1862 g·cm\(^{-3}\) after the heat-treatment at 1050 °C. This dependence evidences the phase separation is accomplished during the heat-treatment at 750 °C, and further crystallization within the regions of inhomogeneity does not lead to a significant density variation.

3.4 Raman spectroscopy study
The Raman spectrum of the initial glass (Figure 6) contains two broad bands, one with a maximum at 440 cm\(^{-1}\) and another one of a complex shape with two local maxima at 800 and 920 cm\(^{-1}\). The bands at 440 and 800 cm\(^{-1}\) are attributed to vibrations of the tetrahedra of the aluminosilicate network. The more intense band at 920 cm\(^{-1}\) is connected with vibrations of TiO\(_4\) tetrahedra entering the aluminosilicate network [2]. The spectrum changes after the heat-treatment at 720 °C for 6 h. There is a change in positions of Raman bands and a redistribution of their intensities. The band at ~920 cm\(^{-1}\) weakens, and the band at ~800 cm\(^{-1}\) shifts to 797 cm\(^{-1}\) and noticeably increases. These changes are associated with the development of liquid phase separation and formation of the amorphous ZAT phase wherein titanium ions form TiO\(_4\) and TiO\(_6\) polyhedrons giving rise to a characteristic band at ~800 cm\(^{-1}\) superimposed on the band due to vibrations of tetrahedra of the aluminosilicate network. After further heat-treatments, phase separations develops with the formation of anatase-like phase, which sigs is the band at ~140 cm\(^{-1}\), the gahnite, and then, at 1000 – 1050 °C, rutile (Figure 5). The multiple vibrations associated with gahnite manifest its disordered structure probably caused by Ti\(^{4+}\) and iron doping into its structure.
3.5 Absorption spectroscopy

The absorption spectrum of the initial glass is formed by a shortwave absorption edge ($E_g = 2.95 \, \text{eV}$), two wide unstructured bands with $\lambda_{\text{max}}$ at about 1070 nm (the $^5T_2 \rightarrow ^5E ({}^5D)$ transition) and about 1850 nm (the $^5E \rightarrow ^5T_2 ({}^5D)$ transition), due to the absorption of $\text{Fe}^{2+}$ ions in octahedral and tetrahedral coordination, respectively, and a wide unstructured band in the region of 2700-3300 nm due to absorption of $\text{OH}^-$-groups in the glass (Figure 7).

As the temperature of heat-treatment increases, the absorption edge shifts to the IR region, hindering the absorption band at 1000 nm; the intensity of the absorption band in the region of 2000 nm decreases.
nm markedly increases, the position of its maximum is shifted to ~ 2030 nm; the absorption band of OH-groups is structured, and its intensity increases. A sharp increase in absorption in the visible region may be due to the Fe$^{2+}$-Fe$^{3+}$ intervalence transitions, Fe$^{2+}$ and Fe$^{3+}$ d $\rightarrow$ d transitions in the ZAT amorphous phase and in gahnite. The absorption at about 2000 nm is associated with the incorporation of Fe$^{2+}$ ions into the gahnite nanocrystals in tetrahedral positions (the $^5E \rightarrow ^5T_2(^5D)$ transition). The structuring of the IR absorption band caused by OH-groups is also connected with gahnite crystallization as the OH groups enter into the gahnite structure.

4. Conclusions
Transparent glass-ceramics based on nanosized Fe$^{2+}$:ZnAl$_2$O$_4$ crystals were developed for the first time. Their structure and spectroscopic properties were studied. The iron ions Fe$^{2+}$ enter the gahnite crystals giving rise to intense absorption band at ~2 μm. The glass-ceramics exhibit a broad (1.5-2.5 μm) absorption due to the $^5E \rightarrow ^5T_2(^5D)$ transition of Fe$^{2+}$ ions in T$_d$ sites and they are promising for applications as saturable absorbers in the short-wave infrared spectral range (2-3 μm).

Acknowledgments
This work was partly supported by RFBR (Project No. 19-03-00855).

References
[1] Basyrova L, Balabanov C, Belyaev A, Drobotenko V, Vitkin V, Dymshits O, Loiko P 2019 J. Phys. Conf. Ser. 1410 012123
[2] Alekseeva I, Dymshits O, Ermakov V, Zhilin A, Tsenter M 2013 Glass Phys. Chem. 39 113–23
[3] Alekseeva I, Baranov A, Dymshits O, Ermakov V, Golubkov V, Tsenter M, Zhilin A, J. 2011 Non-Cryst. Solids 357 3928–39
[4] Alekseeva I, Dymshits O, Ermakov V, Golubkov V, Malyarevich A, Tsenter M, Zhilin A, Yumashev K 2012 Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B 53 167–180
[5] Loiko P, Belyaev A, Dymshits O, Evdokimov I, Vitkin V, Volkova K, Tsenter M, Volokitina A, Baranov M, Vilejshikova E, Baranov A, Zhilin A 2017 J. Alloy Compd. 725 998–05
[6] Golubkov V, Dymshits O, Petrov V, Shashkin A, Tsenter M, Zhilin A 2005 J. Non-Cryst. Solids 351 711–21