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Influence of Fe²⁺ doping concentration on the structure and spectroscopic properties of transparent glass-ceramics based on Fe²⁺:ZnAl₂O₄ nanocrystals

K Ereemeev^{1,*}, O Dymshits^{2,**}, A Khubetsov², I Alekseeva², S Zapalova², M Tsenter², A. Zhilin², L Basyrova³, P Loiko⁴ and V Popkov⁵

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 St. 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 Politekhnikeskaya St., 194021 St. Petersburg, Russia

E-mail: *kirillereemeev42@gmail.com, **vodym1959@gmail.com

Abstract. Zinc aluminosilicate glasses nucleated by titanium dioxide, both undoped and doped with 0.6 and 1.0 wt% FeO were prepared by conventional melt-quenching technique and subsequently converted to glass-ceramics by controlled nucleation and crystallization in the temperature range of 720 – 1200 °C. The glasses and glass-ceramics were characterized by X-ray diffraction, Raman and optical spectroscopy. The addition of FeO speeds up the liquid phase separation of the initial glasses and gahnite (ZnAl₂O₄), rutile (TiO₂) and cristobalite (SiO₂) crystallization. Ferrous ions enter the gahnite crystals leading to a variation of the absorption spectra of glass-ceramics as compared to those of glasses. The glass-ceramics exhibit a broadband (1.5-2.5 μm) absorption due to the ⁵E → ⁵T₂ (⁵D) transition of Fe²⁺ ions in tetrahedral sites in gahnite nanocrystals. They are promising as materials for gain media and saturable absorbers of mid-infrared lasers.

1. Introduction

Coherent light sources emitting in the mid-infrared spectral range (the so-called molecular fingerprint region containing the absorption lines of various bio- and atmospheric species) are of practical use for such applications as molecular spectroscopy, gas sensing and medicine. There is a demand for gain media and saturable absorbers of mid-infrared lasers. Materials doped with tetrahedrally (*T_d*) coordinated ferrous (Fe²⁺) ions and demonstrating intense broadband absorption in the spectral range of 2–3 μm are the suitable candidates. The crystals of ZnS and ZnSe doped with Fe²⁺ ions are clear examples of such materials [1]. Nevertheless, it is of great interest to search for other materials for Fe²⁺ doping. One of the groups of such materials are spinels doped by Fe²⁺ ions, e.g., Fe:MgAl₂O₄, [2]. The structural formula of spinel, AB₂X₄, can be expressed as ^{IV}[A_{1-δ}B_δ]^{VI}[B_{2-δ}A_δ]X₄, where ^{IV}[] and ^{VI}[] represent the tetrahedral (*T_d*) and octahedral (*O_h*) sites, respectively; δ is the so-called inversion parameter reflecting the degree of disorder. There are two ordered configurations of cations in spinels:

the normal spinel with $\delta = 0$ and the inverse spinel with $\delta = 1$. Gahnite, ZnAl_2O_4 , also belongs to the spinel family. It demonstrates a certain degree of disorder with increasing the annealing temperature [3]. Recently, transparent ceramics of $\text{Fe}:\text{ZnAl}_2\text{O}_4$ were fabricated and their spectroscopic parameters were evaluated [4]. The Fe^{2+} content in T_d and O_h sites in gahnite was estimated as nearly equal. As compared to optical ceramics, zinc aluminosilicate (ZAS) transparent glass-ceramics (GCs) containing nanosized gahnite crystals possess an advantage of the flexible and convenient fabrication method based on the glass technology, and, moreover, they allow for alteration of the nanocrystals compositions, structures and sizes. Previously, we developed cobalt-doped transparent GCs in the ZAS system and revealed that the CoO facilitated amorphous phase separation of glasses that resulted in the formation of Co-doped amorphous zinc aluminotitanate (ZAT) phase and gahnite nanocrystals [5,6]. In this work, we developed and studied novel transparent GCs based on $\text{Fe}^{2+}:\text{ZnAl}_2\text{O}_4$ nanocrystals with the aim to elucidate the role of iron ions in their formation.

2. Experimental

We studied the glasses of the $\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system nucleated by TiO_2 , both undoped and doped with 0.6 and 1.0 mol% FeO (400 g in weight). They were melted at 1580°C with stirring, cast onto a metal plate and annealed at 680°C . The initial glasses were transparent. To promote the growth of gahnite nanocrystals, the glasses were subjected to two-stage heat-treatments at temperatures from 750 to 1200°C with a holding time of 6 hours (h) at each stage. The first (nucleation) heat-treatment was always at 720°C . The undoped glass was pale-grey while glasses doped with iron oxide were brown-grey coloured. The colour of the samples steadily changed to black after the heat-treatment at the temperatures ranging from 720 to 1000°C . The obtained GCs were transparent. The samples subjected to heat-treatments at higher temperatures became opaque, Figure 1.

The X-ray powder diffraction (XRD) patterns of the initial glasses and GCs were recorded using a Shimadzu XRD-6000 diffractometer with $\text{Cu K}\alpha$ radiation and a Ni filter. The parameters of the unit cell of gahnite nanocrystals were determined from the Rietveld refinement using the MAUD software. The mean crystal sizes were estimated from the broadening of the X-ray diffraction peak at $2\theta \approx 65.0^\circ$ according to the Scherrer equation [5]. The error of the crystal size estimation was $\sim 5\%$. The Raman spectra were measured with a Renishaw inVia confocal Raman microscope using a Leica $\times 50$ microscope objective and an edge filter. The excitation wavelength was 514 nm (Ar^+ ion laser line). The absorption spectra were measured with a Shimadzu 3600 spectrophotometer in the spectral range of $250 - 3300\text{ nm}$ with a resolution of 1 nm . Plane-parallel polished plates with a thickness of 1 mm were used. The absorption coefficient α_{abs} was calculated taking into account the Fresnel losses.



Figure 1. Photographs of undoped and 0.6 mol% FeO -doped initial glass and GCs obtained by heat-treatments at temperatures of $720 - 1200^\circ\text{C}$ indicated in photographs. The holding time is 6 h.

3. Results and discussion

3.1 Initial glasses

The undoped glass is X-ray amorphous while the traces of gahnite nanocrystals are visible in the XRD patterns of glasses doped with FeO , Figure 2(a). Their Raman spectra are formed by two broad bands, one with two local maxima at ~ 300 and $\sim 445\text{ cm}^{-1}$ and another one with two maxima at about 800 and $920-930\text{ cm}^{-1}$, Figure 2(b). The bands at ~ 445 and 800 cm^{-1} are attributed to vibrations of tetrahedra of the aluminosilicate network in the glass structure. The more intense band at higher frequencies is usually connected with vibrations of TiO_4 tetrahedra entering the aluminosilicate network [5,6]. The shift of positions of the Raman bands centered at ~ 928 and 797 cm^{-1} for the undoped glass to lower frequencies with FeO doping manifests the beginning of liquid phase separation [5,6] during glass

casting and annealing. The absorption spectra of the glasses doped with FeO are drastically different from that of the undoped glass, Figure 2(c). They are formed by the overlapping O-Ti⁴⁺, O-Fe²⁺ and O-Fe³⁺ oxygen-to-metal charge transfer (OMCT) bands, intense, wide and unstructured absorption band in the visible which is assigned to spin-forbidden d-d transitions of ferrous and ferric ions, and the bands with the maxima at ~1080 nm (the ⁵T₂ → ⁵E (⁵D) transition) and ~1860 nm (the ⁵E → ⁵T₂ (⁵D) one) ascribed to absorption of Fe²⁺ ions with O_h and T_d coordination, respectively. A broad asymmetric band at the wavelengths of 2.7 – 3.1 μm is caused by O–H vibrations of hydroxyl groups in the glass. The almost linear dependence of α_{abs} on the concentration of Fe²⁺ ions, Figure 2(d), indicates the implementation of Beer's law, i.e., the distribution of Fe²⁺ ions between the O_h and T_d sites in the initial glasses is almost constant.

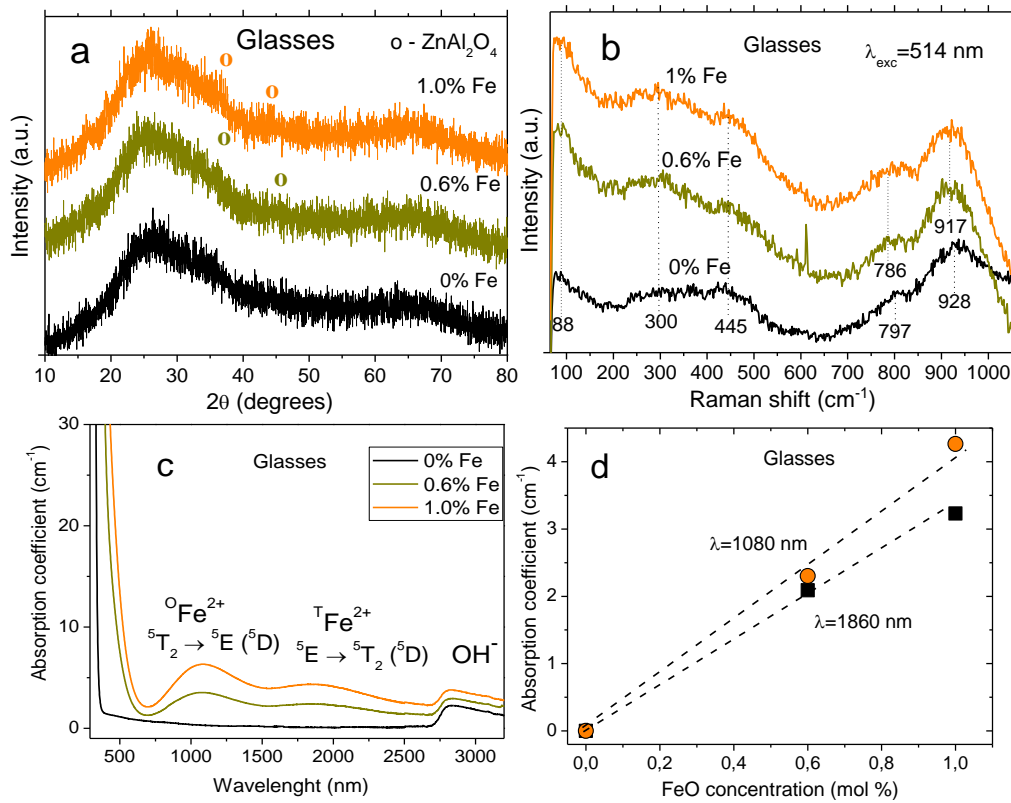


Figure 2(a-d). Characterization of initial glasses, undoped and doped with 0.6 and 1.0 mol% FeO: **(a)** XRD patterns, **(b)** Raman spectra, **(c)** absorption spectra and **(d)** the dependences of α_{abs} in the absorption bands due to the ⁵T₂(⁵D) → ⁵E and the ⁵E → ⁵T₂(⁵D) transitions of Fe²⁺ ions (at 1080 and 1860 nm, respectively) on the FeO concentration.

3.2 Heat-treatment at the first stage

After the heat-treatment of the undoped glass at 720 °C, it contained only traces of gahnite crystals and the gahnite crystallinity fraction increased with the FeO doping, Figure 3(a). The addition of FeO leads to a pronounced change in the Raman spectra, Figure 3(b). There is an intensity redistribution between the bands at 800 - 900 cm⁻¹ in favour of the band at ~800 cm⁻¹. These changes are associated with the development of liquid phase separation and formation of the amorphous ZAT phase wherein titanium ions form TiO₅ and TiO₆ polyhedrons giving rise to a characteristic band at about 800 cm⁻¹ superimposed on the band due to vibrations of tetrahedra of the aluminosilicate network. In the absorption spectra of FeO-doped samples, Figure 3(c), the broad band in the visible is connected with Fe²⁺ + Ti⁴⁺ → Fe³⁺ + Ti³⁺ intervalence charge transfer (IVCT) transitions and spin-forbidden transitions of Fe²⁺ and Fe³⁺ ions in the ligand field. The bands related to the transitions of Fe²⁺ ions in the O_h and

T_d sites in the gahnite nanocrystals are now observed at ~ 1030 and ~ 1820 nm, respectively. The Beer's law is implemented for both bands, Figure 3(d). The structuring of the absorption bands due to the O–H vibrations is connected with OH^- entering the spinel structure in FeO-doped GCs.

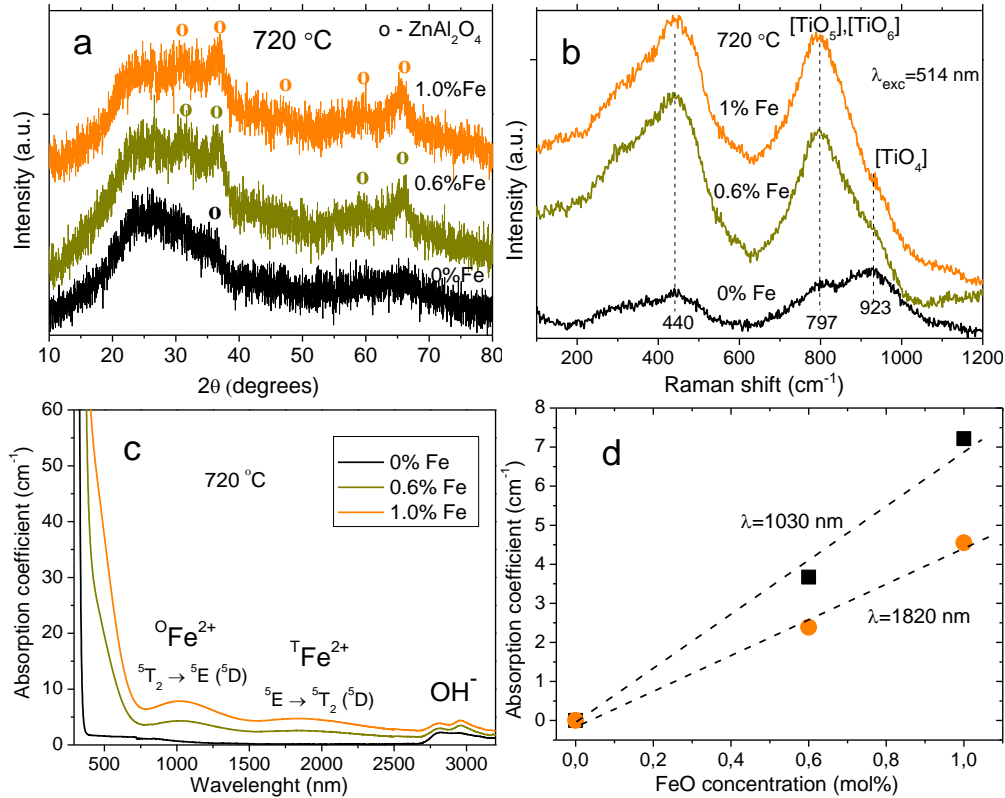


Figure 3(a-d). Characterization of undoped and 0.6 and 1.0 mol% FeO doped glasses after the heat-treatment at 720 °C for 6 h: **(a)** XRD patterns, **(b)** Raman spectra, **(c)** absorption spectra and **(d)** the dependences of α_{abs} in the absorption bands due to the ${}^5T_2({}^5D) \rightarrow {}^5E$ and the ${}^5E \rightarrow {}^5T_2({}^5D)$ transitions of Fe^{2+} ions (at 1030 and 1820 nm, respectively) on the FeO concentration.

3.2 Heat-treatment at the crystallization stage

Gahnite crystallizes within the whole studied temperature range up to 1200 °C, Figure 4(a,b). Simultaneously with gahnite crystallization, the first diffraction maximum in the XRD patterns (an amorphous halo) decreases and shifts to smaller angles (to the position of the diffraction maximum of a quartz glass), because in the course of liquid phase separation and gahnite crystallization the residual glass composition becomes gradually depleted in Zn, Al, Ti and Co oxides [5,6]. According to the XRD data, the GCs prepared in the temperature range of 720 to 950 °C were of single phase nature containing only gahnite nanocrystals. Rutile, the stable modification of TiO_2 , crystallized starting from the temperature of 1000 °C and its amount increased with the FeO addition, Figure 4(a). Cristobalite appeared during the heat-treatment at 1200 °C only in FeO-doped GCs, Figure 4(b). The appearance of the broad band with two maxima at 725 and 765 cm^{-1} , Figure 4(c), and distinct bands at 705 and 737 cm^{-1} , Figure 4(d), in the Raman spectra of FeO-doped GCs reveals disordering of gahnite structure resulting from Fe^{2+} and probably Ti^{4+} entering the gahnite crystals. Anatase and rutile peaks are visible in the Raman spectra of GCs prepared by the heat-treatments with the second stage at 1000 °C, Figure 4(c), rutile peaks are enhanced in the Raman spectra of all FeO-doped GCs, Figure 4(c,d).

In the absorption spectrum of the undoped GC, a broad band spanning from the visible until near IR spectral range is probably connected with the ${}^2T_{2g} \rightarrow E_g$ transition of Ti^{3+} ions in octahedral sites, as well as with the $\text{Ti}^{3+}/\text{Ti}^{4+}$ IVCT band, Figure 5 (a). The absorption edge experiences a notable red-shift

hindering the absorption band at 1000 nm and the intensity of the absorption band around 2000 nm greatly increases. The position of its maximum is now shifted to ~ 2035 nm. Moreover, the absorption band of OH⁻-groups is structured and its intensity raises. A sharp increase in absorption in the visible may be due to the Fe²⁺-Fe³⁺ IVCT transitions, Fe²⁺ and Fe³⁺ d \rightarrow d transitions in the ZAT amorphous phase, in gahnite and a residual glass. The absorption band with a maximum at ~ 2035 nm is associated with the incorporation of Fe²⁺ ions into the gahnite nanocrystals in T_d positions (the ${}^5E \rightarrow {}^5T_2({}^5D)$ transition). The Beer's law is implemented for this band. The structuring of the IR absorption band caused by OH⁻ groups is connected with gahnite crystallization as they enter into the gahnite structure.

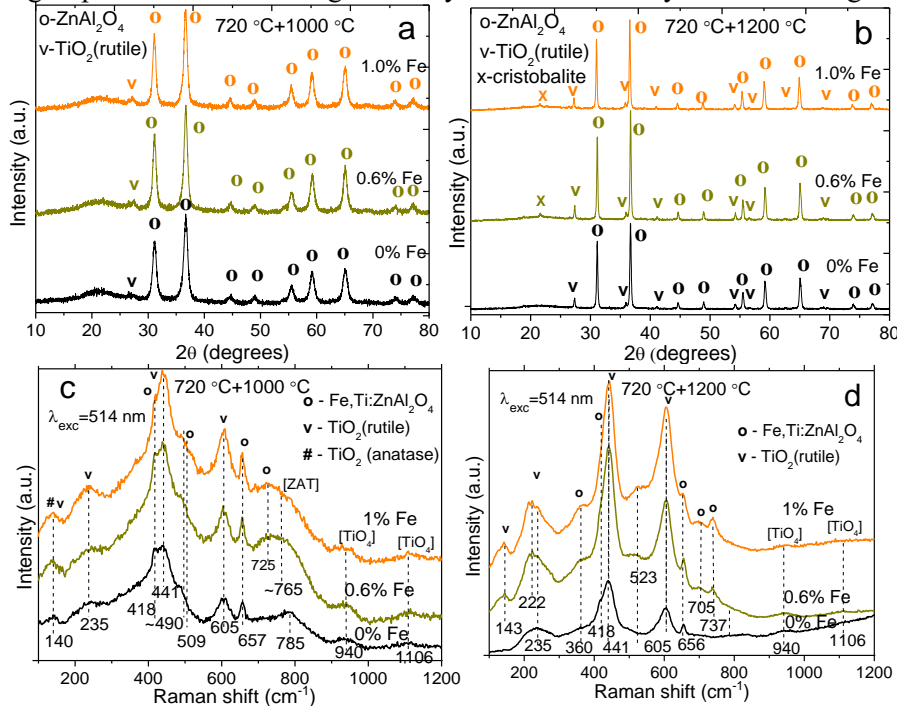


Figure 4(a-d). XRD patterns and Raman spectra of glass-ceramics undoped and doped with 0.6 and 1.0 mol% FeO prepared by the heat-treatments: **(a,c)** at 720 °C and at 1000 °C, **(b,d)** at 720 °C and at 1200 °C. The holding time at each stage is 6 h.

The unit cell parameter of gahnite, Figure 6(a), increases with the FeO content and the heat-treatment temperature. The corresponding crystal sizes are almost independent of the FeO content while increase with the heat-treatment temperature. They vary from about 5 nm to 17 nm as the heat treatment temperature increases from 720 to 1050 °C and drastically increase to about 40 nm as the temperature rises to 1200 °C, Figure 6(b).

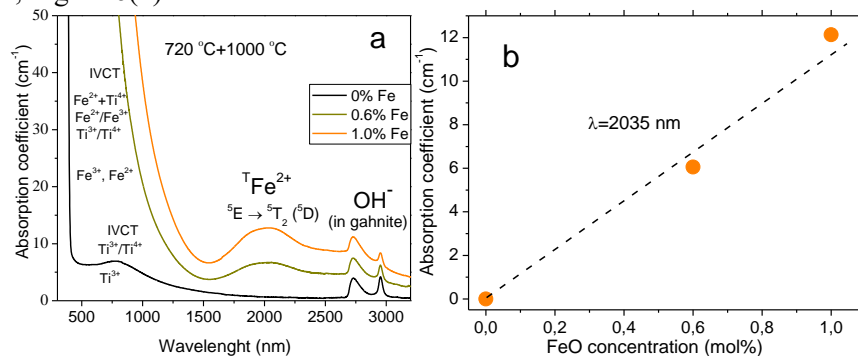


Figure 5(a,b). Absorption spectra of undoped, 0.6 and 1.0 mol% FeO-doped glass-ceramics prepared by the heat-treatment at 720 °C for 6 h and 1000 °C for 6 h **(a)**; the dependence of the absorption coefficient at 2035 nm due to the transition ${}^5E \rightarrow {}^5T_2({}^5D)$ of Fe²⁺ ions on the FeO concentration **(b)**.

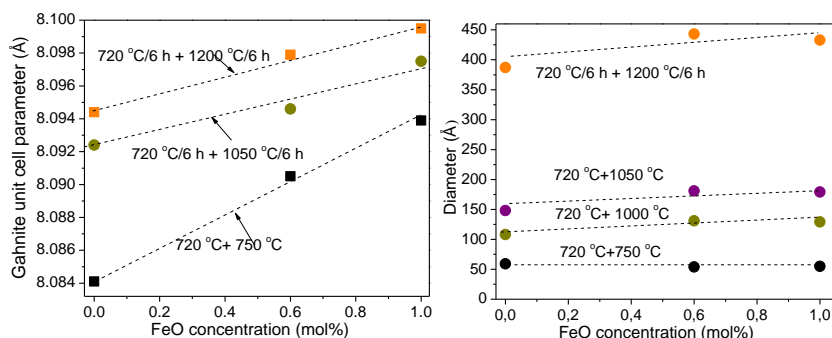


Figure 6(a,b). Dependences of the unit cell parameter **(a)** and the mean size of gahnite nanocrystals **(b)** in the glass-ceramics on the FeO concentration.

4. Conclusions

We report on the synthesis of transparent glass-ceramics based on $\text{Fe}^{2+}:\text{ZnAl}_2\text{O}_4$ nanocrystals and their structure, phase transformation and spectroscopic properties, for the first time, to the best of our knowledge. FeO doping and increasing the FeO concentration in the initial glasses accelerates liquid phase separation and gahnite crystallization during pouring and annealing of the as-cast glasses and during the first (nucleation) stage of the heat-treatment resulting in the formation of zinc aluminotitanate amorphous regions and gahnite nanocrystals. It implies that iron ions enter both phases. The developed transparent glass-ceramics exhibit a broadband (1.5-2.5 μm) absorption due to the ${}^5\text{E} \rightarrow {}^5\text{T}_2$ (${}^5\text{D}$) transition of Fe^{2+} ions in tetrahedral sites in gahnite nanocrystals. In addition, the absorption band of Fe^{2+} ions in the octahedral sites was observed with a maximum at $\sim 1 \mu\text{m}$. The glass-ceramics are promising as saturable absorbers of lasers emitting at 2-3 μm .

Acknowledgements

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