

# Synthesis, structure and spectroscopy of Fe<sup>2+</sup>:MgAl<sub>2</sub>O<sub>4</sub> transparent ceramics and glass-ceramics

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**ABSTRACT.** We report on a comparative study of a transparent Fe:MgAl<sub>2</sub>O<sub>4</sub> (spinel) ceramics and a transparent nanophase Fe:MgAl<sub>2</sub>O<sub>4</sub>-based glass-ceramics. The 0.1 mol% Fe:MgAl<sub>2</sub>O<sub>4</sub> ceramics was synthesized by hot pressing (at 1500 °C / 50 MPa) of powders obtained by the sol-gel method using LiF as a sintering aid. The Fe:MgAl<sub>2</sub>O<sub>4</sub> ceramic is a single-phase material (cubic structure, sp. gr. *Fd3̄m*, *a* = 8.083 Å) with a mean grain size of ~50 μm. The ceramic exhibits a broadband transparency of 0.2–6.0 μm and a high in-line transmission at ~1 μm of 74.4%. The iron ions are presented in the ceramics in the single state of Fe<sup>2+</sup> species in tetrahedral (T<sub>d</sub>) sites. A broad absorption band spanning from ~1.2 to 3.7 μm assigned to the <sup>5</sup>E → <sup>5</sup>T<sub>2</sub> (<sup>5</sup>D) transition of Fe<sup>2+</sup> ions in T<sub>d</sub> sites is observed, corresponding to a ground-state absorption cross section of 0.28×10<sup>-18</sup> cm<sup>2</sup> at 1.90 μm. The glass-ceramics were prepared by secondary two-stage heat-treatments of the magnesium aluminosilicate glass nucleated by titanium oxide and doped with 0.1 mol% FeO. Transparent Fe:MgAl<sub>2</sub>O<sub>4</sub>-based glass-ceramics obtained at the temperature of the second stage of 800 – 1000 °C were multi-phase materials containing two crystalline nanophases, i.e., spinel (mean size: 3.7 – 7.4 nm) and magnesium aluminotitanate solid solution (mean size: 6.4 - 20.6 nm), as well as residual silica-rich glass. Glass-ceramics obtained at the temperature of the second stage of 1050 °C were transparent and based on Fe-doped sapphire. For glass-ceramics, absorption has a much more complex character as it is caused by interplay of iron and titanium ions in different valence states, coordination sites and locations. The iron ions enter the spinel nanocrystals but unlike the ceramic, in the form of both <sup>VI</sup>Fe<sup>2+</sup> and <sup>IV</sup>Fe<sup>2+</sup> species. The developed ceramics and glass-ceramics are promising for saturable absorbers of mid-infrared (2-3 μm) lasers.

**Keywords:** transparent ceramics; glass-ceramics; spinel; iron ions; microstructure; spectroscopy.

## 1. Introduction

Divalent iron ions ( $\text{Fe}^{2+}$ ) embedded in II-IV group materials such as ZnS and ZnSe are known for their intense and broadband absorption and emission in the mid-infrared originating from the  ${}^5\text{E} \leftrightarrow {}^5\text{T}_2$  ( ${}^5\text{D}$ ) transitions of  $\text{Fe}^{2+}$  ions in tetrahedral ( $T_d$ ) crystal field [1]. For example, for  $\text{Fe}^{2+}:\text{ZnSe}$ , the maximum absorption is at  $3.1 \mu\text{m}$  and the emission band is centered at  $4.35 \mu\text{m}$  [2-4]. It makes  $\text{Fe}^{2+}$ -doped chalcogenides suitable for laser gain media [2,5,6] operating in this spectral range with multiple applications in gas sensing, molecular spectroscopy, range finding and medicine. Due to high ground-state absorption (GSA) cross sections for  $\text{Fe}^{2+}$  ions in  $T_d$  sites ( $\sigma_{\text{GSA}} = 0.97 \times 10^{-18} \text{ cm}^2$  for  $\text{Fe}^{2+}:\text{ZnSe}$ ) and the lack of excited-state absorption [1],  $\text{Fe}^{2+}$ -doped materials are also interesting for saturable absorbers (SAs) of mid-infrared lasers [4,7,8].

Because of relatively low hardness and laser-induced damage threshold (LIDT), high temperature coefficient of the refractive index of chalcogenides, and the lack of efficient pump lasers at a wavelength of  $3.1 \mu\text{m}$ , it seems reasonable to find other hosts for  $\text{Fe}^{2+}$  ions doping. One of the possible host candidates is cubic magnesium aluminium spinel,  $\text{MgAl}_2\text{O}_4$  [9]. This broad energy gap material features good thermal and mechanical properties (e.g., high Mohs hardness of 8, high thermal conductivity of  $24.7 \text{ W m}^{-1}\text{K}^{-1}$  for an undoped crystal [10] and relatively low thermal expansion coefficient of about  $9 \times 10^{-6} \text{ K}^{-1}$  between 20 and  $1200 \text{ }^\circ\text{C}$  [11]) together with a broad (for oxide crystals) transparency range of  $0.2\text{--}5.5 \mu\text{m}$ .  $\text{MgAl}_2\text{O}_4$  also exhibits high LIDT well exceeding that of chalcogenides. Spinel demonstrates widely variable occupation of two (tetrahedral,  $T_d$ , and octahedral,  $O_h$ ) sites by various transition metal ions and distribution of the cations between these sites.  $\text{MgAl}_2\text{O}_4$  is known for doping with such transition metal ions as  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  [12-14]. When doped with  $\text{Co}^{2+}$  ions entering predominantly in the  $T_d$  sites, it is recognized as a SA for eye-safe lasers operating at  $\sim 1.5 \mu\text{m}$  [15,16].

Iron-containing spinels are common in both the crust and the Earth's mantle, in meteorites, and in lunar rocks. There is a continuous solid solution between  $\text{MgAl}_2\text{O}_4$ , spinel, end-member and  $\text{FeAl}_2\text{O}_4$ , hercynite, end-member, which also has a normal spinel structure. It is not surprising that there exist structural and optical studies of iron-doped  $\text{MgAl}_2\text{O}_4$  minerals. Andreozzi *et al.* studied the distribution of  $\text{Fe}^{2+}$  ions over the  $T_d$  and  $O_h$  sites in  $\text{MgAl}_2\text{O}_4$  –  $\text{FeAl}_2\text{O}_4$  solid solutions and revealed the tetrahedral preference of  $\text{Fe}^{2+}$  with respect to  $\text{Mg}^{2+}$  [17]. Gaffney described the spectra of  $\text{Fe}^{2+}$  ions in tetrahedral sites in spinel [18], based on an earlier work of Slack [19,20]. Taran *et al.* described optical absorption of natural ( $\text{Fe}^{3+}, \text{Fe}^{2+}$ )-bearing spinels [21]; a study of iron-bearing aluminate spinel under lunar-like redox conditions was performed by Jackson *et al.* [22]. Halenius *et al.* proposed a model of  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  ion pairs in spinels [23].

The melting point of  $\text{MgAl}_2\text{O}_4$  is rather high ( $2135 \text{ }^\circ\text{C}$ ). The single crystals are typically grown by the Czochralski method [24] using iridium crucibles which is challenging because the melting point of iridium is only slightly higher than that of spinel [25]. We found only one paper on  $\text{Fe}^{2+}$ -doped spinel single crystal [26] and one paper on growth of  $\text{FeAl}_2\text{O}_4$ , hercynite, single crystal [19]. According to Sackuvich *et al.* [26],  $\text{Fe}^{2+}$  ions in  $\text{MgAl}_2\text{O}_4$  crys-

tals feature broad absorption band with a maximum near 2  $\mu\text{m}$  and a luminescence signal between 3 and 6  $\mu\text{m}$ .

Thus, it is reasonable to propose other transparent  $\text{MgAl}_2\text{O}_4$ -based materials for doping with transition metal ions, namely, transparent polycrystalline ceramics [16] and transparent nanophase glass-ceramics (GCs) [27-29].

Nowadays, transparent ceramic technology is becoming competitive to traditional single crystal growth methods. It has several advantages [30], such as (i) lower synthesis temperature, (ii) size scalable production, (iii) easier doping with active ions, (iv) the development of compositions which are unstable / hardly reproducible in the single-crystalline form. At the same time, optical ceramics provide spectroscopic and thermal properties similar to those of single crystals. Optical quality of ceramics can be greatly improved by proper adjusting the synthesis procedure. Recently, multiple studies were dedicated to the development of transparent spinel ceramics, such as  $\text{MgAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  (gahnite) both undoped and  $\text{Co}^{2+}$ -doped [16,31-35]. For the consolidation of optical-quality spinel ceramics, either hot pressing with a fluoride-based sintering additive [36] or free sintering with a subsequent hot isostatic pressing (HIP) treatment is used [37]. Less frequent methods are spark plasma sintering (SPS) [38] and microwave sintering [39]. These methods allow to achieve high compaction rates and to preserve the sub- $\mu\text{m}$  structure of ceramics which is responsible for their high micro-hardness. However, optical transmittance of such ceramics is usually lower due to incomplete pore removal during rapid compaction. Many methods in the preparation of spinel powders, such as sol-gel, solid-phase synthesis, pyrolysis of metal salts, *etc.*, have been developed [40]. The advantages of the sol-gel method of obtaining  $\text{MgAl}_2\text{O}_4$  powders with the use of volatile metal alkoxides are high chemical purity of powders and a stable ratio of magnesium-to-aluminum ions of 1:2 [41]. High chemical purity of ceramics is an important requirement for their use in laser, terahertz and microwave technologies, especially for high-power applications [42,43].

Transparent nanophase GCs [44] are obtained by secondary heat-treatments of initial glasses of specially developed compositions. The initial glasses are produced by the melt-quenching technique, and they can be doped by active ions. As a result, the material contains nanosized crystals of one or several crystalline phases uniformly distributed in the residual glass. Fabrication of GCs is in many cases easier than that of transparent ceramics. GCs also benefit from higher LIDT [33]. However, it is important to control the distribution of active ions between the nanocrystalline phase (or phases) and the residual glass. Moreover, thermal conductivity of GCs is typically lower than that of optical ceramics. So far, multiple studies were dedicated to fabrication and characterization of spinel-based transparent GCs doped with  $\text{Cr}^{3+}$  [27,45],  $\text{Co}^{2+}$  [28,29] and  $\text{Ni}^{2+}$  ions [46-48].

In this work, we aim to fabricate and study the microstructure, vibronic and optical properties of novel transparent ceramics and GCs based on  $\text{Fe}^{2+}:\text{MgAl}_2\text{O}_4$  spinel crystals. Previously, the authors from the Institute of Electrophysics UD RAS reported the development of transparent  $\text{Fe}^{2+}:\text{MgAl}_2\text{O}_4$  ceramics [49-51]. The obtained ceramics [49-51] contained secondary oxide phase of  $(\text{MgO})_{0.91}(\text{FeO})_{0.09}$  causing a substantial decrease in transmittance in the visible range. In those ceramics  $\text{Fe}^{3+}$  ions are located both in the primary spi-

nel phase Fe:MgAl<sub>2</sub>O<sub>4</sub> and in the secondary phase Fe:MgO, which results in a very low determined GSA cross sections of Fe<sup>2+</sup> ions in tetrahedral site symmetry [49]. Recently, first GCs based on Fe<sup>2+</sup>:ZnAl<sub>2</sub>O<sub>4</sub> [52,53] nanocrystals in zinc aluminosilicate glass system were prepared and studied. Lin *et al.* reported on the development of transparent GCs based on Fe:(Ga<sub>2-x</sub>Al<sub>x</sub>)O<sub>3</sub> nanocrystals with spinel structure in the sodium-magnesium-alumino-gallosilicate glass system and demonstrated the proof-of-the-concept of their SA performance [54]. Though there exist studies on the iron-doped GCs of the magnesium aluminosilicate system, they aim to develop opaque GCs based of iron-doped cordierite [55-57]. The preliminary results on the development of Fe:MgAl<sub>2</sub>O<sub>4</sub>-based transparent glass-ceramics were first published in [58,59].

## 2. Synthesis of ceramics and glass-ceramics

### 2.1. Synthesis of ceramics

The magnesium aluminium spinel powder doped with Fe<sup>2+</sup> ions was synthesized by the sol-gel method. Metallic magnesium and aluminum (>99% purity) and isopropyl alcohol (99.9% purity) were used as starting materials. Mg and Al metals (31 and 69 wt%, respectively, which corresponds to a molar ratio of 1:2) were melted at 600 °C in an atmosphere of nitrogen. The alloy was crushed, mixed with 0.1 wt% of SnCl<sub>2</sub> and 0.2 wt% of NH<sub>4</sub>Cl, which are the catalysts for the dissolution of the metals in alcohol, and heat-treated in an enclosed stainless steel vessel. MgAl<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub> (Pr<sup>i</sup> stands for the isopropyl groups) was synthesized in a tube reactor at 80–150 °C by an addition of small portions of isopropyl alcohol to the granulated magnesium-aluminum alloy. After that, the final product was purified by vacuum distillation. Under synthesis conditions, other elements do not form volatile isopropylates. Thus, a single vacuum distillation of MgAl<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub> results in its high chemical purity and an exact ratio of 1:2 of magnesium to aluminum metals. The hydrolysis of 50 vol% solution of MgAl<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub> in isopropyl alcohol was conducted by using 1200 ml of isopropyl alcohol-water azeotropic mixture per 1 mol of alkoxide (hydrolysis with pure water leads to a strong agglomeration of hydroxides). The MgAl<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub>:H<sub>2</sub>O ratio was 1:8, which is an equimolar ratio required for complete hydrolysis. The azeotropic mixture contained iron (II) chloride (FeCl<sub>2</sub>) as a source of iron ions. The addition of LiF (the sintering aid) was carried out as follows. 72 ml of suspension prepared by interaction of LiNO<sub>3</sub>·3H<sub>2</sub>O and NH<sub>4</sub>F aqueous solutions was added to 1200 ml of Pr<sup>i</sup>OH–H<sub>2</sub>O azeotrope and further added into 1 mol of MgAl<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub> under stirring. After hydrolysis, the suspensions were cooled down to room temperature (RT) in air. Obtained suspensions were dried at 150 °C under ~1 kPa pressure followed by calcination in air at 750 °C for 3 h. Resulted spinel powders contained 0.1 mol% Fe and about 1.5 wt% of LiF.

To obtain Fe<sup>2+</sup>:MgAl<sub>2</sub>O<sub>4</sub> optical ceramics, the synthesized powders were pre-shaped, loaded into a graphite mold and heated from the RT up to 1600 °C with a heating rate of ~7.5 °C/min and held for 6 h before cooling down. The load was applied at a temperature of 800 °C and then increased up to ~50 MPa in 30 min. The pressure was released before free cooling of the furnace. The transparent ceramic disks were polished to laser-grade quality on both

surfaces using a diamond suspension. The disk had dimensions of  $\text{Ø}13 \times 2.8$  mm (diameter  $\times$  thickness) and a weak grey coloration due to the iron doping, see Fig. 1.

For comparison, undoped  $\text{MgAl}_2\text{O}_4$  ceramic was prepared using a similar approach. The ceramic disk ( $\text{Ø}13 \times 2.0$  mm) was transparent and colorless, Fig. 1.

### 2.2. Synthesis of glass-ceramics

The glass with a composition of 20 MgO, 20  $\text{Al}_2\text{O}_3$ , 60  $\text{SiO}_2$  (mol%) was nucleated by 10 mol%  $\text{TiO}_2$  [60,61] and doped with 0.1 mol% FeO both added above 100% of the base glass composition. The raw materials were reagent grade. The batch for producing 400 g of glass was melted in a crucible made of quartz ceramics at 1550 °C for 3 h with stirring. The glass was poured onto a cold metal plate and annealed at 640 °C.

The transparent pale-yellow glass, Fig. 2, was subjected to double-stage secondary heat-treatments. The first stage was at 750 °C for 6 h and the temperature of the second stage ranged from 800 to 1100 °C with the same holding time of 6 h. As a result, transparent GCs were synthesized. Their color changed with the heat-treatment temperature from the pale yellow to the deep gray-brown (Fig. 2).

## 3. Experimental

### 3.1. Characterization of ceramics

The X-ray powder diffraction (XRD) patterns were measured with a Shimadzu XRD-6000 diffractometer, Cu  $K\alpha$  radiation with a Ni filter. The spinel lattice parameter  $a$  was determined by the Rietveld refinement. Morphology of the fracture surface of ceramics was characterized by scanning electron microscopy (SEM) using a MERLIN SEM microscope (Carl Zeiss). The SEM images were analyzed with the ImageJ software.

The RT Raman spectra were measured with the Renishaw inVia confocal Raman microscope using a Leica x50 objective (N.A. = 0.75). The excitation wavelength  $\lambda_{\text{exc}}$  was 514 nm ( $\text{Ar}^+$  laser line).

The RT transmission spectra in the visible to near-IR and in the mid-IR were measured using a Shimadzu UV-3600 spectrophotometer and a FTIR spectrometer Bruker Tensor 27, respectively.

### 3.2. Characterization of glass-ceramics

The density of the initial glass and GCs was measured by the Archimedes method with toluene. The experimental error was about 0.0005 g/cm<sup>3</sup>.

The XRD patterns were recorded using a Shimadzu XRD-6000 diffractometer with Cu  $K\alpha$  radiation and a Ni filter. The mean crystal size,  $D_{\text{XRD}}$ , was estimated from broadening of the diffraction peaks according to the Scherrer's equation:

$$D_{\text{XRD}} = \frac{K\lambda}{\Delta(2\theta) \cdot \cos\theta}, \quad (1)$$

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 [62]. The error for the crystal size estimation is ~5%. The size of spinel crystals was determined

using the diffraction peak with the Miller's indices  $(hkl) = (440)$  at  $2\theta \approx 65.5^\circ$ . The size of crystals of magnesium aluminotitanate (MAT)  $x\text{MgTi}_2\text{O}_5y\text{Al}_2\text{TiO}_5$  solid solution (ss) with a pseudobrookite structure [60,61] was determined for the (110) diffraction peak at  $2\theta \approx 25.7^\circ$ . The spinel lattice parameter  $a$  was determined using the same diffraction peak with the Miller's indices  $(hkl) = (440)$  at  $2\theta \approx 65.5^\circ$  according to the equation:

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (2)$$

For differential scanning calorimetry (DSC), 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. The heating rate was 10 °C/min. The samples were the initial glass and the glass heat-treated at the nucleation stage of 750 °C for 6 h. To assign the exothermal DSC peaks to certain crystalline phases, bulk samples of about 80 mg in weight were heated in the DSC furnace with the same heating rate of 10 °C/min up to a temperature of the certain exothermal peak appearance, cooled down to RT and subjected to powder XRD analysis.

The microstructure of the initial glass and GCs was studied by transmission electron microscopy (TEM) with the JEOL TEM-1011 microscope (100 kV acceleration voltage, 0.4 nm point resolution). The samples were finely powdered and dispersed in ethanol. The obtained solution was dropped on a TEM grid which was dried for ~30 min. The TEM images were analyzed with the ImageJ software.

The Raman spectra of the initial glass and GCs were recorded with the same confocal Raman microscope as that used for studying the ceramics. For the measurement in the frequency range of 100-1200  $\text{cm}^{-1}$ , an edge filter was used. The Raman spectra in the frequency range of 5-350  $\text{cm}^{-1}$  were measured with a notch-filter. The spatial resolution was about 2  $\text{cm}^{-1}$ .

The absorption spectra of the initial glass and GCs were recorded on a Shimadzu UV-3600 spectrophotometer. Double-sided polished samples (1.0 mm thick) were used. The luminescence spectra were measured using the confocal Raman microscope with  $\lambda_{\text{exc}} = 488 \text{ nm}$  ( $\text{Ar}^+$  laser line).

## 4. Transparent ceramics

### 4.1. Structure

The phase purity and the structure of ceramics were confirmed by XRD, see Fig. 3(a).  $\text{MgAl}_2\text{O}_4$  and  $\text{Fe:MgAl}_2\text{O}_4$  are cubic (sp. gr.  $O_h^7 - Fd\bar{3}m$ , No. 227). The lattice constants of both spinels are similar,  $a = 8.083 \pm 0.003 \text{ \AA}$  (for the  $\text{Fe:MgAl}_2\text{O}_4$  spinel) and  $8.088 \pm 0.003 \text{ \AA}$  (for the undoped  $\text{MgAl}_2\text{O}_4$  one). Quite similar lattice constants  $a = 8.086 \pm 0.002 \text{ \AA}$  and  $8.087 \pm 0.002 \text{ \AA}$  and were reported in [50] for  $\text{MgAl}_2\text{O}_4$  doped with 0.1 and 1wt%  $\text{Fe}_3\text{O}_4$ , respectively. The lattice parameter in  $\text{Fe:MgAl}_2\text{O}_4$  ceramic is slightly larger than that for the initial powder ( $a = 8.063 \text{ \AA}$  [34]), which is most likely due to the presence of a sintering aid of lithium fluoride in the powder that can enter the spinel structure [63]. During hot-pressing, the sintering aid evaporates and the fluorine and lithium ions are replaced by larger ions of oxygen and magnesium or aluminum, respectively.

No traces of any impurity phase were found. Figure 3(a) shows that the intensities of the peaks with the Miller' indices (422) and (533) in the XRD pattern of the Fe:MgAl<sub>2</sub>O<sub>4</sub> ceramics increase as compared with the standard values (see ICSD card No. 82-2424 [64]) and with those of the MgAl<sub>2</sub>O<sub>4</sub> ceramics. The changes in the peak intensity indicate the presence of a disordered spinel phase in the sample [65-67] caused by the iron entering the spinel crystals.

Let us shortly discuss the structure of spinels. Their chemical formula is AB<sub>2</sub>O<sub>4</sub>. Each unit cell contains 32 anions (O<sup>2-</sup>) in a face-centered cubic packing. In the oxygen lattice, the cations (A<sup>2+</sup> and B<sup>3+</sup>) have 32 O<sub>h</sub> and 64 T<sub>d</sub> interstitial sites per unit cell. For a normal spinel, <sup>IV</sup>[A]<sup>VI</sup>[B]<sub>2</sub>O<sub>4</sub>, 1/8 of the tetrahedral sites are occupied by the A<sup>2+</sup> cations and 1/2 of the octahedral ones are occupied by the B<sup>3+</sup> cations. Here the superscripts are the coordination numbers (C.N. = IV and VI for the T<sub>d</sub> and O<sub>h</sub> sites, respectively). Typically, spinels demonstrate a certain degree of cation disorder. It is described by the so-called inversion parameter  $\delta$  - a fraction of trivalent cations in the T<sub>d</sub> sites (or, equivalently, a fraction of A<sup>2+</sup> cations in the O<sub>h</sub> sites). Thus, a general formula for spinels is <sup>IV</sup>[A<sub>1- $\delta$</sub> B <sub>$\delta$</sub> ]<sup>VI</sup>[B<sub>2- $\delta$</sub> A <sub>$\delta$</sub> ]O<sub>4</sub> ( $\delta = 0$  and 1 correspond to a normal / inverse spinel, respectively) [68]. Note that as we mentioned before, there exists Fe-based normal spinel with  $\delta \approx 0$  (FeAl<sub>2</sub>O<sub>4</sub>, hercynite) [69].

The Fe<sup>2+</sup> ions are expected to replace the Mg<sup>2+</sup> ones in T<sub>d</sub> sites owing to the closeness of their ionic radii ( $R_{\text{Fe}} = 0.63 \text{ \AA}$  and  $R_{\text{Mg}} = 0.57 \text{ \AA}$  for IV-fold oxygen coordination [70]). The Fe<sup>2+</sup> doping can also induce an additional cation disorder leading to appearance of both Fe<sup>2+</sup> and Mg<sup>2+</sup> ions in O<sub>h</sub> sites. Andreozzi *et al.* had shown that compared with Fe<sup>2+</sup>, Mg<sup>2+</sup> has some preference in substituting for octahedral Al<sup>3+</sup>, and that in the MgAl<sub>2</sub>O<sub>4</sub> – FeAl<sub>2</sub>O<sub>4</sub> isostructural series of solid solutions, the fraction of Fe<sup>2+</sup> ions in O<sub>h</sub> sites increases with the Fe content while it is near zero for low iron doping (as in our case) [17].

The morphology of the fracture surface was characterized by scanning electron microscopy (SEM), Fig. 4(a). The grain boundaries are clean and there is no secondary phase at the boundaries. This is in agreement with the XRD finding of the absence of any secondary crystal phase (Fig. 3). Due to low-defect grain boundaries, the bonds between the grains have strength comparable to that in the grain volume so that the inter- and intragranular fracture mechanisms compete in ceramics. Usually, when using sintering aid, it tends to accumulate at the grain boundaries, which weakens the bonds between the grains compared to the grain volume. This leads to the intergranular destruction of such ceramics [34]. In our case, the relatively small initial LiF content of 1.5 wt% and the long exposure time at the hot pressing temperature made it possible to completely remove the sintering aid. Another important factor for the absence of impurities at the grain boundaries may be the initially high chemical purity of the powders, achieved by vacuum distillation of the precursor. The ceramic is also almost pore-free. Low porosity and *the absence of secondary phases* make it possible to achieve high optical quality of ceramics (see below). The average grain size is about 50  $\mu\text{m}$  (as determined by analyzing more than 100 grains), see Fig. 4(b). The grain size was obtained by multiplying the measured lengths by a shape factor of 1.2.

#### 4.2. Raman spectra

Vibronic properties of ceramics were studied by Raman spectroscopy, Fig. 5. According to [63], the following vibrational modes are characteristic of the spinel structure:

$$\Gamma = A_{1g}(R) + E_g(R) + 3T_{2g}(R) + 4T_{1u}(IR) + T_{1g} + 2T_{2u} + 2A_{2u} + 2E_u.$$

Among these modes, the Raman-active ones are  $A_{1g}$ ,  $E_g$ , and  $T_{2g}$ , while  $T_{1u}$  is IR-active. The oriented  $MgAl_2O_4$  spinel single crystal has the following vibrational frequencies:  $311\text{ cm}^{-1}$  ( $T_{2g}$ ) – lattice,  $410\text{ cm}^{-1}$  ( $E_g$ ),  $492\text{ cm}^{-1}$  ( $T_{2g}$ ) – both bending,  $671\text{ cm}^{-1}$  ( $T_{2g}$ ) - asymmetric stretching,  $772\text{ cm}^{-1}$  ( $A_{1g}$ ) - symmetric stretching [71].

The same vibrations at  $\sim 195$ ,  $251$ ,  $303$ ,  $405$ ,  $496$ ,  $667$ ,  $721$  and  $764\text{ cm}^{-1}$  are found in the Raman spectra of Fe-doped and undoped ceramics. The Raman bands at  $303$ ,  $405$ ,  $496$ ,  $667$  and  $764\text{ cm}^{-1}$  are close in positions to the data for the  $MgAl_2O_4$  spinel single crystal [71]. Although the Raman spectra of two ceramics are rather similar, the spectrum of the iron-doped spinel is more complex: the band at  $405\text{ cm}^{-1}$  is more broad, asymmetric and intense, the bands at  $496$  and  $721\text{ cm}^{-1}$  are more pronounced, and there are also bands at  $583$  and above  $800\text{ cm}^{-1}$  that are hardly seen in the spectrum of the undoped spinel. The appearance of the band at  $721\text{ cm}^{-1}$  and a low-frequency shoulder on the intense band at  $405\text{ cm}^{-1}$  are typical features of synthetic spinel [72]. The band at  $721\text{ cm}^{-1}$  is assigned to symmetric Al-O stretching vibration of  $AlO_4$  groups created by redistribution of some  $Al^{3+}$  ions from octahedral to tetrahedral sites and evidences a certain disorder of the spinel structure, while the low-frequency shoulder of the  $405\text{-cm}^{-1}$  band appears to be the bending mode for Al ions in tetrahedral sites [73,74]. Apparently, the bands at  $205$  and  $251\text{ cm}^{-1}$ , in the similar manner as the band at  $300\text{ cm}^{-1}$ , can be attributed to the external lattice vibrations in polycrystalline ceramics.

Raman spectroscopy was successfully used to study cation disorder in spinels. It has been suggested [74] that most of extra features in Raman spectra of spinels are related to cation disordering. We speculate that appearance of additional bands in the spectrum of the Fe-doped spinel at  $583$  and at above  $800\text{ cm}^{-1}$  can also stand for a certain degree of its disorder caused by  $Fe^{2+}$  doping. Thus, we can conclude that the comparison of Raman spectra of Fe-doped and undoped spinel proves the increase of the cation disorder in spinel with an addition of iron ions, which is in accordance with the XRD findings. It is also known [74] that the complex Raman spectrum of iron-doped spinel can be affected not only by the substitution  $Fe^{2+} \rightarrow Mg^{2+}$  and the cation disorder, but also by the entrance of small amounts of  $Fe^{3+}$  in the spinel structure. It is not surprising that the addition of  $0.1\%$  Fe does not affect the position of the Raman peaks. According to [75], while the substitution  $Fe^{2+} \rightarrow Mg^{2+}$  proceeds along the  $MgAl_2O_4 - FeAl_2O_4$  series, no change in the wavenumber of the  $E_g$ ,  $T_{2g}$ , and  $A_{1g}$  modes is observed up to the  $Fe^{2+}$  content of  $\sim 20\%$ .

In agreement with the XRD data, no signals attributed to impurities or secondary phases are identified in the Raman spectra of both spinels.

#### 4.3. Optical absorption

The in-line transmission spectrum of the polished Fe: $MgAl_2O_4$  ceramic disk (recalculated for a reference thickness of  $1.0\text{ mm}$ ) is presented in Fig. 6(a) and compared with that for the undoped  $MgAl_2O_4$  ceramic. The transparency range for both samples is similar,  $0.2-6.0$

$\mu\text{m}$ .  $\text{MgAl}_2\text{O}_4$  possesses a large direct bandgap of  $E_g = 7.8$  eV (the corresponding wavelength of the UV absorption edge  $\lambda_{\text{UV}} \sim 0.16$   $\mu\text{m}$ ) [76]. For the undoped ceramic, the in-line (small-signal) transmission  $T$  at the wavelength of  $\sim 1$   $\mu\text{m}$  is 82.2% (compare with the theoretical value set by the Fresnel losses,  $T_0 = 87.0\%$  for a refractive index  $n = 1.704$  [9]). For the Fe-doped ceramics at the same wavelength of  $\sim 1$   $\mu\text{m}$ ,  $T$  is reduced to a value of 74.4%.

In the spectrum of the Fe-doped ceramics, there is an intense absorption band in the near-mid-IR, spanning from  $\sim 1.2$  to  $3.7$   $\mu\text{m}$  with the local maxima at  $1.90$  and  $2.82$   $\mu\text{m}$ . It is assigned to the absorption of  $\text{Fe}^{2+}$  ions in  $T_d$  sites in spinel. The electronic configuration of  $\text{Fe}^{2+}$  ion is  $[\text{Ar}]3d^6$ . Thus, the energy-level scheme for the  $\text{Fe}^{2+}$  ion in the tetrahedral ligand field is equivalent to a  $3d^{(10-n)} = 3d^4$  ion in the octahedral ligand field. The ground state of the free ion is the  ${}^5D$  one and it is split in the tetrahedral ligand field into the  ${}^5E$  and  ${}^5T_2$  levels separated by an energy  $\Delta = 10Dq$ . The spin-allowed transitions between these levels determine the intense absorption and emission bands of  ${}^{\text{IV}}\text{Fe}^{2+}$  ions. Indeed, an intense absorption band in the NIR range centered at  $\sim 5000$   $\text{cm}^{-1}$  has been widely attributed to the spin-allowed electronic d–d transition ( ${}^5E \rightarrow {}^5T_2$ ) in tetrahedrally coordinated  $\text{Fe}^{2+}$  [18–22,77–80]. The band is characterized by a distinct shoulder at  $\sim 3500$   $\text{cm}^{-1}$ , due to the dynamic Jahn–Teller effect for tetrahedral  $\text{Fe}^{2+}$  ions in the spinel structure [21,79]. Our data are in agreement with Gaffney [18] who reported on the following energies of this transition in absorption:  $3600$  and  $4900$   $\text{cm}^{-1}$  ( $\lambda = 2.78$  and  $2.04$   $\mu\text{m}$ ). For tetrahedrally coordinated  $\text{Fe}^{2+}$  ions, there also exist higher-lying triplet states ( ${}^3H$ ,  ${}^3P$ ,  ${}^3F$ ,  ${}^3G$ ), however, the transitions to these states are spin-forbidden and thus very weak.

Apart from  ${}^{\text{IV}}\text{Fe}^{2+}$  ions, as pointed out above, there can exist  ${}^{\text{VI}}\text{Fe}^{2+}$  ones in the disordered spinel structure. In general, because the  $O_h$  site has a center of symmetry, the transition intensities for transition metal ions located in the ligand field of octahedral symmetry are by several orders of magnitude weaker than those in the field of tetrahedral symmetry. Absorption of  ${}^{\text{VI}}\text{Fe}^{2+}$  ions was observed before mainly in highly doped samples. Gaffney [18] assigned transitions at  $9500$  and  $10800$   $\text{cm}^{-1}$  ( $\lambda = 1.05$  and  $0.93$   $\mu\text{m}$ , respectively) to the spin-allowed  ${}^5T_2 \rightarrow {}^5E$  ( ${}^5D$ ) absorption transition in the octahedral ( $O_h$ ) field. No absorption at these wavelengths is found in the ceramic sample under study. Dickson *et al.* predicted the molar extinction coefficient  $\varepsilon$  for this absorption band to be  $0.51$   $\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  [81] (compare with the value of  $59$   $\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for the  ${}^{\text{IV}}\text{Fe}^{2+}$  absorption [23]. According to [17], in spinel,  $\text{Fe}^{2+}$  shows a marked preference for tetrahedral coordination with respect to  $\text{Mg}^{2+}$ , thus, the absence of absorption caused by the  ${}^{\text{VI}}\text{Fe}^{2+}$  ions is not surprising.

Another possibility for Fe ions to be accommodated in the spinel lattice is to do it in the form of  $\text{Fe}^{3+}$  (in the  $O_h$  sites, by replacing  $\text{Al}^{3+}$  ions). The corresponding ionic radii are  $R_{\text{Fe}} = 0.645$   $\text{\AA}$ , high-spin, and  $R_{\text{Al}} = 0.535$   $\text{\AA}$  for VI-fold oxygen coordination [70]. The presence of  $\text{Fe}^{3+}$  ions in oxide crystals can be manifested by absorption transitions of both isolated  $\text{Fe}^{3+}$  ions (d-d transition) and  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  ion pairs (intervalence charge transfer, IV CT, transition) [23]. The characteristic transitions are at  $21700$  and  $21300$   $\text{cm}^{-1}$  ( $\lambda = 0.46$  and  $0.47$   $\mu\text{m}$ , respectively) – for the  ${}^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g$  ( ${}^4G$ ) transitions for the isolated  ${}^{\text{VI}}\text{Fe}^{2+}$  ions and ion pairs, respectively [23]. None of these bands were observed in the studied ceramics. This finding is in accordance with [82], which states the iron atoms at low concentration are dilut-

ed in the system and located far from each other. However, we cannot rule out that we noticed no trace of  $\text{Fe}^{3+}$  ions in the  $\text{O}_h$  sites due to the low intensity of their absorption bands.

In the previous works [49-51,83-85], the presence of  $\text{Fe}^{3+}$  was detected by measuring the visible luminescence spectra of iron-doped samples revealing emissions centered at  $\sim 0.51$ ,  $0.62$  and  $0.72$   $\mu\text{m}$  and originated from the  ${}^4\text{G}$  excited states. The emission spectrum for our ceramic sample is shown in Fig. 7. In fact, Fig. 7 demonstrates a typical red fluorescence spectrum of  $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$  [86,87]. The red emission at  $687$  nm is assigned to the  ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$  spin-forbidden transition of  $\text{Cr}^{3+}$  ions located at the  $\text{Al}^{3+}$  sites [87]. A very weak luminescence of  $\text{Fe}^{3+}$  ions can probably reveal itself by the broad band of low intensity in the range of  $540 - 650$  nm and partly be concealed in the luminescence spectrum of the  $\text{Cr}^{3+}$  ion. The absorption spectrum of  $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$  consists of two broad bands in the visible spectral range, at  $\sim 390$  nm (the  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$  transition) and at  $\sim 540$  nm (the  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  transition). We did not observe the characteristic absorption bands of  $\text{Cr}^{3+}$  ion in the absorption spectrum of our  $\text{Fe}:\text{MgAl}_2\text{O}_4$  ceramic sample (see Fig. 6). Therefore, the concentration of this uncontrolled impurity ion in the ceramic sample is extremely low. According to the study of Bubnova and Solomonov [51], the characteristic luminescence bands of  $\text{Cr}^{3+}$  ions are not observed in spinels containing  $\text{Fe}^{3+}$  ions due to the quenching originating from the nonradiative energy transfer between chromium excited-states and the lower-lying levels of iron ions. Consequently, the fact that the luminescence spectrum of our  $\text{Fe}:\text{MgAl}_2\text{O}_4$  spinel ceramic presents the luminescence of  $\text{Cr}^{3+}$  ions is an evidence of the absence or an extremely low content of  $\text{Fe}^{3+}$  ions in the material.

In the UV part of the absorption spectrum of the  $\text{Fe}:\text{MgAl}_2\text{O}_4$  ceramic, there is an absorption band centered at  $0.26$   $\mu\text{m}$ . This band is too intense for the spin-forbidden  ${}^{\text{IV}}\text{Fe}^{2+}$  transitions. It can originate from the oxygen to  $\text{Fe}^{2+}$  and probably to  $\text{Fe}^{3+}$  charge transfer (oxide to metal charge transfer, OMCT). The corresponding absorption peaks are located at about  $250$  nm and  $210$  nm, respectively [88]. This suggestion is in accordance with Gaffney's finding [18] that  $\text{Fe}^{3+}$  impurities do not contribute directly to the visible spectra of most of these minerals, with the exception that  $\text{Fe}^{3+}$  probably contributes to the intense ultraviolet absorption.

The ground-state absorption (GSA) cross section,  $\sigma_{\text{GSA}}$ , for the  ${}^5\text{E} \rightarrow {}^5\text{T}_2$  ( ${}^5\text{D}$ ) transition of  $\text{Fe}^{2+}$  in  $\text{MgAl}_2\text{O}_4$  was calculated assuming that all the iron ions in the ceramic are optically active and there is no contribution of  ${}^{\text{VI}}\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species. The results are shown in Fig. 6(b). Here, we use the nominal iron concentration  $N_{\text{Fe}} = 1.516 \times 10^{19}$   $\text{cm}^{-3}$  (as calculated for the theoretical spinel density  $\rho = 3.578$   $\text{g}/\text{cm}^3$ ). The maximum  $\sigma_{\text{GSA}}$  is calculated to be  $0.28 \times 10^{-18}$   $\text{cm}^2$  at  $1.90$   $\mu\text{m}$ .

For comparison, in Fig. 6(b), we also plotted the GSA cross section spectra for  $\text{Fe}^{2+}$  ions in  $\text{ZnS}$  and  $\text{ZnSe}$  crystals (measured in this work using samples fabricated at G.G. Devyatikh Institute of Chemistry of High-Purity Substances, RAS). The absorption band in the Fe-doped spinel is blue-shifted by  $\sim 1$   $\mu\text{m}$  as compared to that for the  $\text{Fe}:\text{ZnSe}$  material while showing a very similar shape. The value of  $\sigma_{\text{GSA}}$  for the  $\text{Fe}:\text{MgAl}_2\text{O}_4$  spinel is reduced by a factor of  $\sim 3$  (compare with  $\sigma_{\text{GSA}} = 0.97 \times 10^{-18}$   $\text{cm}^2$  at  $3.11$   $\mu\text{m}$  for the  $\text{Fe}:\text{ZnSe}$  sample). We believe that this difference mainly originates from the host matrix. In part, it may also originate from the presence of traces of  ${}^{\text{VI}}\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species that do not contribute to the

absorption at 1.90  $\mu\text{m}$ ). Another possible mechanism responsible for decreasing the concentration of optically active iron ions in the ceramic compared to its initial concentration in the powder may be reduction of the  $\text{Fe}^{2+}$  ions to the metallic state due to the presence of residual hydrocarbons and carbon monoxide from the graphite equipment of the hot press. However, one of the features of LiF as a sintering additive is effective removal of carbon-containing impurities from ceramics at the open porosity stage. This prevents intensive reduction of  $\text{Fe}^{2+}$  ions. We believe that the concentration of optically active iron is close to its initial concentration in the powder.

It is worth mentioning that the described reduction mechanism can be partly responsible for the appearance of optically inactive iron in [47], as supported by much lower  $\sigma_{\text{GSA}}$  of only  $(1.66 \pm 0.14) \times 10^{-20} \text{ cm}^2$  reported in that work. Its indication is the dark coloration of samples in [47]. Another reason for such a low  $\sigma_{\text{GSA}}$  is the presence of  $^{\text{VI}}\text{Fe}^{2+}$  in this ceramics, as manifested by intense absorption band at  $\sim 1 \mu\text{m}$  [47].

## 5. Transparent glass-ceramics

### 5.1. Structure

The density variation for the initial glass with the heat-treatment temperature is shown in Fig. 8. It demonstrates a complex behavior typical for density variation of spinel based GCs [29]. The density of the initial glass is  $2.6120 \text{ g/cm}^3$ . After the heat-treatment at  $750 \text{ }^\circ\text{C}$ , the density slightly increases to  $2.6151 \text{ g/cm}^3$ , and after two-stage heat-treatments in the temperature range of  $800\text{--}900 \text{ }^\circ\text{C}$  it rapidly increases up to  $2.7147 \text{ g/cm}^3$ . The GCs prepared at the second stage in the temperature range of  $950\text{--}1000 \text{ }^\circ\text{C}$  have lower densities (the GC prepared at  $1000 \text{ }^\circ\text{C}$  has a density of  $2.6809 \text{ g/cm}^3$ ). The density of GC prepared at  $1050 \text{ }^\circ\text{C}$  is higher, namely  $2.7148 \text{ g/cm}^3$ .

The DSC curves for the initial glass and the glass heat-treated at  $750 \text{ }^\circ\text{C}$  for 6 h are drastically different, Fig. 9. Though the glass transition temperature,  $T_g$ , is about  $740 \text{ }^\circ\text{C}$  for both glasses, in the temperature range of  $800\text{--}1000 \text{ }^\circ\text{C}$  they behave differently. For the initial glass, there is an intense narrow peak with the crystallization onset temperature ( $T_{\text{on}}$ ) of  $880 \text{ }^\circ\text{C}$  and the maximum crystallization temperature of  $909 \text{ }^\circ\text{C}$ . This peak demonstrates an asymmetric wing from the low-temperature side. For the glass heat-treated at  $750 \text{ }^\circ\text{C}$  for 6 h, there are three rather broad exothermal peaks with the crystallization onset temperatures of  $795$ ,  $934$  and  $1085 \text{ }^\circ\text{C}$  and maximum crystallization temperatures of about  $859$ ,  $973$  and  $1160 \text{ }^\circ\text{C}$ , respectively, Fig. 10. It was challenging to determine the origin of these peaks for both DSC curves. That is why, after the crystallization onset temperatures were determined, the samples of the initial glass and the glass preliminary heat-treated at  $750 \text{ }^\circ\text{C}$  for 6 h, both about 80 mg in weight, were heated in the DSC instrument up to the crystallization onset temperatures.

According to the XRD data, Fig. 10(a), in the DSC curve of the initial glass, the first exothermal peak is associated with crystallization of the magnesium aluminotitanate (MAT) solid solution (ss) (probably, its crystallization corresponds to the low-temperature wing of the exothermal peak) and of the magnesium aluminosilicate with a quartz-like structure. The sample heat-treated up to the temperature of the second exothermic peak ( $1160 \text{ }^\circ\text{C}$ ) had a rich

phase composition of the MAT ss, magnesium aluminosilicate with a quartz-like structure, sapphirine, rutile, traces of indialite, a high-temperature modification of cordierite, and traces of mullite.

The XRD patterns of GCs prepared from the glass heat-treated at 750 °C for 6 h showed that the first crystallization peak is due to formation of spinel and traces of MAT ss. The sample heated up to 970 °C contained crystals of both MAT ss and spinel, while after heating up to 1150 °C, the sample contained the MAT ss and sapphirine crystals, as shown in Fig. 10(b).

The XRD patterns of the initial glass and GCs obtained by secondary heat treatments in the temperature range from 750 to 1050 °C are shown in Fig. 11. The initial glass and the glass heat-treated at the nucleation stage (at 750 °C for 6 h) are X-ray amorphous. The color change (Fig. 2) and density increase (Fig. 8) after the heat treatment at 750 °C suggest amorphous phase separation of the initial glass. This assumption will be confirmed below using TEM, Raman and optical spectroscopy data.

The XRD patterns show that after two-stage heat-treatments with the second stage in the temperature range of 800–1000 °C, two crystalline phases, MAT ss and spinel, crystallize and grow. With increasing the heat-treatment temperature, intensities of the peaks on the XRD patterns increase, and the intensity of the amorphous halo decreases. It means that the crystallinity fraction in GCs increases with the heat-treatment temperature. When the temperature rises from 800 to 1000 °C, the spinel mean crystal size grows from 37 to 74 Å, while the size of MAT crystals increases from 64 to 206 Å (see Table 1). The spinel unit cell parameter  $a$  increases with the heat-treatment temperature from 8.002 Å (at 800 °C) to 8.079 Å (at 1000 °C). As it was mentioned before, there exists an infinite solid solution in the  $\text{MgAl}_2\text{O}_4$ – $\text{FeAl}_2\text{O}_4$  system with the unit cell parameter  $a$  variation from 8.0855 to 8.1646 Å [17]. Therefore, one would expect larger spinel unit cell parameter in GCs. The low value of the parameter  $a$  implies that the composition of the spinel under study is enriched in alumina, which agrees with our previous observations [61]. An increase of the lattice constant of spinel under study with the heat-treatment temperature could be explained mainly by the decrease of the excess of aluminum in the spinel composition and additionally by an increase of the order in the spinel structure [29].

As soon as the crystals of spinel and MAT ss are formed at 800 °C, there is a shift of the amorphous halo position to smaller angles, which manifests a change in the composition of the residual glass. With increasing the heat-treatment temperature, the position of the amorphous halo becomes close to that of the vitreous silica, as the residual glass composition becomes more and more silica enriched.

In the temperature range of 1050–1100 °C, sapphirine, the solid solution with a composition lying between  $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 1\text{SiO}_2$  and  $7\text{MgO}\cdot 9\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$  [89] is also formed. After the two-stage heat treatment with the second hold at 1050 °C, the GC is transparent, while after the heat treatment at 1100 °C, it is translucent. It is the first time to our knowledge that transparent GC based on sapphirine are prepared (see Fig. 2 and Fig. 11, 1050 °C).

A typical TEM image of the initial glass, Fig. 12(a), shows amorphous phase separation in accordance with our previous studies [61]. Note that the XRD pattern of the sample indi-

cates the lack of any crystalline phase. The phase separation develops after the nucleation stage of the heat treatment at 750 °C, Fig. 12(b). The phase separated regions (mean size:  $D_{\text{TEM}} \sim 3.3$  nm) are still X-ray amorphous. In the TEM image of the GC sample obtained at 950 °C, nanocrystals ( $D_{\text{TEM}} \sim 6.4$  nm) with a rectangular and elongated shape are observed. They are most probably the spinel nanocrystals. Indeed, the corresponding  $D_{\text{XRD}} = 7.4$  nm (spinel) and 20.6 nm (MAT ss), see Table 1.

The complex character of the density variation with the heat-treatment temperature, when the density first increases and then slightly decreases, cf. Fig. 8, is related to a complex structure of the GCs described above and, in particular, to different densities of the spinel and MAT solid solutions and the amorphous phase with composition close to the vitreous silica, whose ratio changes with temperature. In addition, the composition of solid solutions also change in a complex way. The density increase is observed for the GC prepared at 1050 °C and containing sapphirine nanocrystals and increased fraction of MAT ss, Fig. 10. It could not be associated with the crystallization of sapphirine as the densities of spinel ( $\sim 3.58$  g/cm<sup>3</sup> [9]) and sapphirine (3.40-3.58 g/cm<sup>3</sup>, depending on its composition [90]) are similar. Thus, this effect is probably connected with increased fraction of the MAT ss containing Fe ions (see below). Note that the armalcolite density is  $\sim 4.94$  g/cm<sup>3</sup> [91].

### 5.2. Raman spectra

The Raman spectra of the initial and heat-treated glasses demonstrate the structural evolution of the material, see Fig. 13(a). The spectrum of the initial glass contains two broad bands, one with a maximum at 478 cm<sup>-1</sup>, and another of a complex shape with several maxima at 802, 920 and 1025 cm<sup>-1</sup>. The bands at 478, 802 and 1025 cm<sup>-1</sup> are attributed to vibrations of tetrahedra of the aluminosilicate network. The very intense band at 920 cm<sup>-1</sup> is attributed to vibrations of the [TiO<sub>4</sub>] tetrahedra incorporated into the aluminosilicate network [60].

After the heat-treatment of the glass at 750 °C for 6 h (the nucleation stage), its Raman spectrum changes. The broad band at 478 cm<sup>-1</sup> shifts to 466 cm<sup>-1</sup> and the band intensities in the high-frequency region are redistributed: the band at 920 cm<sup>-1</sup> shifts to 910 cm<sup>-1</sup> and attenuates, and the band at 800 cm<sup>-1</sup> shifts to 814 cm<sup>-1</sup> and enhances. These changes are caused by development of the phase separation of the glass: the magnesium aluminotitanate amorphous phase (with a characteristic band at 810 cm<sup>-1</sup>) and the phase enriched in magnesia and alumina are formed in the residual silica-rich phase (the manifestation of the latter phase is the shift of the band characteristic for the glass network from 478 cm<sup>-1</sup> to 466 cm<sup>-1</sup>). Thus, the so-called three-phase immiscibility [61] is developed. The high intensity of the 814 cm<sup>-1</sup> band can be explained by the superposition of vibrations of the [SiO<sub>4</sub>] tetrahedra and those of the Ti–O bonds in [TiO]<sub>5</sub> and in [TiO]<sub>6</sub> polyhedrons in the amorphous magnesium aluminotitanate phase [60].

The Raman spectra of GCs prepared by two-stage heat treatments are different from those previously discussed. In the Raman spectrum of GC prepared at 750 °C (the first stage) and at 800 °C (the second one), there is a broad band at 450 cm<sup>-1</sup> (note that for pure SiO<sub>2</sub>, it is located at 440 cm<sup>-1</sup>), an intense band of 810 cm<sup>-1</sup> with an inflection at 915 cm<sup>-1</sup>, and a number

of weak bands at 148, 285 and  $\sim 690$   $\text{cm}^{-1}$ . These changes indicate further phase separation of the glass and beginning of the MAT ss crystallization. The bands at 148, 285, 603 and  $\sim 690$   $\text{cm}^{-1}$  and the intense band at 810  $\text{cm}^{-1}$  which is superimposed on the band of the amorphous magnesium aluminotitanate phase, can be attributed to the spectrum of the MAT ss with a rather high alumina content [60]. After further increasing the temperature of the second stage of the heat treatment to 850  $^{\circ}\text{C}$ , the bands at 219, 272, 385,  $\sim 487$ ,  $\sim 690$  and 802  $\text{cm}^{-1}$  appear in the Raman spectrum that can be attributed to the MAT ss crystals. Note that the weakest bands in the frequency range of 334–496  $\text{cm}^{-1}$  are superimposed on the band at  $\sim 450$   $\text{cm}^{-1}$  originating from the residual glass phase, and it is difficult to determine their position more precisely. With a successive increase in the heat-treatment temperature of the glass from 900 to 1000  $^{\circ}\text{C}$ , almost all bands of the MAT ss are observed in the Raman spectrum. They are located at 167, 209, 261,  $\sim 375$ ,  $\sim 487$ , 668, 789 and  $\sim 900$   $\text{cm}^{-1}$  (a weak wing of the intense band near 800  $\text{cm}^{-1}$ ), and their positions slightly vary reflecting the variation of the ratio of magnesium and aluminum in the MAT ss at the particular temperature. After the heat-treatment with the second stage at 1050  $^{\circ}\text{C}$ , the bands are shifted to higher frequencies of 170, 215, 266,  $\sim 383$ ,  $\sim 487$ , 681, and 797  $\text{cm}^{-1}$ , which indicates an additional enrichment of the solid solution with alumina (note that the weak band at 456  $\text{cm}^{-1}$  does not belong to the spectrum of the MAT ss).

We speculate that iron ions  $\text{Fe}^{2+}$  can enter the crystals of MAT ss. There exist a mineral armalcolite, which has a general chemical formula of  $(\text{Mg}^{2+}, \text{Fe}^{2+})\text{Ti}_2\text{O}_5$ . Together with MAT, it belongs to the pseudobrookite group. The Raman spectrum of armalcolite [92] is similar to that of the MAT ss. Thus, one can expect that entering the  $\text{Fe}^{2+}$  ions into the structure of MAT ss should not disturb the structure and will not cause a serious change of the Raman spectrum.

After the two-stage heat treatments with a second stage at 950–1000  $^{\circ}\text{C}$ , a weak and then more distinct maximum appears at 409  $\text{cm}^{-1}$ , which corresponds to the most intense band of spinel [70]. Note that, apparently, due to the large difference in the scattering cross sections for crystals of MAT ss and spinel, in the Raman spectra of the heat-treated glass the bands of MAT ss are always the most intense, and spinel is hard to be observed.

After increasing the heat-treatment temperature to 1050  $^{\circ}\text{C}$ , according to XRD data, Fig. 11, sapphire crystals are detected in addition to spinel and MAT ss. We tried to find any signs of sapphire in this Raman spectrum. In the RRUFF database [93], there are Raman spectra of several sapphire minerals with peak positions at about 220, 410, 495, 565, 685, 750, 825, 915 and 985  $\text{cm}^{-1}$ . Two of these bands are the most intense, i.e., at 565 and 685  $\text{cm}^{-1}$ , of which the second is about 1.6 times more intense than the first. Figure 13(a) shows that the position of the most intense Raman band of sapphire at 685  $\text{cm}^{-1}$  nearly coincides with the position of the band of MAT ss at 681  $\text{cm}^{-1}$ . A very weak trace of the second most intense sapphire band is found at 562  $\text{cm}^{-1}$ . The trace of the band at  $\sim 409$   $\text{cm}^{-1}$  is the superposition of spinel and sapphire bands. The sapphire band of intermediate intensity at 915  $\text{cm}^{-1}$  is superimposed on the high-frequency tail of the intense band of the MAT ss at 795  $\text{cm}^{-1}$ . Thus, there is no significant impact of sapphire crystallization on the Raman spectrum

of GC since intensities of all the bands do not change noticeably when comparing the spectrum of the GC prepared at 1000 °C with that of the GC prepared at 1050 °C.

### 5.3. Low-frequency Raman spectra

The Raman spectra of the initial glass and the glass subjected to heat-treatment at the nucleation stage (at 750 °C for 6 h) did not show any low-frequency band. This band appears after two-stage heat-treatments and its position shifts to lower frequencies with increasing the heat-treatment temperature, Fig. 13(b).

There is a correlation between the position of the low-frequency Raman band and the size of inhomogeneous regions [94,95]:

$$\nu_{02}^s = \frac{\xi_{02}^s \nu_l}{2\pi R \cdot c}, \quad (3)$$

where  $\nu_{02}^s$  is the frequency of the spheroidal vibration mode corresponding to the low-frequency peak, which is mostly active in Raman scattering,  $\xi_{02}^s$  is the phenomenological coefficient depending on the relation between the transversal,  $\nu_t$ , and longitudinal,  $\nu_l$ , velocities of sound in the inhomogeneous regions and on the particle interface,  $R$  is the radius of the inhomogeneous region (assuming its nearly-spherical shape) and  $c$  is the speed of light. The mean size ( $D_{\text{Raman}}$ ) of inhomogeneous regions is [96]:

$$D_{\text{Raman}} \approx \frac{0.8\nu_l}{c\nu_{02}^s}. \quad (4)$$

Our earlier study of phase separation in heat-treated magnesium aluminosilicate glasses nucleated by TiO<sub>2</sub> using small-angle X-ray scattering [61,97] showed that a bidispersed system of inhomogeneities is formed at the initial stages of phase separation. The sizes of the smaller regions were found to be consistent with the sizes obtained from the position of the low-frequency Raman band under an assumption that at the beginning of the process, these are amorphous silicate inhomogeneities enriched in magnesium and aluminum, in which spinel crystallizes with increasing the heat-treatment temperature. Large-size inhomogeneities, at first also of amorphous nature, form magnesium-aluminum-titanate phase, from which the MAT ss crystallizes with increasing the heat-treatment temperature.

The sound velocity for spinel crystals  $\nu_l = 10 \times 10^5 \text{ cms}^{-1}$  [98]. When calculating the sizes of inhomogeneous regions  $D_{\text{Raman}}$  listed in Table 1, we have chosen a slightly lower sound velocity,  $\nu_l = 8 \times 10^5 \text{ cms}^{-1}$ , since a certain amount of SiO<sub>2</sub> is always present in magnesium aluminate regions of inhomogeneity. For SiO<sub>2</sub>,  $\nu_l$  is less than  $6 \times 10^5 \text{ cms}^{-1}$  [98]. The results presented in Table 1 allowed us to conclude that these regions of inhomogeneity are not completely crystallized, since the diameter of spinel crystals according to the XRD and TEM data is approximately half of that calculated from the position of the low-frequency Raman band.

### 5.4. Optical absorption

The absorption spectra of the initial glass and GCs are presented in Fig. 14(a-c). For the initial glass, the UV absorption edge is observed at  $\lambda_{\text{UV}} = 0.34 \text{ }\mu\text{m}$ . The spectrum contains a

broad band in the range of 400–600 nm, a maximum of which is superimposed with the absorption edge, a weak and broad band at 0.75–1.5  $\mu\text{m}$  with a peak at  $\sim 1.05 \mu\text{m}$  and a weak shoulder extending until 2.5  $\mu\text{m}$ , and a broad asymmetric band in the in the range of 2.7 – 3.1  $\mu\text{m}$ . The spectrum of the glass heat-treated at 750  $^{\circ}\text{C}$  for 6 h (the nucleation stage) is different from the spectrum of the initial glass mainly in the UV and visible ranges: the absorption edge is red-shifted by about 7 nm, and a broad band in the visible intensifies and becomes broader, it now spans until 700 nm.

The spectrum of the GC prepared by the two-stage heat-treatment with the second stage at 800  $^{\circ}\text{C}$  demonstrates a similar evolution: the absorption edge is further red-shifted by about 6 nm, and a broad band in the visible spectral range intensifies and becomes even broader now spanning until 900 nm.

With increasing the temperature of the heat-treatment at the second stage (850–1000  $^{\circ}\text{C}$ ), the spectra of the GCs change in a different way. The slope of the UV absorption edge becomes smoother, while its position is slightly changing in the range of  $\lambda_{\text{UV}} = 0.34\text{--}0.35 \mu\text{m}$ . There is also a great raise of absorption in the visible with a maximum at  $\sim 0.55 \mu\text{m}$  and in the near IR, and an increase in intensity of the broad absorption band at 0.75–1.5  $\mu\text{m}$ , Fig. 14(b). A broad band at 1.4–2.5  $\mu\text{m}$  with a maximum at  $\sim 1.88 \mu\text{m}$  appears and grow with increasing the heat-treatment temperature. The mid-IR absorption is structured with two components at 2.73 and 2.92  $\mu\text{m}$ , Fig. 14(c).

Finally, for the GC obtained at 1050  $^{\circ}\text{C}$ , the absorption edge experiences a notable red-shift to  $\lambda_{\text{UV}} = 0.37 \mu\text{m}$ . The absorption at  $\sim 1.88 \mu\text{m}$  decreases. Simultaneously, the absorption in the visible and at  $\sim 1.1 \mu\text{m}$  raises.

The interpretation of the absorption spectra is complicated because in the initial glass and in GCs, there are two polyvalent transition metal ions that can be responsible for light absorption, i.e., titanium and iron ones, and both ions participate in phase transformations caused by heat-treatments, which alternates their surrounding.

In general, titanium ions are found in glasses and minerals under two oxidation states of  $\text{Ti}^{3+}$  ( $3d^1$ ) and  $\text{Ti}^{4+}$  ( $3d^0$ ). The absorption band due to the  ${}^2\text{T}_{2g} \rightarrow \text{E}_g$  transition of the  $\text{Ti}^{3+}$  ion in  $\text{O}_h$  site symmetry is located at about 500 – 625 nm depending on the ligand field strength and distortions of its symmetry [99,100], while the band due to the  $\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition of  $\text{Ti}^{3+}$  in  $\text{T}_d$  site symmetry is located at about 1000 nm [100,101]. The O- $\text{Ti}^{3+}$  OMCT band is predicted in the UV spectral range at about 240 nm [102].  $\text{Ti}^{4+}$  ions do not exhibit any d-d transition while they are responsible for the O- $\text{Ti}^{4+}$  OMCT band which is located in the UV spectral range at about 300 nm [102], as well as participate in homonuclear IV CT  $\text{Ti}^{4+}/\text{Ti}^{3+}$  and heteronuclear  $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$  transitions that give rise to intense absorption bands in the visible spectral range. In different minerals, IV CT  $\text{Ti}^{4+}/\text{Ti}^{3+}$  transition gives rise to a band at about 480 nm [103], 660 - 670 nm [104].

Iron ions in glasses exist under two oxidation states, ferrous,  $\text{Fe}^{2+}$  ( $3d^6$ ) and ferric,  $\text{Fe}^{3+}$  ( $3d^5$ ). The analysis of the absorption spectra caused by iron ions in glasses is difficult because all transitions of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions, except of those giving rise to bands in the region of 1 and 2  $\mu\text{m}$ , are spin-forbidden and therefore have weak intensities; the corresponding bands are superimposed on very intense (especially in case of  $\text{Fe}^{3+}$  ions) IV CT (at least 10 times more

intense) and OMCT (100 to 1000 more intense) bands. Moreover, Fe<sup>3+</sup> and Fe<sup>2+</sup> ions often coexist, they can be fourfold-, fivefold- and sixfold-coordinated, and similar forbidden bands fall into the same spectral range and overlap [101,105]. For the assignment of absorption bands in the spectra of glasses, a comparison with absorption spectra of minerals with well-established structure is employed [105], additional methods of analysis are used, i.e., high-resolution X-ray absorption near-edge structure (XANES) spectra [106] or Mössbauer spectra [100,107].

In the spectra of ferric ions in silicate glasses, the OMCT Fe<sup>2+</sup>-O band is located at about 235 nm, while weak spin-forbidden bands can be found around 21500 and 23400 cm<sup>-1</sup> (at 465 and 430 nm, respectively) [105] and are assigned to the Fe<sup>2+</sup> spin-forbidden transitions <sup>5</sup>T<sub>2</sub>(D) → <sup>3</sup>T<sub>1</sub>(H) and <sup>5</sup>T<sub>2</sub>(D) → <sup>3</sup>T<sub>2</sub>(H), respectively. The broad bands at about 1000 and 2000 nm are attributed to the spin-allowed electronic d-d transitions <sup>5</sup>T<sub>2</sub> → <sup>5</sup>E and <sup>5</sup>E → <sup>5</sup>T<sub>2</sub> for octahedrally and tetrahedrally coordinated Fe<sup>2+</sup> ions, respectively [100,101].

In the spectra of ferric ions in silicate glasses, the OMCT Fe<sup>3+</sup>-O band is located at about 270 nm [105] and it spans until the visible spectral range. It often even overlaps with peaks located at about 370, 380, 420, 440, and 480 nm and assigned to d-d transitions of [<sup>4</sup>]Fe<sup>3+</sup>, [<sup>5</sup>]Fe<sup>3+</sup> and [<sup>6</sup>]Fe<sup>3+</sup> ions [105].

Fe<sup>2+</sup>-Fe<sup>3+</sup> and Fe<sup>2+</sup>-Ti<sup>4+</sup> coordination clusters may coexist in the same structure, and give rise to homonuclear Fe<sup>2+</sup> → Fe<sup>3+</sup> and heteronuclear Fe<sup>2+</sup> → Ti<sup>4+</sup> intervalence transitions in the visible region, thereby complicating the assignment of absorption bands [104]. The Fe<sup>2+</sup>-Ti<sup>4+</sup> IV CT transition is believed to contribute to the UV-visible spectra of synthetic Fe-Ti silicate glasses [108]. In [100], it was found at about 450 nm contributing to the absorption edge of the glass. IV CT Fe<sup>2+</sup> → Fe<sup>3+</sup> transitions are observed in the range of 540 - 660 nm, as well as at around 730-770 nm [104].

The spectral changes observed upon the heat-treatments of the initial glass under study confirm that the titanium and iron ions are involved in phase transformations. The absorption edge of the initial glass is caused by the O-Ti<sup>4+</sup>, O-Fe<sup>2+</sup>, and O-Fe<sup>3+</sup> OMCT overlapping spectral bands. According to Mysen [109], in magnesium aluminosilicate glasses, iron exists in the forms of ferrous (Fe<sup>2+</sup>) and ferric (Fe<sup>3+</sup>) ions with 4-, 5-, and 6-fold coordination states. The absorption band in the range of 400-600 nm is probably due to spin-forbidden d-d absorption bands of ferrous and ferric ions [105], while the weak and broad absorption band at 0.75–1.5 μm with a peak at ~1.05 μm can be associated with Fe<sup>2+</sup> ions in O<sub>h</sub> sites in the glass network. A weak shoulder extending until 2.5 μm can be connected with a minor fraction of Fe<sup>2+</sup> ions in T<sub>d</sub> sites. A broad asymmetric band in the in the range of 2.7 – 3.1 μm is caused by very intense absorption bands due to O–H vibrations of hydroxyl groups in glass.

The variation of the absorption spectrum after the heat-treatment at the nucleation stage is connected with the development of the three-phase immiscibility. Ferrous ions probably enter magnesium aluminate and magnesium aluminotitanate amorphous regions resulting in Fe<sup>2+</sup>+ Ti<sup>4+</sup> → Fe<sup>3+</sup> + Ti<sup>3+</sup> IVCT transitions.

The red shift of the absorption edge and a great raise of absorption in the visible spectral range after secondary heat treatments is consistent with crystallization of spinel and MAT ss and possible entering of iron ions into these phases. Absorption spectra of iron-doped

spinel is well-documented and discussed [18,20-23,77-81,110]. The broad absorption bands in the visible part of spectra of Fe-doped spinels are usually attributed to different spin-forbidden d-d transitions of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in the spinel ligand field [21,110], while the additional weak band at ~15000 cm<sup>-1</sup> (~670 nm) can be assigned to the Fe<sup>2+</sup>-Fe<sup>3+</sup> exchange interaction [110]. In the spectra of GCs under study we can undoubtedly see the signs of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in the spinel structure, as well as IV CT transitions associated with Ti<sup>3+</sup>/Ti<sup>4+</sup>, Fe<sup>2+</sup>/Fe<sup>3+</sup> and Fe<sup>2+</sup>+ Ti<sup>4+</sup> → Fe<sup>3+</sup> + Ti<sup>3+</sup>. It should be noted that broad d-d absorption bands of Ti<sup>3+</sup> ions in synthetic magnesium aluminate spinel are localized in the spectral region of 510 and 760 nm [111]. We cannot exclude their appearance in absorption spectra of GCs under study. An appearance and growth of the bands in the IR spectral range is due to the entry of Fe<sup>2+</sup> ions into spinel nanocrystals in both the tetrahedral (predominantly) and octahedral positions. The mid-IR absorption with two components at 2.73 and 2.92 μm is developed on the basement of the broad asymmetric unstructured band of OH<sup>-</sup> groups in the residual glass. It is interesting to note that the position of the short wavelength component of this band experiences a gradual blue-shift from 2.8 to 2.73 μm with increasing the temperature of the heat-treatment, Fig. 14(c). We connect the structuring of the absorption bands due to O–H vibrations with spinel crystallization because it is observed only in the spectra of samples containing spinel nanocrystals. Note that in synthetic spinel, the structuring of the band associated with OH groups was observed and assigned to OH groups entering the spinel structure [112,113]. However, the positions of these bands at 2985 nm (3350 cm<sup>-1</sup>) and 2818 nm (3548 cm<sup>-1</sup>) are different from those observed in our GCs while the reason for this discrepancy still remains unclear.

For the GC obtained at 1050 °C, a notable red-shift of the UV absorption edge reflects an increase in light scattering by relatively large sapphirine crystals. The absorption at ~1.88 μm associated with Fe<sup>2+</sup> ions in T<sub>d</sub> sites in spinel decreases. Simultaneously, the absorption in the visible and at ~1.1 μm raises. This correlates with the decrease in the amount of precipitated spinel and appearance of sapphirine. In sapphirine, Mg<sup>2+</sup> ions are in sixfold coordination while Al<sup>3+</sup> ions are in four- and sixfold coordinated sites [114]. Sapphirine accommodates iron ions and exhibits the substitutions Mg → Fe<sup>2+</sup> (predominantly) and Al → Fe<sup>3+</sup> [113] with Fe<sup>3+</sup> ions assigned to tetrahedral positions [115]. Thus, upon sapphirine formation from spinel and residual highly siliceous glass, iron ions are present as the <sup>VI</sup>Fe<sup>2+</sup> and <sup>IV</sup>Fe<sup>3+</sup> species, which is reflected in absorption spectra.

Due to the complex distribution of iron ions over several phases, as well as the presence of iron species with different coordination and valence states, it is very difficult to make a reliable estimation of the fraction of iron ions located in spinel nanocrystals. The determination of the ground-state absorption cross-section for Fe<sup>2+</sup> ions in MgAl<sub>2</sub>O<sub>4</sub> (e.g., in an absorption saturation experiment) may facilitate such estimates.

#### 5.4. Luminescence

The luminescence spectrum of GCs (Fig. 15) strikingly resembles that of ceramic (Fig. 7) that was assigned to impurity Cr<sup>3+</sup> ions in O<sub>h</sub> sites of spinel. This means that the evolution of the luminescence properties on the initial glass with the heat-treatment should be

connected with impurity  $\text{Cr}^{3+}$  ions located in different phases. Let us discuss the spectral-luminescence properties of  $\text{Cr}^{3+}$  ions in the initial glass and in GCs. In oxide glasses,  $\text{Cr}^{3+}$  ions occupy a variety of sites with different crystal field strengths due to site variability and compositional disorder.  $\text{Cr}^{3+}$  is generally recognized as being in  $O_h$  symmetry with certain distortions [116]. According to [117], for trivalent chromium in octahedral coordination, the  ${}^4T_{2g} \rightarrow {}^4A_{2g}$  transition is typical in the low crystal field materials with a substantial participation of the site-to-site disorder, i.e., in glasses. The  $\text{Cr}^{3+}$  luminescence in silicate glasses in low-crystal field is at  $\sim 800$  nm [116,118,119]. The luminescence spectrum of the initial glass in the visible contains a weak broad band with a maximum at about 750 nm (Fig. 15). After the heat-treatment at 750 °C, the intensity of the luminescence band increases. A disproportional increase in intensity of the short-wavelength wing changes the shape of the luminescence band, while the peak position at about 750 nm does not change. After two-stage heat-treatments and with increasing the temperature at the second stage (800–1050 °C), the luminescence spectra of the GCs further change. Sharp peaks with maxima at 667, 676, 688, 698, 709, and 717 nm are formed on the basement of the broad unstructured band. Their intensities sequentially increase with the heat-treatment temperature in the range of 800–1000 °C while the intensity of the broad unstructured band has a non-monotonic behavior. The maximum intensity of the latter band is observed in GC prepared by the heat-treatment at the second stage of 850 and 900 °C, then it slightly decreases and remains unchanged for GCs prepared at 950-1050 °C (Fig. 16). The intensities of the peaks with maxima at 667, 676, 688, 698, 709, and 717 nm slightly decrease in the spectrum of the GC prepared at 1050 °C.

The luminescence spectra of GCs prepared by heat-treatments at the second stage at 850 – 1050 °C can be considered as a superposition of spectral features of the  $\text{Cr}^{3+}:\text{MgAl}_2\text{O}_4$  luminescence and the band underlying these features and the longer wavelength band attributed to high- and low-crystal field  $\text{Cr}^{3+}$  sites, respectively, in the amorphous residual phase [116,119].

## 6. Discussion

In this section, we aimed to describe our results by comparing the structure of ceramic and GC and the behavior of iron and impurity chromium ions in these two hosts, wherever it is possible. Previously, we used this approach in the study of  $\text{Co}:\text{ZnAl}_2\text{O}_4$  transparent ceramic and GC [33]. Such a comparison clearly demonstrates the characteristic features of both materials. The XRD pattern of ceramics presents a single-phase spinel material. The XRD pattern of the  $\text{Fe}:\text{MgAl}_2\text{O}_4$ -based GC reveals a multiphase material exhibiting the strongly broadened diffraction peaks of spinel located at the same positions as for the ceramic, as well as broad peaks of low intensity due to precipitation of MAT ss nanosized crystals and a massive halo due to a high content of the residual highly siliceous glass, Fig. 16(a). A relatively low spinel crystalline fraction in GC becomes evident.

A comparison of Raman spectra of ceramic and GC helped us to find characteristic vibrations of spinel nanocrystals in the complex Raman spectrum of GC containing the features of the MAT ss and those of the residual glass. Previously, we were certain that spinel vibrations are too weak in intensity to be noticed in the spectra of GCs at the background of in-

tense vibrations of MAT ss [60]. The most intense spinel band located at  $409\text{ cm}^{-1}$  can be easily found because in this spectral range there are no modes of the MAT ss. Moreover, we managed to find the other bands typical for spinel nanocrystals only by comparison with the spectrum of ceramics. Now we can notice the peaks at 200, 251, 306, 409, 496, 668, 724 and  $764\text{ cm}^{-1}$  in the spectrum of GC and attribute them to vibrations connected with spinel crystals, Fig. 16(b).

The comparison of absorption spectra of ceramic and GC, Fig. 16(c), clearly indicates the presence of iron ions in ceramics only in one oxidation state,  $\text{Fe}^{2+}$ , and predominantly in the  $T_d$  sites as opposed to multiple valence states and different coordinations in GCs. This difference is the result of different phase compositions of the materials. The ceramic is a single-phase spinel while the GCs are multiphase materials containing spinel nanocrystals. Indeed, the glass under study demonstrates the three-phase immiscibility, i.e., formation of the magnesium aluminotitanate amorphous phase and an amorphous phase enriched in magnesia and alumina. These phases are located in the residual silica-rich glass. In fact, Fe ions are distributed between these three phases according to a partition coefficient. During further crystallization within amorphous regions enriched in magnesia and alumina and magnesium aluminotitanate amorphous regions, iron ions become a component of the spinel and MAT ss crystals, as well as remain in the residual glass. In the GCs, iron ions are located in spinel nanocrystals as  $^{\text{IV}}\text{Fe}^{2+}$  and  $^{\text{VI}}\text{Fe}^{2+}$ ,  $^{\text{IV}}\text{Fe}^{3+}$  and  $^{\text{VI}}\text{Fe}^{3+}$  species, in the MAT ss probably as  $^{\text{IV}}\text{Fe}^{2+}$  species and predominantly in the form of  $\text{Fe}^{3+}$  species in the residual glass enriched in silica. The spinels in the ceramic and GCs are very different due to their different structures (i.e., different degree of inversion determined by composition and fabrication conditions), compositions (in GCs as opposed to ceramics, there are solid solutions of spinel enriched in alumina and containing titanium ions) and sizes (nm-sized in GCs vs.  $\mu\text{m}$ -sized in ceramic).

The luminescence spectra of both materials are very similar, Fig. 16(d). They are formed by luminescence of  $\text{Cr}^{3+}$  ions substituting for  $\text{Al}^{3+}$  ions in spinel crystals. The only difference in the spectra is the presence of a broad unstructured band with two maxima at about 720 and 750 nm observed in the spectrum of GCs. It is connected to a multiphase nature of GCs: this broad unstructured luminescence band is typical for  $\text{Cr}^{3+}$  ions in glass and reflects the presence of the residual glass in GCs. The maximum at about 720 nm on this broad band can be connected with the luminescence of  $\text{Fe}^{3+}$  ions in  $O_h$  symmetry in the  $\text{Al}^{3+}$  position in spinel nanocrystals in GCs [49-51].

We are aware that spinel ceramic often contains an admixture of secondary phases, i.e., kyanite ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) [51],  $(\text{MgO})_{0.91}(\text{FeO})_{0.09}$  or periclase (MgO) [49,50]. These phases are manifested by luminescence of  $\text{Fe}^{3+}$  ions. The absence of  $\text{Fe}^{3+}$  ion luminescence in spinel ceramics proves that it is a single-phase material that does not contain  $\text{Fe}^{3+}$  ions.

Let us also comment on the synthesis method of our ceramics. In contrast to [47] where the  $\text{Fe}^{2+}:\text{MgAl}_2\text{O}_4$  powders were obtained by laser ablation followed by free vacuum sintering, in our work the powders were synthesized by sol-gel method, and their consolidation was carried out by hot pressing in the presence of LiF sintering additive. This approach made it possible to obtain higher optical quality ceramics, which is especially noticeable in the visible and near-IR wavelength ranges. In addition, the main part of the iron remained in the +2 oxi-

dation state in  $T_d$  sites. Thus, at close initial concentration of iron in spinel powders as compared to [47], the absorption of  $Fe^{2+}$  ions in our ceramics is several times greater, see Fig. 6(a).

## 7. Conclusions

We fabricated and studied the structure, phase transformations, optical and spectroscopic properties of the  $Fe:MgAl_2O_4$  (spinel) transparent ceramic and  $Fe:MgAl_2O_4$ -based transparent nanophase glass-ceramics. The main difference of two materials is their phase composition which determines the valence state and coordination of the iron ions leading to different spectroscopic properties. The 0.1 mol%  $Fe:MgAl_2O_4$  ceramic obtained by hot-pressing at 1600 °C / 50 MPa of powders obtained by the sol-gel method and using LiF as a sintering aid is a single-phase material being isostructural to undoped spinel (sp. gr.  $Fd\bar{3}m$ , the lattice constant  $a = 8.083 \pm 0.003$  Å). Its microstructure is determined by relatively large grains (mean size: 50  $\mu m$ ) with clean grain boundaries and the lack of any secondary phases at their boundaries. The iron ions are replacing the  $Mg^{2+}$  ones in tetrahedral ( $T_d$ ) sites. The optical absorption and visible luminescence studies indicated that the content of the  $^{VI}Fe^{2+}$  and  $Fe^{3+}$  species, if present, is very low. The absorption of the  $Fe:MgAl_2O_4$  ceramic is determined by a broad and intense band related to the  $^5E \rightarrow ^5T_2$  ( $^5D$ ) transition of  $Fe^{2+}$  ions in  $T_d$  sites and corresponding to a ground-state absorption cross section of  $0.28 \times 10^{-18}$  cm<sup>2</sup> at the peak wavelength of 1.90  $\mu m$ . This absorption band is similar in shape to that observed in  $Fe^{2+}$ -doped zinc chalcogenides (ZnS, ZnSe) while is blue-shifted.

This is for the first time that transparent  $Fe:MgAl_2O_4$ -based glass-ceramics were obtained. They were fabricated by secondary two-stage heat-treatment of the initial magnesium aluminosilicate glass nucleated by 10 mol%  $TiO_2$  and doped with 0.1 mol%  $FeO$ . A complex picture of phase transformations in the initial glass and further in the GCs was determined. For the second stage of the heat-treatment at 800 – 1000 °C for 6 h (the first, nucleation, stage, was at 750 °C for 6 h), nanosized spinel crystals (mean size: 3.7 – 7.4 nm, lattice constant:  $a = 8.002 - 8.079$  Å, both increasing with the heat-treatment temperature) precipitated. The transparent GCs were multi-phase materials containing, together with the spinel nanophase magnesium aluminotitanate solid solution (MAT ss) nanocrystals (mean size: 6.4-20.6 nm), as well as enriched in silica residual glass phase. The iron ions in these GCs were present as  $^{IV}Fe^{2+}$ ,  $^{VI}Fe^{2+}$  and  $Fe^{3+}$  species in the spinel structure, as well as  $Fe^{2+}$  and  $Fe^{3+}$  species in magnesium aluminotitanate solid solutions and in the residual glass. The presence of  $Ti^{3+}$  and  $Ti^{4+}$  ions (from the crystallization catalyst) determined the absorption of GCs in the UV-visible spectral range. Absorption is partly caused by interplay of iron and titanium ions in different valence states, coordination sites, and locations while the  $Cr^{3+}$  ions in spinel and in the residual glass (an uncontrolled impurity) determined the spectrum of visible luminescence.

In the present paper, we focused on revealing the nature of the optically active iron centers in spinel transparent ceramic and GCs. This is of key importance for potential applications of such materials, e.g., as laser gain media and saturable absorbers of mid-infrared lasers emitting at the wavelength of 2-3  $\mu m$ . For applications, particularly the  $Fe^{2+}$  ions in  $T_d$

sites are preferable. Besides, one cannot neglect the difference in the thermo-mechanical properties of the host materials and especially their resistance to the laser-induced damage which is much higher for GCs. Further work on Fe:MgAl<sub>2</sub>O<sub>4</sub> based transparent materials should focus on revealing their mid-infrared emission properties (the spectrum and the lifetime), as well as the saturable absorption properties. The latter may serve as an independent tool to confirm the ground-state absorption cross sections for <sup>IV</sup>Fe<sup>2+</sup> species in spinel.

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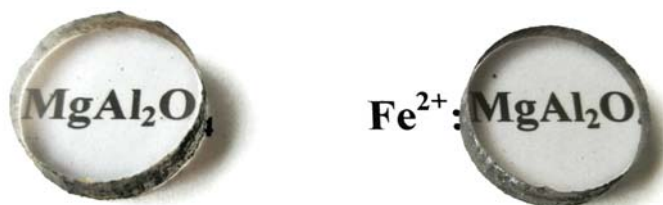
**Table 1.** Mean size of nanocrystals  $D$  in transparent GCs estimated by different methods\* and the unit-cell parameter of spinel nanocrystals  $a$ .

Heat-treatment regime	XRD			Raman	TEM
	Spinel	MAT		$D_{\text{Raman}}, \text{Å}$	$D_{\text{TEM}}, \text{Å}$
	$a, \text{Å}$	$D_{\text{XRD}}, \text{Å}$	$D_{\text{XRD}}, \text{Å}$		
750 °C/6 h + 800 °C/6 h	8.002	37	64	98	-
750 °C/6 h + 850 °C/6 h	8.020	41	103	115	-
750 °C/6 h + 900 °C/6 h	8.074	60	127	115	-
750 °C/6 h + 950 °C/6 h	8.079	74	146	124	64
750 °C/6 h + 1000 °C/6 h	8.079	74	206	137	-

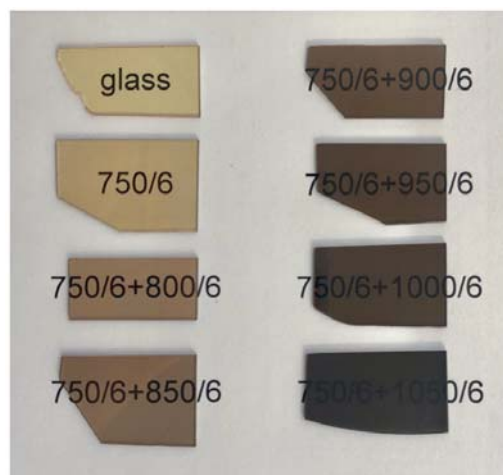
\* $D_{\text{XRD}}$  – size determined from the XRD studies using the Scherrer formula, Eq. (1);  $D_{\text{Raman}}$  – size determined from small-frequency Raman spectra, Eq. (4);  $D_{\text{TEM}}$  – size determined from TEM images.

### List of figure captions

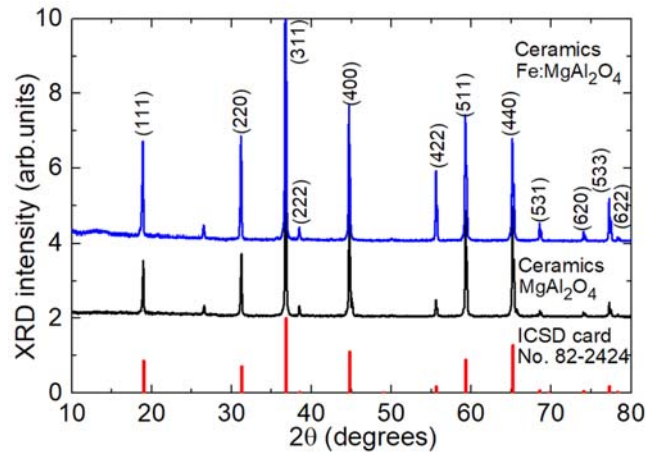
**Figure 1.** Photograph of the laser-grade-polished undoped  $\text{MgAl}_2\text{O}_4$  (*left*) and 0.1 mol%  $\text{Fe}:\text{MgAl}_2\text{O}_4$  (*right*) transparent ceramic disks.



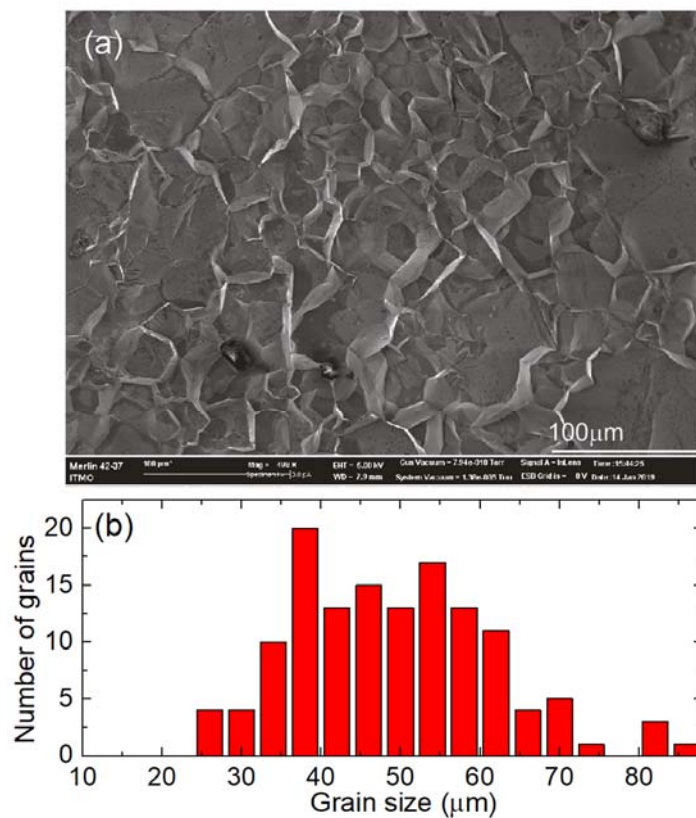
**Figure 2.** Photographs of the initial glass and transparent GCs obtained by various secondary heat-treatments, (temperature, °C / duration, h).



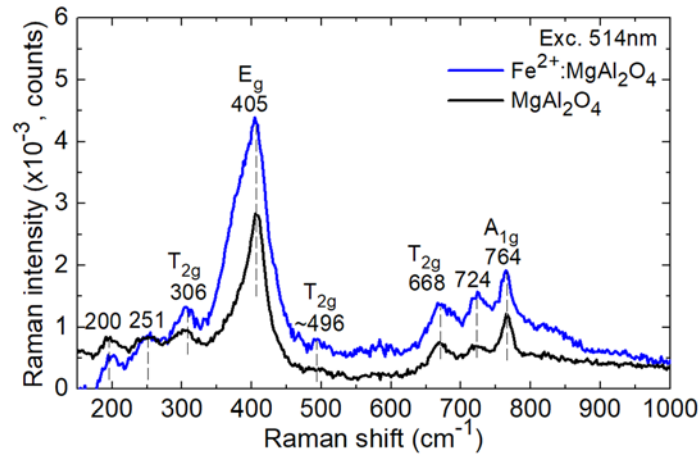
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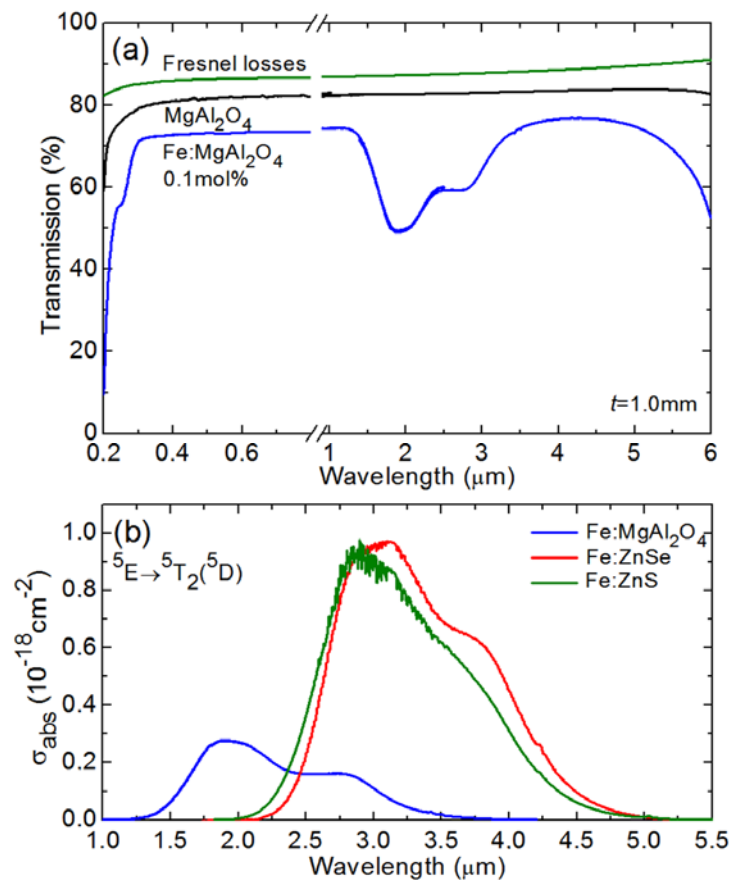
**Figure 4.** (a) SEM image of a fracture surface of a 0.1 mol%  $\text{Fe}:\text{MgAl}_2\text{O}_4$  ceramic; (b) a typical grain size distribution.



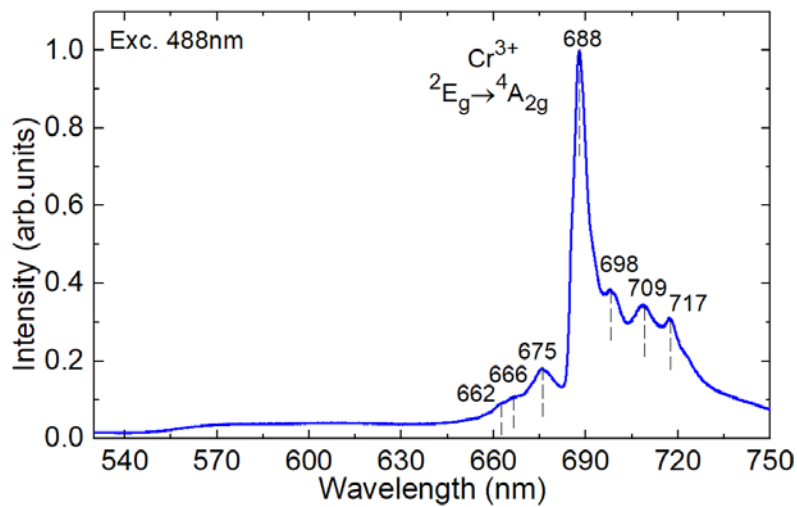
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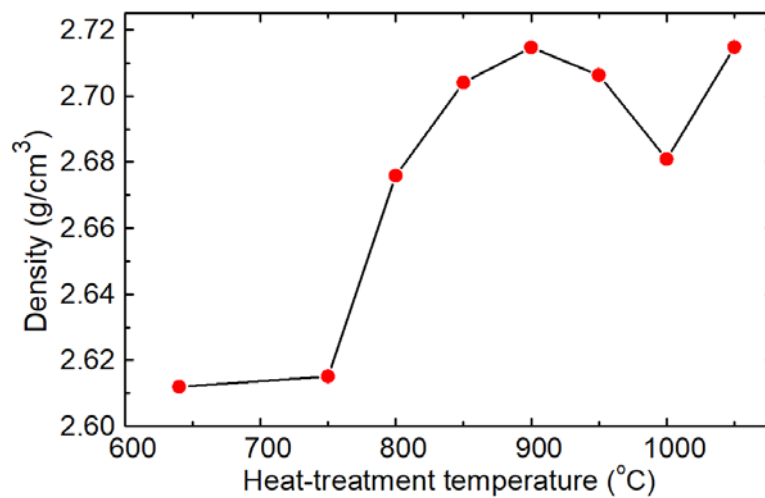
**Figure 6.** (a) In-line transmission spectra of laser-grade-polished undoped  $\text{MgAl}_2\text{O}_4$  and 0.1 mol%  $\text{Fe}:\text{MgAl}_2\text{O}_4$  ceramic disks ( $t = 1.0 \text{ mm}$ ), *green curve* indicates the theoretical Fresnel losses; (b) the absorption cross sections,  $\sigma_{\text{abs}}$ , for the  ${}^5E \rightarrow {}^5T_2({}^5D)$  transition of  $\text{Fe}^{2+}$  ions in  $T_d$  sites in  $\text{MgAl}_2\text{O}_4$  ceramic, ZnSe and ZnS materials.



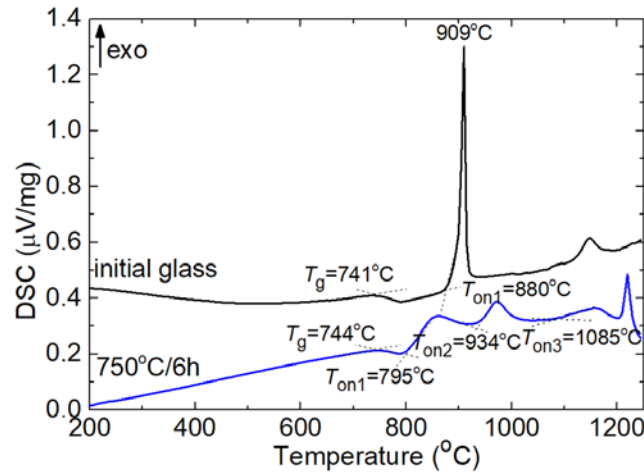
**Figure 7.** Luminescence spectrum of the 0.1 mol% Fe:MgAl<sub>2</sub>O<sub>4</sub> ceramic. The excitation wavelength is 488 nm. Numbers denote the positions of the emission peaks in nm.



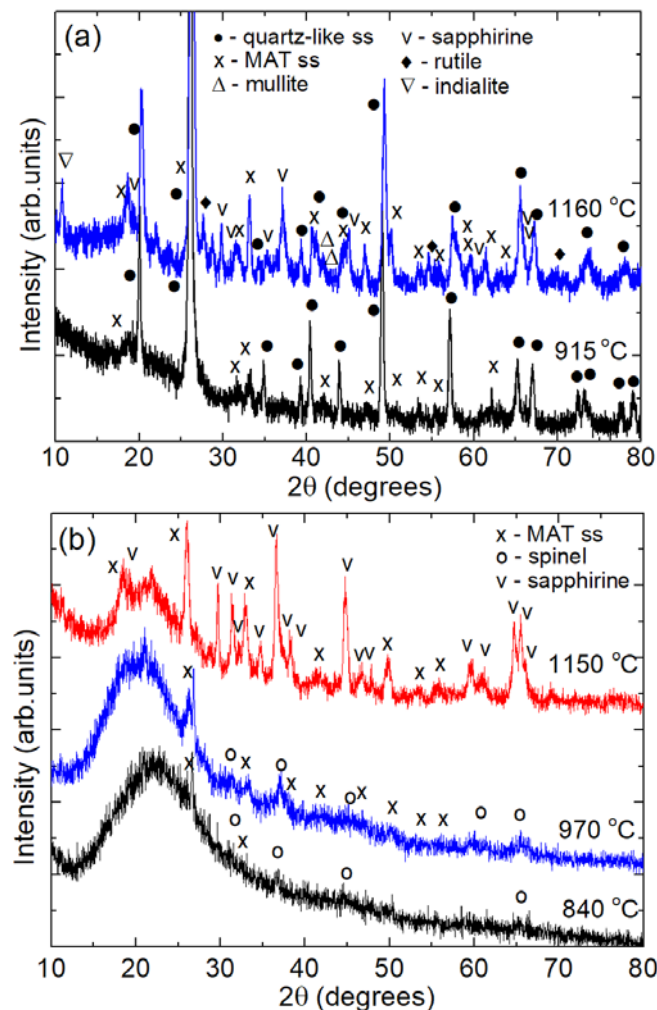
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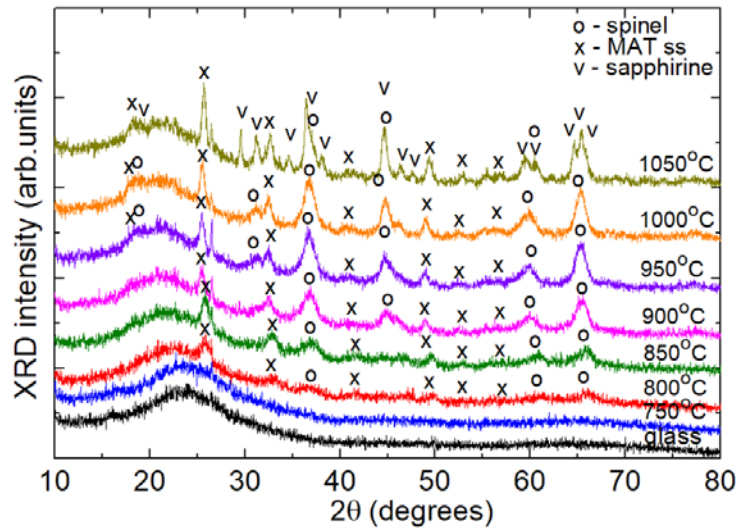
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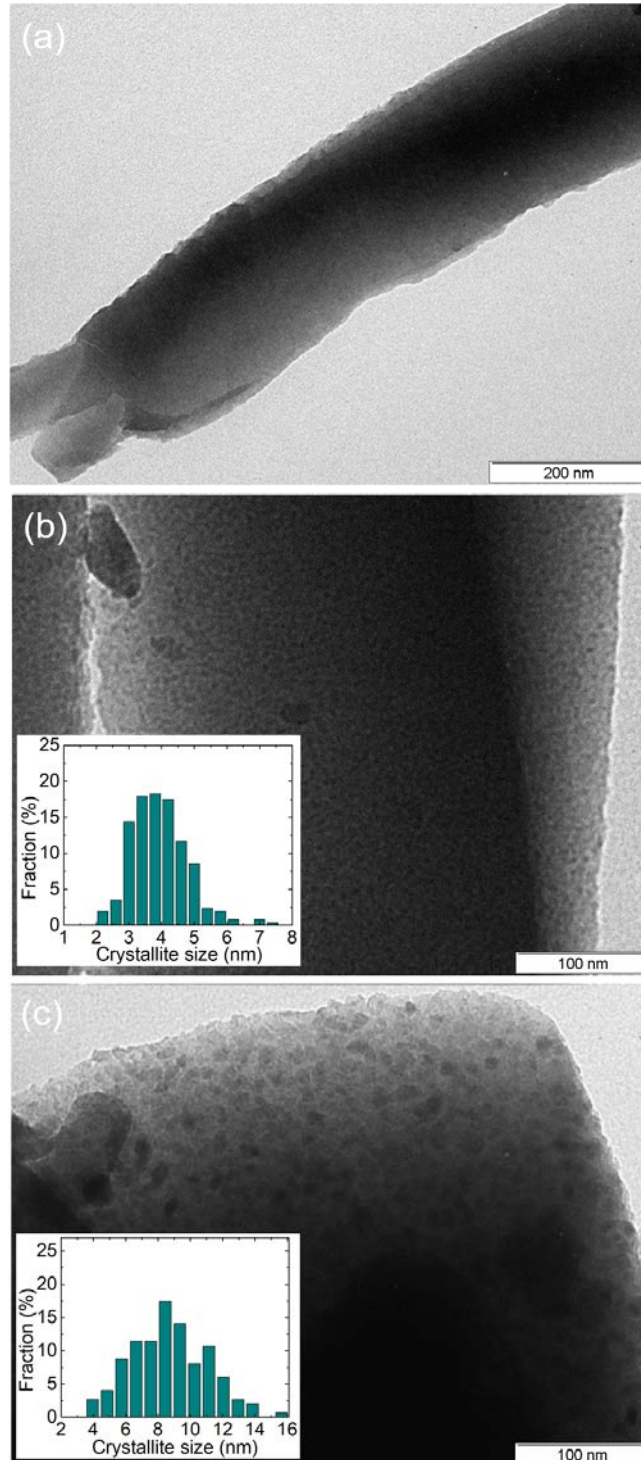
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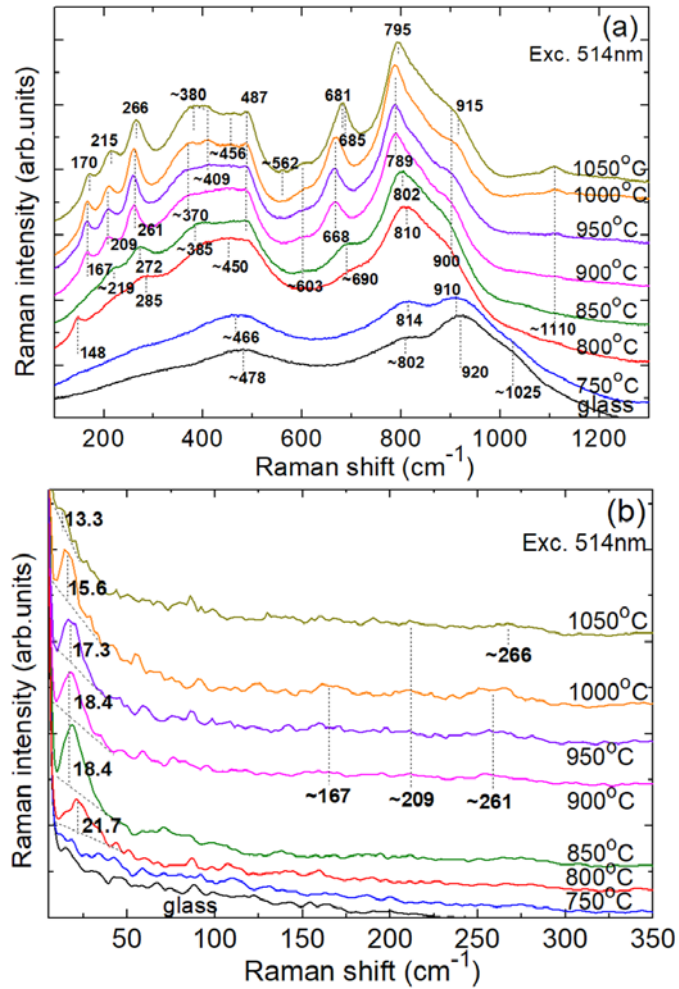
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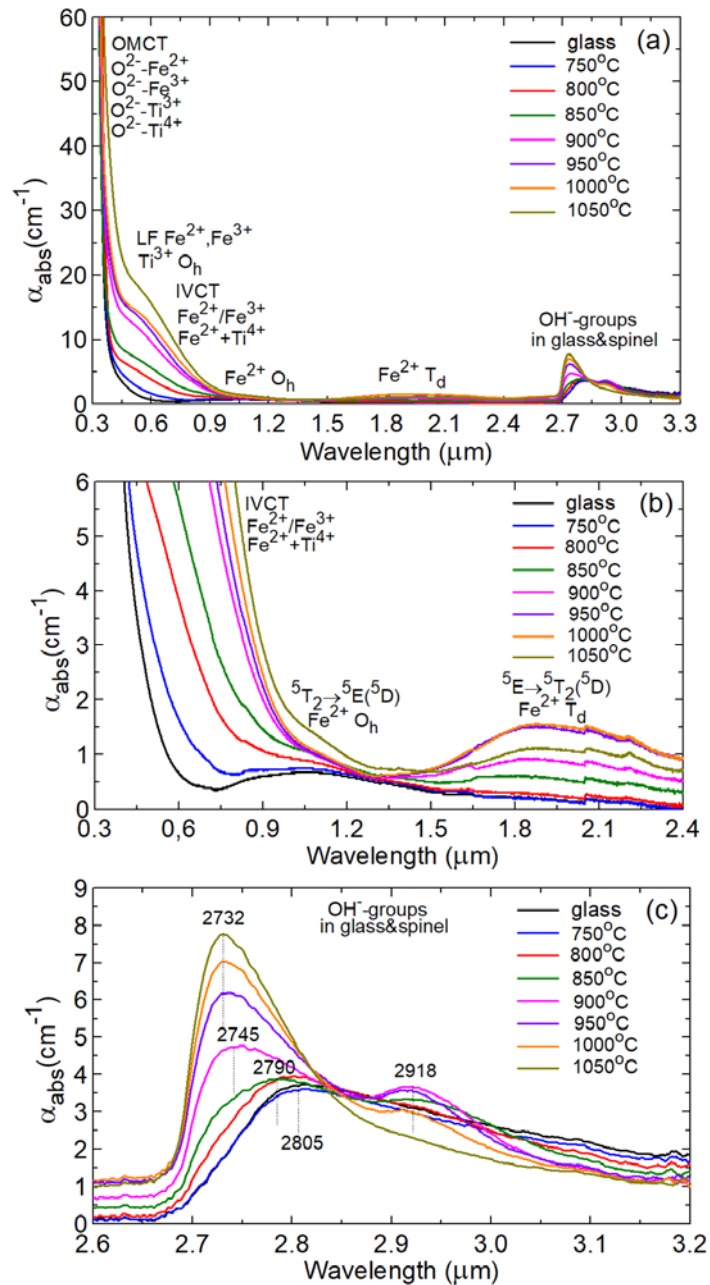
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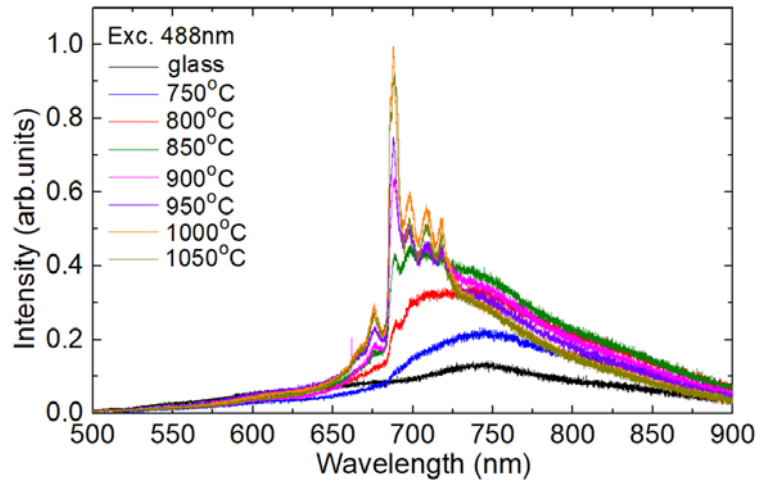
**Figure 13.** Unpolarized Raman spectra of the initial glass and transparent glass-ceramics: (a) the overview of the frequency range of 100-1300  $\text{cm}^{-1}$ , (b) a close look at the frequency range of 5-350  $\text{cm}^{-1}$  with a notch filter. Labels 800 – 1050  $^{\circ}\text{C}$  indicate the heat-treatment temperature at the second stage.  $\lambda_{\text{exc}} = 514 \text{ nm}$ , numbers denote the position of the Raman peaks in  $\text{cm}^{-1}$ . The curves are shifted for the convenience of observation.



**Figure 14.** Absorption spectra of the initial glass and transparent glass-ceramics in different spectral ranges: (a) overview spectrum, (b) a close look on the 0.3-2.4  $\mu\text{m}$  range, (c) a close look on the OH<sup>-</sup>-group absorption at 2.6 – 3.2  $\mu\text{m}$ . *Labels* 800 – 1050 °C indicate the heat-treatment temperature at the second stage. The first stage of the heat-treatment is always at 750 °C for 6 h. *Numbers* in (c) indicate the peak positions in nm.



**Figure 15.** Spectra of visible luminescence from the initial glass and transparent glass-ceramics. Labels 800 – 1050 °C indicate the heat-treatment temperature at the second stage.  $\lambda_{exc} = 488$  nm.



**Figure 16.** Comparison of a 0.1 mol% Fe:MgAl<sub>2</sub>O<sub>4</sub> ceramic and Fe:MgAl<sub>2</sub>O<sub>4</sub> based glass-ceramics prepared by the heat-treatment with the second stage at 1000 °C for 6 h: (a) XRD patterns, (b) Raman spectra,  $\lambda_{exc} = 514$  nm, numbers denote the Raman frequencies in cm<sup>-1</sup>, (c) absorption spectra (for ceramics, the scattering losses are subtracted), and (d) spectra of visible luminescence,  $\lambda_{exc} = 488$  nm, numbers denote the positions of the emission peaks in nm.

