Structure and spectral properties of Fe:ZnAl$_2$O$_4$ transparent glass-ceramics and ceramic

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Abstract. Transparent glass-ceramics based on iron-doped ZnAl$_2$O$_4$ (gahnite) nanocrystals were prepared by melt-quenching (at 1580 °C) with subsequent heat-treatments (at 720 – 1050 °C). Polycrystalline transparent Fe:ZnAl$_2$O$_4$ ceramic was synthesized by hot pressing of powders (at 1600 °C, 50 MPa) using the sintering additive, ZnF$_2$. A comparative study of the structure, Raman spectra and absorption properties of these materials was performed.

1. Introduction

Gahnite (ZnAl$_2$O$_4$) is a promising optical material belonging to the family of spinels, AB$_2$O$_4$. It is very suitable for doping with transitions metal ions [1,2]. Divalent iron ions (Fe$^{2+}$) are of interest because of their broadband absorption extending into the mid-infrared [3]. The growth of gahnite single crystals is technologically complicated. Thus, it is relevant to develop other ZnAl$_2$O$_4$-based transparent materials, such as transparent nanophase glass-ceramics (GCs) and transparent ceramics. Recently, first GCs based on Fe$^{2+}$:MgAl$_2$O$_4$ [4] and on Fe$^{2+}$:ZnAl$_2$O$_4$ [4,6] nanocrystals were prepared and studied. In the present work, we report on the fabrication of such materials doped with iron ions, as well as their structure and optical properties.

2. Experimental

2.1. Synthesis of glass-ceramics

The model glass of the ZnO-Al$_2$O$_3$-SiO$_2$ system nucleated by TiO$_2$ [1] was doped with 1.0 mol% FeO and melted in a quartz ceramic crucible at 1580 °C for 4 h with stirring, cast onto a metal plate and annealed at 620 °C. The batch weight was 400 g. Transparent gahnite-based GCs were prepared from...
the glass by two-stage heat-treatments with the first (nucleation) stage at 720 °C and the second stage in the range from 750 to 1200 °C (the duration of each stage was 6 h).

2.2. Synthesis of ceramic

Metallic aluminum A99 (≥99.99% purity), anhydrous isopropyl alcohol (reagent grade), zinc formate (99.99% purity), zinc fluoride (99.99% purity) and iron (II) formate (99.99% purity) were used as starting materials. Firstly, aluminum isopropoxide Al[OCH(CH₃)₂]₃ was synthesized by direct interaction of aluminum with isopropyl alcohol. The obtained aluminum isopropoxide was distilled in vacuum at a temperature of ~160 °C and an absolute pressure ~0.5 kPa. Then, an alcoholic solution of aluminum isopropoxide was hydrolyzed with an aqueous solution of zinc formate, zinc fluoride and iron (II) formate by dropping with intense stirring. The Zn(form) / (Al + Fe) molar ratio was 1:2. The contents of zinc fluoride and iron ions were 3 wt% ZnF₂ and 1 at.% Fe²⁺, respectively. After vacuum drying at the final temperature of 300°C, the resulted precursor xerogel was ground in a planetary ball mill, and then calcined in air at 700 °C for 20 min. The obtained 3 wt% ZnF₂, 1 at.% Fe²⁺:ZnAl₂O₄ powder was compacted in a steel mold with a diameter of 20 mm at 50 MPa, then wrapped into a graphite foil and hot pressed at a temperature of 1520 °C under uniaxial pressure of 40 MPa for 4 h in a ~10 Pa vacuum. After polishing, transparent Fe²⁺-doped ZnAl₂O₄ ceramic with a thickness of ~2 mm and a diameter of 20 mm was obtained, Figure 1.

![Figure 1](image)

**Figure 1.** Photographs (a) of the laser-grade polished 1 at.% Fe:ZnAl₂O₄ ceramic (thickness: ~2 mm); (b) the 1.0 mol% FeO-doped initial glass and ZnAl₂O₄-based GCs Labels 750 – 1050 °C indicate the heat-treatment temperature at the second stage. The heat-treatment at the nucleation stage is at 720 °C for 6 h.

2.3. Characterization methods

The differential scanning calorimetry (DSC) study for glasses was carried out using a simultaneous thermal analyzer NETZSCH STA 449 F3 Jupiter at a heating rate of 10 K/min in a dynamic flow atmosphere of Ar in the temperature range between room temperature and 1250 °C. A bulk sample of about 15 mg in weight was used. The X-ray powder diffraction (XRD) patterns of the ceramic and GCs were measured with a Shimadzu XRD-6000 diffractometer with Ni-filtered Cu Kα radiation. The mean sizes of crystals with spinel structure in the GCs were estimated from broadening of the X-ray diffraction peak at 2θ ≈ 65.0° according to the Scherrer equation. Their unit cell parameter a was determined using the same diffraction peak with the Millers’ indices (440). The error for the crystal size estimation was ~5%. The Raman spectra were measured using a Renishaw inVia confocal Raman microscope equipped with a Leica ×50 objective and an edge filter. The excitation wavelength was 514 nm (an Ar⁺ ion laser line). The absorption spectra were recorded with a Shimadzu 3600 spectrophotometer in the spectral range 250 - 3300 nm with a resolution of 1 nm. Plane-parallel polished plates with a thickness of 1 mm were used.
3. Results and discussion
Let us first describe the properties of transparent GCs. Figure 2 presents the results of the DSC study of the initial glass and glass heat-treated at 720 °C for 6 h (the nucleation stage). An intense peak on the DSC curve of the initial glass with the crystallization onset temperature \( T_{\text{on}} \) of 804 °C and the maximum crystallization temperature \( T_{\text{max}} \) of 840 °C evidences the gahnite crystallization. The peaks of low intensity in the high-temperature part of the DSC curve are assigned to rutile (TiO₂) and probably cristobalite (SiO₂) crystallization. The nucleation affects the kinetics of crystallization: the glass transition temperature \( T_g \) decreases by ~10 °C, the temperature of gahnite crystallization decreases by ~35 °C and the exothermal peak broadens, the temperatures of crystallization of high-temperature phases also decrease.

![Figure 2. DSC curves of the initial glass and glass heat-treated at 720 °C for 6 h. \( T_g \) is the glass transition temperature, \( T_{\text{on}} \) and \( T_{\text{max}} \) are the onset and maximum crystallization temperatures.](image)

![Figure 3. (a) XRD patterns of the initial and heat-treated glasses; (b) the average size of ZnAl₂O₄ crystals; (c) the intensity of the ZnAl₂O₄ diffraction peak at \( 2\theta = 36.6^\circ \); (d) the unit cell parameter \( a \) of the ZnAl₂O₄ crystals as a function of the heat-treatment temperature of the initial glass. The heat-treatment duration is 6 h. The heat-treatment at the nucleation stage is at 720 °C for 6 h.](image)
The XRD pattern of the initial glass (Figure 3a) shows an amorphous halo with a maximum at 20 = 26.1° and no signs of any crystalline phases. The traces of gahnite crystals are seen after the heat-treatment at 720 °C. As the temperature of the heat-treatment increases, the Scherrer diameter of gahnite crystals gradually increases from 5 to 19 nm, Figure 3b. The crystallinity of gahnite also increases (Figure 3c). The parameter of the gahnite unit cell a changes with increasing the heat-treatment temperature in a complex manner (Figure 3d) and ranges from 8.102 Å (at 750 °C) to 8.119 Å (at 1050 °C). The maximum value of a = 8.123 Å is observed after the heat-treatment at 900 °C. These changes reflect a complex variation in the composition and structure of the crystals with heat-treatment temperature. Rutile crystallizes during the heat-treatment at 1000 °C and the corresponding nanocrystals have a size of 24 nm.

The Raman spectrum of the initial glass, Figure 4, contains two broad bands, one with a maximum at 460 cm⁻¹ and another one of a complex shape with two local maxima at 800 and 920 cm⁻¹. The bands at 440 and 800 cm⁻¹ are attributed to vibrations of tetrahedra of the aluminosilicate network. The more intense band at 920 cm⁻¹ is connected with vibrations of TiO₄ tetrahedra entering the aluminosilicate network [4]. The spectrum changes after the heat-treatment at 720 °C for 6 h. There is a change in the positions of Raman bands and a redistribution of their intensities. The band at ~920 cm⁻¹ weakens, and the band at ~800 cm⁻¹ shifts to ~790 cm⁻¹ and noticeably increases. These changes are associated with the development of liquid phase separation and formation of the amorphous zinc aluminotitanate phase wherein titanium ions form TiO₄ and TiO₆ polyhedrons giving rise to a characteristic band at ~790 cm⁻¹ superimposed on the band due to vibrations of tetrahedra of the aluminosilicate network. After further heat-treatments, the phase separation develops with a formation of gahnite, and then, at 950 – 1050 °C, rutile (Figure 3). The multiple vibrations associated with gahnite manifest its partly inversed structure probably caused by Ti⁴⁺, Ti⁶⁺, Fe²⁺ and Fe³⁺ ions entering its structure.

[Figure 4. Unpolarized Raman spectra of the initial glass and transparent GCs, the labels 750 – 1050 °C indicate the heat-treatment temperature at the second stage, λexc = 514 nm. The heat-treatment at the nucleation stage is at 720 °C for 6 h.]

The absorption spectrum of the initial glass reveals a short-wave absorption edge (E₉ = 2.95 eV), two broad and smooth bands with maxima at about 1070 nm (the 3T₂ → 5E (1D) transition) and about 1850 nm (the 3E → 3T₂ (1D) transition), assigned to the absorption of Fe³⁺ ions in octahedral (predominantly) and tetrahedral coordination, respectively, and a broad band in the region of 2700-3300 nm due to absorption of OH-groups in the glass (Figure 5). As the temperature of the heat-treatment increases, the short-wavelength absorption edge shifts to longer wavelengths, hindering the absorption band centered at 1000 nm, the intensity of the absorption band at ~2 μm markedly increases, the position of its maximum is shifted to ~2030 nm, the absorption band of OH-groups is structured and its intensity increases. A sharp increase in absorption in the visible and near-IR regions is connected with the Fe²⁺→Fe³⁺ intervalance transitions, Fe²⁺ and Fe³⁺ 4d→d transitions in the zinc aluminotitanate amorphous phase and in gahnite (Fe³⁺ and Fe²⁺ in octahedral site symmetry positions). The absorption at ~2030 nm is associated with incorporation of Fe²⁺ ions into the gahnite nanocrystals.
in tetrahedral positions (the $^5E \rightarrow ^5T_2(5D)$ transition). The structuring of the IR absorption band caused by the OH- groups is also connected with gahnite crystallization as the OH- groups can enter the gahnite structure.

We have performed a comparative study of the structural and optical properties of the transparent GC prepared by the heat-treatment at 720 °C for 6 h and at 1050 °C for 6 h and the ceramic. Scanning electron microscopy (SEM) revealed a close-packed microstructure of ceramic, Figure 6a, while the TEM photograph of GC revealed its multiphase nature. Intense diffraction peaks in the XRD pattern of the ceramic, Figure 6c, belong to gahnite, ZnAl$_2$O$_4$, with a cubic structure (sp. gr. Fd3m). The unit cell parameter of gahnite ceramic $a$ is 8.12 Å. The increased $a$ value as compared to that of undoped Figure 5. Absorption spectra of the initial glass and transparent GCs. The labels 750 – 1050 °C indicate the heat-treatment temperature at the second stage.

![Figure 5](image5.png)

**Figure 5.** Absorption spectra of the initial glass and transparent GCs. The labels 750 – 1050 °C indicate the heat-treatment temperature at the second stage.

![Figure 6](image6.png)

**Figure 6.** Structural characteristics of the Fe:ZnAl$_2$O$_4$-based transparent GC prepared by the heat-treatment at 720 °C for 6 h and at 1050 °C for 6 h and the Fe:ZnAl$_2$O$_4$ ceramic: (a) SEM image of the fractured surface of ceramic; (b) TEM image of GC; (c) XRD patterns, numbers denote the Miller's indices $(hkl)$; (d) Raman spectra, $\lambda_{exc} = 514$ nm.
ZnAl$_2$O$_4$ ($a = 8.088$ Å) indicates a certain degree of inversion. A comparison of the XRD patterns of the GC and ceramic, Figure 6c, revealed that they differ in phase composition, size and fraction of gahnite crystals. The XRD pattern of the GC shows broad peaks of gahnite, broad peaks of low intensity due to rutile, TiO$_2$, and a weak halo due to the residual highly siliceous glass phase. The mean size of gahnite nanocrystals in the GC is 18 nm and their unit cell parameter $a$ is 8.098 Å, also manifesting a certain degree of inversion. The average size of rutile crystals is 39 nm. The complex phase composition of the GC is also revealed in its Raman spectrum, see Figure 6d.

The absorption spectra of both the GC and ceramic demonstrate absorption of Fe$^{2+}$ ions in tetrahedral (T$_d$) sites in gahnite crystals due to the $^5$E $\rightarrow$ $^5$T$_2$(^5D) transition, Figure 7. The inversion of Fe:ZnAl$_2$O$_4$ is confirmed by absorption of Fe$^{2+}$ ions in octahedral (O$_h$) sites (the $^5$T$_2$(^5D) $\rightarrow$ $^5$E transition). The profound red-shift of the UV absorption edge for the GC as compared with that of the ceramic is due to intervalent and charge-transfer transitions in multiphase GC.

![Absorption spectra of Fe:ZnAl$_2$O$_4$-based transparent GC prepared by the heat-treatment at 720 °C for 6 h and at 1050 °C for 6 h and Fe:ZnAl$_2$O$_4$ ceramic.](image)

### Figure 7.

Absorption spectra of Fe:ZnAl$_2$O$_4$-based transparent GC prepared by the heat-treatment at 720 °C for 6 h and at 1050 °C for 6 h and Fe:ZnAl$_2$O$_4$ ceramic.

### 4. Conclusions

Transparent materials based on iron-doped gahnite (glass-ceramics and ceramic) were prepared. Their structure and spectral properties were evaluated and compared. A broad absorption band at 1.5-3 μm due to the $^5$E $\rightarrow$ $^5$T$_2$(^5D) transition of Fe$^{2+}$ ions in T$_d$ sites in gahnite crystals makes these materials promising for saturable absorbers of lasers emitting in the short-wave infrared spectral range.

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