Crystallization, mechanical, and optical properties of transparent, nanocrystalline gahnite glass-ceramics

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Abstract
This paper describes the preparation of a transparent glass-ceramic from the SiO2-K2O-ZnO-Al2O3-TiO2 system containing a single crystalline phase, gahnite (ZnAl2O4). TiO2 was used as a nucleating agent for the heat-induced precipitation of gahnite crystals of 5-10 nm. The evolution of the ZnAl2O4 spinel structure through the gradual formation of Al-O bonds was examined by infrared spectroscopy. The dark brown color of the transparent precursor glass and glass-ceramic was eliminated using CeO2. The increase in transparency of the CeO2-doped glass and glass-ceramics was demonstrated by UV-visible absorption spectroscopy. EPR measurements confirmed the presence of Ce3+ ions, indicating that CeO2 was effective in eliminating the brown color introduced by Ti3+ ions via oxidation to Ti4+. The hardness of the glass-ceramic was 30% higher than that of the as-prepared glasses. This work offers key guidelines to produce hard, transparent glass-ceramics which may be potential candidates for a variety of technological applications, such as armor and display panels.

KEYWORDS
glass, glass-ceramics, mechanical properties, optical materials/properties, spinels

1 | INTRODUCTION

In recent times, numerous applications have been found for glass-ceramics (GCs) in both domestic and technological areas. In most cases, after the transformation from glass to glass-ceramic, the material loses optical quality, limiting some of its possible applications. For instance, the development and production of transparent colorless glass-ceramics containing important crystal phases, such as spinel, represents a significant challenge because the synthesis of precursor glasses, which leads to spinel glass-ceramics through crystallization, is quite difficult due to their high...
meltng temperature and high viscosity. Highly transparent spinel glass-ceramics can be fabricated from glasses in the SiO₂-Al₂O₃-ZnO-MgO-ZrO₂ system, containing very fine spinel crystallites with sizes in the range of 10-50 nm. However, a major drawback of high alumina content glasses is their very high melting temperatures (>1650°C) and high viscosity, which make them difficult to melt, homogenize and refine. Given this fact, it has been suggested that the use of TiO₂ rather than ZrO₂ as a nucleating agent lowers the melting temperature of the system. Nucleation is premised on the concept of an ultra-fine scale, highly uniform liquid phase separation into SiO₂ and TiO₂/Al₂O₃-rich areas when TiO₂ is used. Ti⁴⁺ can occupy the octahedral site of the spinel structure via charge balanced substitution.

Glass-ceramics can transmit visible light if either one of the following conditions is met: (1) the crystallites of all the phases are much smaller than the wavelength of visible light, or (2) the optical anisotropy within the crystals and the difference between the refractive index of the crystals and the glass matrix are very small. These conditions can be achieved in some aluminosilicate glass-ceramics systems containing solid solutions of β-quartz, spinel and mullite as major crystalline phases. There are numerous potential applications for transparent crystalline materials, which can be shaped by the (fast) glass-forming process. However, glass-ceramics produced with TiO₂ as nucleating agent present a yellowish-brown coloration, whose intensity increases with crystallization. The evolution of the optical absorption and coloration of lithium-alumina-silicate (LAS) glasses and glass-ceramics nucleated using TiO₂ was recently explained by Chavoutier et al. based on the Ti⁴⁺-O₂⁻ charge transfer mechanism. Also, the Ti³⁺ cation with 3d¹ electronic configuration has a d-d absorption close to 500 nm, which generates dark brown coloration in glasses. The Ti⁺⁺ cation with its 3d⁰ electronic configuration does not give rise to d-d absorption, but it can contribute to the optical absorption of the glass in the near UV due to O-Ti charge transfer. In contrast, ZrO₂ is not known to produce any color in glass. Indeed, the Zr³⁺ ion presents a 4d⁰ electronic configuration (absence of d-d transition) and the O-Zr charge transfer band probably occurs at wavelengths below 200 nm.

In view of the above, CeO₂ can be used to eliminate the coloration introduced by Ti³⁺ ions. CeO₂ yields a pale-yellow coloration, probably due to Ce(IV)-O(-II) charge transfer. CeO₂ can be reduced to become the hexagonal sesquioxide Ce₂O₃ by following the reaction below.

\[
4\text{CeO}_2 \rightarrow 2\text{Ce}_2\text{O}_3 + \text{O}_2 \quad (1)
\]

The residual oxygen can oxidize Ti³⁺ to Ti⁴⁺ and the dark coloration can be eliminated, leaving the glass with a pale yellow color and greater transparency. In addition, cerium oxide is often added in small quantities to commercial glass-forming melts to prevent solarization, and its fining (elimination of bubbles) action is also considered a beneficial side effect. Spinel glass-ceramics exhibit excellent thermal stability with a very high strain point and low thermal expansion coefficient, similar to elemental silicon, which makes them suitable for use in photovoltaic substrates and flat panel displays. In addition, ZnO, used as flux in glasses, is fully consumed during generation of the garnite crystal phase, leaving a residual glass with fewer non-bridging oxygen atoms. The resulting siliceous glass matrix is then suitable for use at high temperature, and has excellent chemical durability and a suitable combination of mechanical properties, making this material suitable for various structural applications. The potential use of transparent garnite glass-ceramics, doped with transition metals or rare-earth ions, in optical devices is another option but still needs to be determined. A possible use is in ballistic armor structures.

In a pioneering work, Beall and Duke reported on the development of transparent glass-ceramics containing the ZnAl₂O₄ spinel phase after a phase separated precursor glass was heat-treated at about 900°C. They also stated that a cristobalite phase forms at the air glass-ceramics interface if it is held at 1000°C for several hours. In order to suppress such surface crystallization, they used Cs₂O. In this work, Cs₂O is replaced with K₂O and the garnite phases can precipitate in the glass interior if heat-treatment is performed at 880°C for up to 100 hour. In addition, in this paper we also discuss the use of CeO₂ to eliminate the brownish-gray color caused by the presence of Ti³⁺. In the same subject, Pinckney’s US patent describes a transparent glass-ceramic, gray in color, containing garnite crystals, which is generated when a certain mother glass is heat-treated at 800°C for 2 hour for nucleation and held at 1000°C for 4 hour for crystal growth. The glass batch was melted at 1600°C for 16 hours. In the composition, they used 1.5 wt% each of Rb₂O and Cs₂O, whereas in the glass investigated here, those oxides are replaced by 3 wt% K₂O. We are not aware of any other study on garnite transparent glass-ceramics containing only the garnite crystal phase. In the two previous studies referred above, other crystal phases, such as zirconia were present.

Thus, the aim of this work was to develop relatively easy melting, transparent, high hardness garnite glass-ceramics. In order to achieve that goal, we have investigated: (1) the role of CeO₂ to improve the transparency of the TiO₂ nucleated garnite spinel glass-ceramics; (2) the ideal temperature to maximize the nucleation and crystallization rates—these temperatures were determined using differential scanning calorimetry (DSC). (3) The absorption coefficients of undoped and CeO₂-doped glass-ceramics crystallized during different periods of time. (4) The hardness of the resulting nanometric glass-ceramics. The systematic studies of properties are correlated with the
nanostructures of the glass-ceramics. The EPR technique was employed to investigate the presence and environment of Ce$^{3+}$ ions in the CeO$_2$-doped glass-ceramics.

2 EXPERIMENTAL PROCEDURE

The composition of the precursor glass (Gn1) in wt% is based on 50.6SiO$_2$, 23.0Al$_2$O$_3$, 18.4ZnO, 3K$_2$O, and 5TiO$_2$. This is a slightly modified composition from that reported by Pinckney, which contains K$_2$O instead of CsO and Rb$_2$O. In the second composition, 0.5 wt% CeO$_2$ in excess was added to investigate its effect on the optical properties of the glass, which herein after is referred to as Gn2. Batches were prepared from high-purity precursors such as SiO$_2$ (99%, Vitrovita, São Carlos, Brazil), anhydrous K$_2$CO$_3$ (99%, Nuclear, São Carlos, Brazil), ZnO (99.7%, J. T. Baker, Phillipsburg, New Jersey, USA), Al$_2$O$_3$ (99%, Almatis, Leetsdale, Pennsylvania, USA), TiO$_2$ (99.5%, Riedel De Haen, Seelze, Germany), and CeO$_2$ (99.0%, Vetec, Duque de Caxias, Brazil), using the conventional melt-casting technique. A batch of about 100 g of glass was pre-mixed in an agate-mortar, then thoroughly mixed for 12 hour in a planetary mixer (Turbula®, System Schatz, Maschinenfabrik, Basel, Switzerland), and melted in a platinum crucible in an electric furnace at 1620°C for 4 hour, in air. The glass melt was poured onto a preheated cast iron mold, followed by annealing at 600°C for 12 hour to remove the internal stresses of the glass, and then slowly cooled to room temperature at 2°C/min. A much lower annealing temperature than the $T_g$ (670°C) was used in order to prevent nucleation in this stage. The as-prepared glass blocks were cut and shaped into the desired dimensions and optically polished for spectroscopic characterization. The transparent gahnite GCs were derived from Gn1 and CeO$_2$-doped (Gn2) glasses by controlled heat-treatment at 670°C, for 3 hour for nucleation, and at 880°C, with varying times of 2, 25, 50, and 100 hour, for crystallite growth.

The Archimedes principle was used to determine the densities of the glasses and GCs, using water as the immersion liquid, in a single pan electrical balance with 0.0001 g precision. The error in density measurement is estimated to be ±0.004 g/cm$^3$. In order to determine the nucleation mechanism and the Avrami index, DSC studies were performed on powder samples (10 mg -18-22 µm diameter) and bulk (2.0 mm x 2.0 mm x 1.5 mm) samples. The samples were subjected to different heating rates ($\beta$=10, 15, 20, 25, and 35°C/min) in a temperature range of ambient to 1100°C. All the DSC experiments were performed in air atmosphere in platinum crucibles, using a NETZSCH STA 449F3 simultaneous thermal analyzer (Gerätebau GmbH, Selb, Germany).

To identify the crystalline phases developed in the heat-treated glass-ceramics, X-ray diffraction (XRD) data were recorded in a Rigaku Ultima IV X-ray diffractometer (Tokyo, Japan), using anchor scan parameters of CuK$\alpha$ radiation wavelength=1.5406 Å at 25°C, equipped with a 40 kV power supply and 20 mA output. Scanning was performed from 20=10 to 80° with a step size of 0.02° (20). The average crystallite diameter, $t$, can be estimated from the full-width at half-maximum (FWHM) of the intense X-ray diffraction peak by Scherrer’s formula:

$$ t = \frac{0.9\lambda}{\beta \cos \theta} $$

where $\lambda$ is the wavelength of X-ray radiation (CuK$\alpha$=1.5406 Å) and $\beta$ is the FWHM of the peak at 20 in radian. The FWHM of the peaks were measured after fitting the data using Gaussian fitting parameters.

Images of the microstructure of the very fine powdered glass-ceramic samples were obtained using transmission electron microscopy (TEM; Tecnai G2, FEI Company, Hillsboro, Oregon, USA) coupled with energy-dispersive X-ray spectroscopy. The samples for TEM measurements were prepared by dispersing fine powder in an acetone medium and drying it on a carbon grid. The experiment was performed at 200 kV. Fourier transform infrared (FTIR) reflectance spectra of the polished bulk samples were recorded using an FTIR spectrometer (Tensor 27, Bruker, Ettlingen, Germany), in the wavenumber range of 400-2000 cm$^{-1}$ with a resolution of ±4 cm$^{-1}$ after 16 scans.

The optical absorption spectra of polished samples with ~2 mm thickness were recorded in a Perkin Elmer UV-Vis-NIR spectrophotometer (model Lambda 25, Perkin-Elmer Corporation, Waltham, Massachusetts, USA) in the wavenumber range of 400-1100 nm, with an accuracy of ±1%.

The polished surfaces of the GC samples were subjected to microindentation hardness testing using a hardness tester (Model-FM-7E, Future-tech Corporation, Tokyo, Japan) equipped with a conical Vickers indenter for glasses and GCs and applying a load of 300 g. Five indentations were made on each sample under identical loading conditions. The diagonals of the Vickers indentations were measured on each sample and the hardness was calculated using the standard equation for the Vickers geometry,

$$ HV = \frac{1.8544P}{d^2} $$

where $HV$ is the Vickers hardness number (VHN) in kg/mm$^2$, $P$ is the normal load in kg, and $d$ is the average diagonal length of the indentation in mm.

Continuous wave, CW, and pulsed Electron Paramagnetic Resonance, EPR, experiments were carried in an E-580 BRUKER ELEXIS X-band spectrometer operating
at a microwave frequency of around 9.5 GHz. The temperature was controlled by continuous flow liquid helium cryostats ESR-900 (CW) and CF-935 (pulsed) and PID controller ITC503, all from Oxford Instruments (Witney, Oxfordshire, England). CW measurements were taken at room temperature, 294 K, and at 25 K. Pulsed experiments were performed at 8 K. All the glass and glass-ceramic samples were in powder form and an amount of 10-40 mg was placed at the bottom of a 3 mm inner diameter quartz tube and introduced in the center of the microwave cavity. All the EPR data were normalized to the corresponding sample mass. Electron spin echo envelope modulation (ESEEM) spectra were recorded at various external field strengths, using the two-pulse echo sequence \((\pi/2)-\tau-(\pi/2)-\tau\)-echo with a typical \(\pi/2\) pulse width of \(T_p=16\) ns and a repetition time of \(T_r=2\) ms. The lower limit of the delay between the first and second pulse, \(\tau\), is dictated by the instrument’s dead time and was set to 120 ns and incremented 1024 times in 4 ns steps. The echo signal appearing at time \(2\tau\) was integrated in a 148 ns time window and two scans were added for signal averaging. The resulting ESEEM data were processed as follows: (1) the modulated echo decay was first processed by the Krylov Basis Diagonalization Method (KBDM)\(^{12,13}\) to isolate the zero (or low) frequency decay component; (2) for further analysis, this zero frequency component was fitted to an exponential decay function, as will be described later herein; (3) the KBDM-edited low frequency component was subtracted from the experimental signal in order to leave behind the pure decaying modulation; and (4) the modulation decay was Fourier-transformed, resulting in the ESEEM spectrum. The echo-detected field-sweep absorption spectra, EDFS, were recorded using a similar two-pulse sequence. The pulse spacing, \(\tau\), was set to 800 ns and the integrated echo intensities were measured as a function of the magnetic field strength over the range of 0.1-12.1 kG.

3 | RESULTS AND DISCUSSION

3.1 | Thermal and physical properties

DSC runs were employed to determine the glass transition temperature \((T_g)\), crystallization onset temperature \((T_x)\), crystallization peak temperatures \((T_p)\), and a qualitative curve for nucleation rates \((k(T))\). After this, the Avrami index of crystallization was determined.

Figure 1 depicts part of the DSC curves obtained for Gn1 (powder and bulk) and Gn2 (bulk). The samples were heated at 10°C/min from room temperature up to the point where the crystallization peak became completely visible. Note that the \(T_P\) values for Gn1 glasses (powder and bulk) appear at exactly the same temperature, 868°C (±1°C). This is strong evidence that the crystallization mechanism in this glass is predominantly volumetric. If the surface mechanism were predominant, the crystallization peak of the powder sample would appear at a lower temperature than that of the bulk samples, since powder samples present higher surface areas than bulk ones.\(^{14}\) Still in Figure 1, also note that the \(T_g\) and \(T_p\) values decrease, in the same experimental conditions, by 30°C and 14°C, when the garnet glass is doped with 0.5 wt% CeO\(_2\). This indicates that CeO\(_2\) strongly influences the properties of this glass.

The densities of undoped glass, Ce-doped glass, and Ce-doped heat-treated glass-ceramics vary in the range of 2.81-2.94 g cm\(^{-3}\), making them favorable, for instance, for armor applications because of their lighter weight compared to that of some ceramic counterparts. The increase in density is due to crystallization.

DSC studies were also conducted to determine the qualitative nucleation curve for Gn2 glass. Bulk samples were treated for 3 hour at different nucleation temperatures \((T_N)\) in the temperature range close to \(T_g\) (640°C-700°C). Subsequently, the samples were heated in a DSC furnace at 10°C/min and the corresponding crystallization peak temperature \((T_p)\) was recorded. Our reasonable assumption is that the concentration of nuclei follows the same trend as the inverse of the crystallization peak temperature, 1/\(T_p\) vs nucleation temperature \((T_N)\).\(^{15,16}\) Thus, Figure 2 shows a qualitative nucleation curve obtained by plotting 1/\(T_p\) as a function of \(T_N\). An analysis of this nucleation curve indicates that the temperature at which the crystal nucleation rate is highest coincides with \(T_p\), ie, ~670°C. The knowledge of the maximum crystal nucleation rate is important to tailor the optical and mechanical properties of glass-ceramics, since relevant parameters such as the number and

![FIGURE 1 DSC curves of precursor Garnet glass with and without CeO\(_2\) doping](image-url)
size of nanocrystals strongly influence the transmittance and mechanical properties of glass-ceramics.

In order to investigate the crystallization mechanism of the Gn2 glass, the Avrami index of crystallization was determined. Samples with dimensions of 2.0 mm × 2.0 mm × 1.5 mm were heated in a DSC furnace at different heating rates (10°C, 15°C, 20°C, 25°C, 30°C and 35°C per minute) from room temperature until the complete appearance of the crystallization peak, as demonstrated in Figure 3.

The Avrami index (n) can be determined using the Ozawa method,17 which relates (n) to the crystallized fraction (x) resulting from the integration of the DSC curves obtained at different heating rates, φ, according to Equation 4:

$$-n = \frac{\ln(-\ln(1-x))}{\ln(\phi)}$$

The procedure to obtain n values from DSC measurements involves calculating the temperature dependence of the crystallized fraction and then plotting ln(-ln(1-x)) vs ln φ, as shown in Figure 4. A linear dependence was observed and the Avrami index, calculated from the slope of the straight lines, was found to be ~3 in the temperature range of 875°C to 885°C. This indicates, at least in this temperature range, that the crystallization mechanism is predominantly volumetric.18,19 Therefore, the crystal growth treatments for measuring mechanical properties were performed in this same temperature range.

3.2 | X-ray diffraction

The XRD patterns of Gn2 glass-ceramics shown in Figure 5 confirm the sole presence of ZnAl2O4 spinel crystals, according to PDF file no. 71-968, corresponding to cubic spinel ZnAl2O4, with lattice parameter a=8.088 Å, space group Fd-3m. No other crystalline phase was detected in the glass-ceramic samples. The peak intensity was found to increase as the duration of the heat-treatment at growth temperature (880°C) increased, but no additional peaks were developed. All the samples heat-treated in different time ranges of 2-100 hour showed broad peaks. The broader peaks in the XRD pattern are attributed to extremely small crystallite sizes, while the sharp peaks are ascribed to the formation of comparatively larger crystallite sizes with higher volumes. The average crystallite sizes of the ZnAl2O4 were estimated by Equation 2. The average crystallites size of the Gn2 samples was found to increase monotonically with the increase in heat-treatment duration. The sample heat-treated at 880°C for 2 hour developed...
crystallites of about 4.1 nm, as calculated using Scherrer’s equation, whereas samples heat-treated for 25, 50, and 100 hour show crystallites sizes of 5.8, 6.6, and 6.8 nm, respectively. These findings allow us to infer a very low crystal growth rate, likely due to the depletion of both Zn and Al in the glass matrix, which is the reason why transparent glass-ceramics were obtained even after heat-treatment for 100 hour at the chosen crystal growth temperature. In addition, the glass-ceramics heat-treated for different periods of time were subjected to TEM studies to observe and confirm the sizes of resulting crystallites.

3.3 | TEM analysis

The microstructure of the heat-treated glass-ceramics was also studied by transmission electron microscopy (TEM). The TEM bright field, as well as high-resolution images, along with their respective selected area of electron diffraction (SAED) patterns and EDS, were recorded for Gn2 spinel glass-ceramic samples. High-resolution bright-field TEM and EDS images of ZnAl₂O₄ spinel glass-ceramics nucleated at 670°C for 3 hour and subsequently subjected to a crystal growth treatment at 880°C for 2 hour are shown in Figure 6A. Cubic crystals with a uniform size of up to 5 nm dispersed in the highly siliceous continuous glassy matrix are clearly visible. The EDS spectrum revealed the presence of the ions that constitute gahnite crystals, ie, Zn, Al, O, and other elements such as Si, Ti, and K, likely originating from the glass matrix.

Bright-field TEM images along with their SAED pattern and the EDS for glass-ceramics nucleated at 670°C for 3 hour and developed at 880°C for 100 hour are shown in Figure 6B. These images also reveal the presence of individual spinel crystallites with an average size of 5-10 nm.
The crystal shapes and morphologies are distinctly visible. The nanocrystalline nature is further confirmed by the nature of the SAED pattern, which shows characteristic ring patterns along with fewer distinct spot patterns, corroborating the presence of some larger crystals. Indexing of the SAED ring patterns of the crystals yielded the hkl planes, which were found to match those of the ZnAl₂O₄ spinel crystals. Prominent hkl planes like (311), (220), (511), and (440) were visible in the continuous ring pattern and are shown in the inset of Figure 6B. This TEM observation provides strong support regarding the crystallite sizes, which were calculated from the XRD pattern.

3.4 | FT-IR reflectance spectroscopy analysis

As will be discussed later, the glass doped with CeO₂ showed a significant decrease in the optical absorption coefficients when compared to the undoped material. The FTIR technique was employed to gain a better understanding of the structure of our glasses, such as the coordination number of network formers and the change in oxygen bonds induced by CeO₂ doping and heat treatments. Figure 7 shows the FTIR spectra for the as prepared glass (Gn1), CeO₂-doped glass (Gn2), and CeO₂-doped glass (Gn2) nucleated at 670°C for 3 hour, with further crystal growth at 880°C for 2, 25, 50, and 100 hour.

The crystal shapes and morphologies are distinctly visible. The nanocrystalline nature is further confirmed by the nature of the SAED pattern, which shows characteristic ring patterns along with fewer distinct spot patterns, corroborating the presence of some larger crystals. Indexing of the SAED ring patterns of the crystals yielded the hkl planes, which were found to match those of the ZnAl₂O₄ spinel crystals. Prominent hkl planes like (311), (220), (511), and (440) were visible in the continuous ring pattern and are shown in the inset of Figure 6B. This TEM observation provides strong support regarding the crystallite sizes, which were calculated from the XRD pattern.

3.5 | UV-Vis optical absorption spectroscopy

As can be seen in the photographs in Figure 8, the Gn1 sample is a dark colored glass unsuitable for transparent

<table>
<thead>
<tr>
<th>Band position (cm⁻¹)</th>
<th>Band assignment</th>
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<tbody>
<tr>
<td>460</td>
<td>O-Si-O bending vibration²³,²⁶</td>
</tr>
<tr>
<td>565</td>
<td>Al-O bending vibration of [AlO₆]²⁴ and Zn-O vibration of [ZnO₄]²⁷</td>
</tr>
<tr>
<td>680</td>
<td>Al-O stretching vibration of [AlO₄]²⁶</td>
</tr>
<tr>
<td>790</td>
<td>Si-O-Si and Al-O-Al stretching vibration²⁴</td>
</tr>
<tr>
<td>897</td>
<td>Si-O asymmetric stretching vibration²⁵</td>
</tr>
<tr>
<td>912</td>
<td>Si-O non-bridging oxygen stretching vibration²⁶</td>
</tr>
<tr>
<td>1103</td>
<td>Si-O and Si-O-Al asymmetric stretching vibration²³</td>
</tr>
<tr>
<td>1200-1250</td>
<td>Si-O stretching vibration²⁵</td>
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armor or photonic applications. The reason why the gahnite glass (Gn2) was doped with CeO2 was to improve its optical transparency. Figure 9 shows the absorption coefficient as a function of frequency of undoped and CeO2-doped as-prepared glasses or heat-treated at 880°C for 2, 25, 50, and 100 hour, preceded by nucleation at 670°C for 3 hour. A comparison of the spectra of as-prepared Gn1 and Gn2 samples clearly reveals a marked improvement in transparency resulting from the use of 0.5 wt% of CeO2 dopant, resulting in a yellowish colored sample (Figure 8). The brownish color of Gn1 is due to the reduction of TiO2 to Ti2O3 during the glass melting process.27 Ti3+ cations with 3d1 electronic configuration present a d-d absorption close to 488 nm,4,5 but the introduction of CeO2 causes oxygen to be released at the elevated melting temperature, leading to the oxidation reaction

$$\text{Ti}^{3+} + \text{Ce}^{4+} \leftrightarrow \text{Ti}^{4+} + \text{Ce}^{3+}$$

(5)

Ce3+ has an absorption band near 314 nm, which does not affect the transparency of the glass in the visible spectrum, and Ti4+ does not give rise to visible absorption. For the Gn1 composition, heat treatment leads not only to a red shift of the UV absorption edge by approximately 30 nm but also to light scattering, possibly due to the formation of the crystalline phase, and/or the increased presence of defects and/or surface roughness. The Gn2 samples show a similar behavior and their spectral features do not change substantially in heat treatment times longer than 2 hour. However, it is interesting to note a (desirable) decrease in the absorption coefficient of the Gn2 sample heat treated during 50 hours. This is likely due to a combined effect of the decreased difference in the refractive index of the crystal and residual glass (because the composition of the glass phase changes), and sufficiently small crystal size. This effect has already been demonstrated in a soda-lime silicate glass-ceramic.29 In fact, the crystallites size only slightly increases with the duration of heat treatment, whereas the composition of the residual glassy matrix changes continuously with the precipitation of ZnAl2O4, leading to a lower refractive index difference and lower absorption coefficient (for λ>480 nm) for the Gn2 sample heat treated during 50 hour. Thus, a compromise between the optical quality and formation of the crystalline phase that improves mechanical resistance is established, and one must find the optimum conditions according to the desired application.

### 3.6 Mechanical properties

The hardness of the Gn2 glasses and heat-treated glass-ceramic samples was evaluated with a Vickers indenter, applying an indent load of 300 g and using the average diagonal lengths of the hardness impressions. Representative images of the indentation impressions of gahnite spinel glasses and glass-ceramic samples heat-treated for 25, 50, and 100 hour observed by optical microscopy are shown in Figure 10, together with their respective hardness values. The average hardness values obtained for the precursor glass is about 580 VHN, while values obtained for the heat-treated glass-ceramics vary from 700 to 750 VHN. The heat-treated glass-ceramics showed an increase of ~20%-30% in hardness when compared to that of the glass. This is due to the generation of hard gahnite crystals, whose hardness in the spinel glass matrix is approximately...
A trend of decreasing hardness, within experimental error, was observed when the duration of the heat-treatment was longer than 50 hour.

### 3.7 Electron paramagnetic resonance

Figure 11 shows the CW EPR spectra obtained for samples Gn1, Gn2, and Gn2/2 hour at room temperature (294 K) and at 25 K. The main feature in all these data is the presence of a broad line covering the entire field range. In addition, two small sharp lines are visible at $g \approx 4.3$ ($\approx 1500$ G) and $g \approx 1.94$ ($\approx 3500$ G). The first line can be assigned to Fe$^{3+}$ impurities resulting from contamination after Ce doping. No Fe was detected in Ce free glass.

The second line, which seems to disappear when the glass is doped with Ce, can be assigned to paramagnetic centers associated to defects in the glass structure. Since these two spectral features do not pertain to the main focus of this work, no further efforts were made to make a detailed physical interpretation of them. The broad lines are similar in all the samples, including the undoped Gn1 sample, indicating that they cannot be related to Ce$^{3+}$ paramagnetic ions.

The electron spin-echo-detected EPR (EDFS) spectrum was recorded by measuring the transient signal (echo) generated by a two-pulse sequence with fixed time separation and varying external magnetic field. Thus, signal absorption was measured directly, which is a considerable advantage over the usual CW-EPR methods applied in the case of broad line EPR spectra. EDFS spectra for the glasses doped with Ce (Gn2) are depicted in Figure 12. The undoped sample Gn1 produced no EDFS signal and is not shown. This led us to assign the absorption lines observed in Figure 13 to Ce$^{3+}$ paramagnetic centers, which can be observed only by the EDFS method. Furthermore, note that all the samples show similar signal amplitudes, indicating that the amount of Ce$^{3+}$ in the sample is not influenced by heat treatment.

The EDFS spectra of Ce-doped samples in Figure 12 showed a complex unresolved broad signal spanning about

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**FIGURE 10** Images of indentation impressions and Vickers hardness numbers vs heat treatment time (micron bar=20 μm), for Gn2 glass heat-treated at 880°C for the indicated periods of time, preceded by nucleation at 670°C for 3 hour.

**FIGURE 11** CW-EPR spectra of samples Gn1, Gn2, and Gn2-2 hour obtained at room temperature (top) and at 25 K (bottom). The sharp line at around 1590 G (25 K) for samples Gn2 and Gn2/2 hour is attributed to Fe$^{3+}$ impurities ($g=4.3$). The sharp line at around 3500 G (294 K and 25 K) for sample Gn1 has not yet been assigned ($g=1.94$). Microwave frequency: $\approx 9.48$ GHz.

**FIGURE 12** EDFS-EPR spectra of Gn2 samples obtained at 8 K. Arrows indicate the field positions in which ESEEM measurements were taken. All the spectra intensities are normalized by the corresponding sample mass and relaxation decay, as described in the text. Microwave frequency: $\approx 9.39$ GHz.
The prominent bumps, or oscillations, in the upper part of the spectra represent nuclear modulation effects and are not real absorption features. A relatively small pulse separation (τ=800 ns) was used to increase the signal-to-noise ratio. As the pulse separation increases further, the signal intensity decreases and the oscillations disappear, as a consequence of relaxation decay of the modulation pattern (not shown in the figure).

It is important to remark that the intensity of the spectra plotted in Figure 12 is proportional to the echo intensity at τ=800 ns and is therefore strongly dependent on the values of relaxation times. Since these values could be estimated at the central position of the absorption band (Figure 13 (C)), the absorption curves were also normalized by their corresponding decay factors as well as by their sample masses.

Assigning a particular Hamiltonian spin that can simulate such broad resonance is not easy for the following reasons. First, the line shape of this broad signal arises from the $^2F_{5/2}$ ground state of Ce$^{3+}$ ions and is probably strongly influenced by both an anisotropic zero-field splitting and an anisotropic g-tensor. The energy gap from the lowest excited state $^2F_{7/2}$ is 2250 cm$^{-1}$, owing to the spin-orbit coupling interaction. This excludes any significant contribution of the $^2F_{7/2}$ state in determining g-values. Therefore, the wave function of the $^2F_{5/2}$ ground state for a specific crystal field symmetry results from the linear combination of three Kramers doublets, which mixes the $|M_f=\pm 1/2\rangle$, $|M_f=\pm 3/2\rangle$ and $|M_f=\pm 5/2\rangle$ eigen functions. In general, the mixing coefficients of the doublets depend on the distortion of the Ce$^{3+}$ environment, giving rise to a wide range of experimental g-tensor values, a fact that has been reported innumerable single crystal studies. In the case of glasses or partially crystallized glasses, it is even more difficult to predict the Hamiltonian spin parameters because of the large distribution of ion symmetries in the crystal fields in both amorphous and crystalline matrices. Possible sources of distortions that cause excessive broadening of the resonance can be the presence of lattice defects such as vacancies or substitutional ions, or when the Ce$^{3+}$ electric charge differs from that of the substitutional site. To the best of our knowledge, only a few EPR studies of Ce$^{3+}$-doped glasses have been reported so far, where broad and poorly resolved line shapes of this kind have been observed for various glass compositions. Because of these difficulties, our study still lacks an explicit simulation of the signals shown in Figure 13.

In the two-pulse ESEEM experiment, the intensity of the primary echo is recorded as a function of the time interval τ and the integrated area of the echo is determined as a function of τ. The results obtained for samples Gn2, in a magnetic field of 6100 G, are shown in Figure 13. The plot of inset (A) in linear scale shows a typical example in which the zero-frequency decay function and spectral modulation function are separated from the experimental data. The sum of the decay (red) and modulation (green) functions closely reproduces the acquired signal (black). The decay function for all the studied samples is shown in (B). Note that the data shown in (B) are plotted in a semi-log scale and shifted vertically to better visualize their time decay behavior. Note also that data acquisition starts at τ=120 ns, owing to the instrumental dead time. In a comparison of the decays, note the exponential behavior of samples Gn2/25 hour, Gn2/50 hour, and Gn2/100 hour over about two decades, while samples Gn2 and Gn2/2 hour show a marked deviation from this exponential behavior.

KBDM is a parametric nonlinear method for fitting time-domain signals and was used to separate the zero-frequency decay and spectral modulation functions from the ESEEM data. The goal of the KBDM is to model the time-domain signal as a sum of exponentially damped sinusoids. Pure exponential decays are described by zero-frequency components while non-zero-frequency components describe the modulation function and noise. In this study, only samples Gn2/25 hour, Gn2/50 hour, and Gn2/100 hour had a zero frequency decay that could be fitted by a single exponential component. In the case of samples Gn2 and Gn2/2 hour, the same fitting could not be accomplished by a single exponential component; instead, at least two components with frequencies close to zero and different decay times resulted from each fitting. The deviation from pure exponential decay observed for samples Gn2
and Gn2/2 hour is a small but real effect, as can be appreciated from Figure 13 in comparison with the corresponding decay of the remaining samples, which can be assigned to pure exponential decays with every confidence. The echo intensity decay is mainly governed by the mutual interaction between magnetic dipoles of the Ce3+ ions, or spin-spin relaxation processes then, if we assume that the thermal treatment has not modified the spatial distribution of the Ce3+ ions with respect to the untreated glass, we believe that the shape of the decay function should be the same for both, treated and untreated samples. Indeed, the calculated relaxation time, $T_M$, shows only small variations, remaining in the range 350-400 ns for all samples as can be seen in Figure 13 (C), indicating that the average distance between Ce3+ ions does not change markedly upon heat treatment. However, the small differences seen in the relaxation shape, that is nonexponential for samples Gn2 and Gn2/2 hour, represents a puzzle in this scenario. A possible explanation for this discrepancy may arise if we must focus on other process, like spin-lattice relaxation, which is due to phonons in the lattice, is also influencing the echo decay. In this case, crystallization may be responsible for the observed behavior. Finally, owning to the complexity of the observed behavior, we have not reached a better understanding of this issue.

Notwithstanding the above, all the decay data were fitted to a single exponential function, enabling the determination of relevant parameters such as signal amplitude extrapolated at $t = 0$, characteristic decay time (known as “memory time, $T_M$”, in the EPR literature), and a constant offset. The offset was subtracted from the decay signal in the plots in Figure 13 (B). In Figure 13, inset (C) shows the values determined for $T_M$ and the signal amplitude of all the samples. For comparison, the values of the signal amplitudes were normalized by the corresponding sample mass. Note that the slight variations in the amplitude values are small and not systematic, and in fact, indicate that these data are uncorrelated to sample treatment. The values found for $T_M$ in increasing order, are: 350.5, 356.8, 372.6, 385.7, and 391.3 ns for samples Gn2/25 hour, Gn2/50 hour, Gn2/100 hour, Gn2/2 hour and Gn2, respectively. The relationship between the amplitudes of modulation and decay functions is known in the EPR literature as the “modulation depth, $k$” and is also plotted in the same inset. A noticeable increase in the values of $k$ is observed for samples Gn2 and Gn2/2 hour, indicating the presence of a larger anisotropy of the hyperfine interaction, which is consistent with the amorphous phase.

ESEEM, one of the few techniques for determining the structure of disordered systems, can enable the determination of local structures beyond the first coordination sphere. In the two-pulse ESEEM experiment, the echo amplitude is modulated as a function of pulse separation, $\tau$, by frequencies associated with nearby nuclear spins weakly coupled to the electron spin by anisotropic dipolar interactions. This process is evidenced by a decaying oscillatory transient (such as that plotted in green in Figure 13 (A)) and the ESEEM spectrum is calculated by Fourier transformation of the transient. A typical result of the application of this procedure to our data is shown in Figure 14. As can be seen, the ESEEM spectra are entirely dominated by the hyperfine coupling to 27Al nuclei. The peaks in different fields clearly reveal the Larmor frequencies of 27Al (natural abundance 100%, gyro-magnetic ratio $\gamma=1.11$ kG/MHz), suggesting that these nuclei interact with the electron spins in the orbitals of the Ce3+ ions at the weak coupling limit, where the hyperfine coupling constant is small compared to the nuclear Zeeman frequencies. Therefore, we conclude that these signals belong to 27Al nuclei in second or higher order Ce3+ coordination spheres (distance range 4-8 Å).

4 | CONCLUSIONS

Transparent glass-ceramics containing 5-10 nm ZnAl2O4 crystals were produced from a SiO2-K2O-ZnO-Al2O3-TiO2 glass. TiO2 was used as a nucleating agent to trigger internal crystallization of the garnet phase. DSC studies have provided evidence of internal crystallization, with an Avrami index of 3. However, the glasses and glass-ceramics were dark brown because Ti^{+4} was partially reduced to Ti^{+3} at the high melting temperatures required to synthesize the glass, thus making the GC unsuitable for optical applications. However, CeO2 proved to be an efficient addition,
which minimized the color by oxidizing Ti$^{3+}$ to Ti$^{4+}$, as confirmed by the presence of Ce$^{3+}$ in the EPR spectra.

Moreover, the addition of CeO$_2$ reduced the glass transition, melting, and refining temperatures. XRD and TEM analysis substantiated the formation of nanocrystallites. FTIR experiments confirmed the gradual formation of the Al-O bonds after heat treatment of the precursor glass, due to the formation of spinel structure. The hardness of the glass-ceramics increased by up to 30% compared to that of the parent glass. The heat treatments did not change substantially the optical properties of the G02 glass-ceramic.

The presence of Ce$^{3+}$ was confirmed by pulsed EPR techniques and results indicate that the concentration of Ce$^{3+}$ in the untreated doped glass remains the same upon heat treatment. However, ESEEM measurements pointed a small difference in the spin relaxation behavior of samples heat treated. EPR measurements pointed a high strain point spinel glass-ceramics.

The hard, transparent glass-ceramics obtained here may be potential candidates for some applications, such as armor and display panels.

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REFERENCES


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