

Article

Effect of Increasing Fe₂O₃ Content on the Structural, Thermal, and Optical Characteristics of Soda–Lime–Silica Glass-Ceramics

Raluca A. Mereu ¹, Alexandru Turza ², Oana Raita ² and Mioara Zagrai ^{2,*}

¹ Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos Street, 400028 Cluj-Napoca, Romania; raluca.mereu@ubbcluj.ro

² Department of Materials, Energy and Advanced Technologies—META, National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat, 400293 Cluj-Napoca, Romania; alexandru.turza@itim-cj.ro (A.T.); oana.raita@itim-cj.ro (O.R.)

* Correspondence: mioara.zagrai@itim-cj.ro

Abstract

In this study, a series of xFe₂O₃–Na₂O–CaO–SiO₂ glass-ceramics containing 0–28 wt.% Fe₂O₃ were prepared via the conventional melt-quenching technique. The resulting samples, designated S1–S4, were subsequently subjected to thermal treatment and investigated with respect to their structural, thermal, and optical characteristics. Differential scanning calorimetry analysis revealed the influence of the Fe₂O₃ concentration on the glass transition temperature and crystallization behavior of the samples. Structural analysis of the samples revealed that crystalline silicate and iron oxide phases constituted the predominant crystalline phases, with their overall crystallinity being strongly dependent on the Fe₂O₃ content and thermal treatment. Fourier transform infrared spectroscopy evidenced structural modifications of the silicate network induced by iron incorporation, while ultraviolet–visible–near infrared spectroscopy highlighted the presence of Fe²⁺/Fe³⁺ ions and their associated electronic transitions. The results indicate that increasing the Fe₂O₃ content significantly affects the network structure, redox state, and thermal behavior of the glass-ceramic system, leading to enhanced absorption properties.

Keywords: soda–lime–silica glass-ceramic system; Fe₂O₃; X-ray diffraction; crystallization; FTIR spectroscopy; UV–Vis–NIR spectroscopy

1. Introduction

In recent years, glass and glass-ceramic systems have gained increasing attention due to their multifunctional applications, ranging from storage medium in high-temperature Thermal energy storage (TES) systems [1,2] and thermal insulation to the valorization of industrial wastes and the immobilization of radioactive waste. The performance of TES systems is strongly dependent on the thermophysical, chemical, optical, environmental, and economic properties of the storage material, particularly in applications such as concentrated solar power (CSP) [3]. The ability of storage materials to operate at elevated temperatures significantly enhances the efficiency of heat-to-electricity conversion, making the development of high-temperature TES materials an important research topic [4].

Among different materials investigated for TES applications, glasses and glass-ceramics have attracted considerable attention due to their excellent thermal stability, chemical durability, corrosion resistance, relatively low cost, and ease of processing [5]. Furthermore, their chemical stability enables long-term heat storage, while their recyclability and abundance make them environmentally sustainable alternatives to conventional



Academic Editor: Jiamin Wu

Received: 12 June 2026

Revised: 17 July 2026

Accepted: 19 July 2026

Published: 21 July 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

TES materials. The possibility of tailoring their composition over a wide range allows the optimization of structural, thermal, and optical properties according to specific application requirements [6]. Also, the incorporation of waste-derived raw materials, including industrial by-products and metallurgical slags, into glass and glass-ceramic matrices provides both ecological and economic benefits by reducing environmental pollution while enabling the development of sustainable value-added materials [7–10]. In addition, the excellent chemical durability and long-term stability of glass-based systems make them promising candidates for radioactive waste immobilization. Recent advances in glass, glass-ceramic, and composite processing technologies have further expanded the functional capabilities of these materials, particularly regarding magnetic properties, structural integrity, and tailored radiation-absorption characteristics [11]. Although integrating multiple functionalities into a single material remains a considerable challenge, significant progress has been achieved in tailoring the structure and properties of these systems for advanced technological applications [12]. Moreover, glass foams and glass-ceramic foams have indicated excellent potential as thermal insulation materials for buildings, contributing to reduced heating and cooling demands and consequently improving energy efficiency [13].

The Na_2O – CaO – SiO_2 (soda–lime–silica) system is the most widely used glass family, accounting for approximately 90% of all commercially produced glasses. Besides its traditional applications in windows, containers, and flat glass products, this system has also found use in advanced technological fields, including structural engineering components and coating systems [14]. Owing to its good glass-forming ability, low production cost, and compositional flexibility, the soda–lime–silica system represents an attractive matrix for the development of functional glass and glass-ceramic materials.

The incorporation of transition metal oxides into silicate glasses is a well-established strategy for modifying their physical and functional properties. Among these oxides, iron oxide (Fe_2O_3) is of particular interest due to its ability to exist in multiple oxidation states (Fe^{2+} and Fe^{3+}) and coordination environments within the glass network. Numerous studies have shown that Fe_2O_3 significantly influences the thermal and structural behavior of soda–lime–silica glasses, including glass transition, crystallization kinetics, optical absorption, and network connectivity [14,15]. When added in relatively small amounts, iron oxide can act as a nucleating agent, affecting both the nucleation rate and crystal growth processes during glass-ceramic formation [16].

The structural role of iron depends strongly on its oxidation state and coordination geometry. Fe^{2+} ions generally behave as network modifiers, disrupting Si–O–Si linkages and creating non-bridging oxygen atoms, which decrease the connectivity of the glass network. In contrast, Fe^{3+} ions may participate as network formers by entering tetrahedral sites and contributing to network stabilization. Consequently, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio has a significant influence on the glass structure, density, thermal stability, crystallization tendency, and mechanical performance [17]. Recent studies on CaO – Al_2O_3 – SiO_2 -based glasses have indicated that increasing the Fe_2O_3 content promotes network depolymerization through the formation of non-bridging oxygens, resulting in substantial modifications of the structural organization and physical properties of the glass matrix [18].

In addition to their structural effects, iron oxides contribute significantly to the optical behavior of glasses. The coexistence of Fe^{2+} and Fe^{3+} ions gives rise to characteristic electronic transitions and intervalence charge-transfer processes, leading to strong absorption in the UV–visible and near-infrared regions. Such absorption characteristics are particularly attractive for thermal energy-storage applications, where efficient solar radiation absorption and conversion into thermal energy are desirable [19,20].

The present work focuses on the influence of Fe_2O_3 substitution for CaO in the Na_2O – CaO – SiO_2 soda–lime silicate system and on the effect of thermal treatment on the

structural evolution and redox state of iron ions. Glasses with compositions of $16\text{Na}_2\text{O}-(44-x)\text{CaO}-40\text{SiO}_2\cdot x\text{Fe}_2\text{O}_3$ ($x = 0, 14, 21$, and 28 wt.%) were synthesized using the conventional melt-quenching method and subsequently subjected to controlled heat treatment. The obtained glass and glass-ceramic materials were characterized by density measurements, differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and UV-Vis-NIR spectroscopy in order to evaluate their structural, thermal, and optical properties.

The results indicate that Fe_2O_3 incorporation significantly modifies the glass network structure, affects crystallization behavior, and influences the optical absorption characteristics of the investigated materials. Therefore, this study provides valuable insights into the role of iron oxide in controlling the structure-property relationships of soda-lime-silica glasses and contributes to the development of advanced glass-ceramic materials.

2. Materials and Methods

2.1. Sample Preparation

Materials belonging to the $16\text{Na}_2\text{O}-(44-x)\text{CaO}-40\text{SiO}_2\cdot x\text{Fe}_2\text{O}_3$ system, with $x = 0, 14, 21$, and 28 wt.% Fe_2O_3 , were synthesized via the conventional melt-quenching method in order to investigate the influence of iron oxide on the structural, thermal, and optical properties of the obtained glass-ceramics. The starting mixtures were prepared from analytically pure reagents: anhydrous sodium carbonate (Na_2CO_3), calcium carbonate (CaCO_3), silicon dioxide (SiO_2), and iron(III) oxide (Fe_2O_3).

The glass-ceramic samples were prepared under normal atmospheric conditions by melting 5 g batches in alumina crucibles at 1350°C in an air atmosphere. For the composition containing 28 wt.% Fe_2O_3 , the melting temperature was increased to 1400°C to ensure complete melting and proper pouring of the sample from the crucible. The molten mixtures were subsequently poured and rapidly quenched onto a stainless-steel plate at room temperature to obtain the samples.

Two series of samples were investigated in this study. The first series consisted of the as-quenched samples, denoted S1–S4, while the second series, labeled S'1–S'4, underwent an additional thermal treatment in air at 500°C for 1 h in order to relieve internal stresses, followed by slow cooling to room temperature at a rate of $1^\circ\text{C}/\text{min}$.

2.2. Characterizations

The structural, thermal, and optical characteristics of the prepared materials were investigated via X-ray diffraction (XRD) (Bruker AXS, Karlsruhe, Germany the manufacturer, city, and country), differential scanning calorimetry/differential thermal analysis (DSC/DTA), Fourier transform infrared (FT-IR) spectroscopy, and UV-Vis spectroscopy.

The density (ρ) of the prepared samples was measured at room temperature using the Archimedes method with an analytical balance of four-digit precision.

Thermal behavior was investigated using a simultaneous thermal analyzer (SDT Q600, TA Instruments, New Castle, DE, USA). Approximately 25 mg of powdered sample was placed in alumina crucibles and analyzed under a dynamic air atmosphere. The measurements were carried out under non-isothermal conditions up to 1000°C , employing a constant heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

The crystalline phases of the glass-ceramic samples were identified via X-ray diffraction (XRD) using a D8 ADVANCE diffractometer (Bruker, Karlsruhe, Germany). Diffraction patterns were collected in the 2θ range of 20 – 80° with a scanning rate of $4^\circ/\text{min}$.

Fourier transform infrared (FTIR) spectra were recorded using a JASCO FTIR-6200 spectrometer (Jasco, Tokyo, Japan) in a 400 – 4000 cm^{-1} spectral range with a spectral resolution of $\pm 2\text{ cm}^{-1}$. The measurements were performed using the KBr pellet technique.

Optical absorption measurements were carried out using a PerkinElmer Lambda 45 UV–Vis spectrometer (PerkinElmer Inc Waltham, MA, USA) equipped with an integrating sphere. The powder samples were mixed with BaSO₄ and uniaxially pressed into transparent pellets under a load of 10 tons/cm², resulting in disks with a diameter of 13 mm and a thickness of approximately 2 mm. The spectra were recorded in the wavelength range of 200–2000 nm, with a wavelength accuracy of ± 2 nm.

3. Results and Discussions

3.1. Physical Properties of the Samples

The physical properties of the prepared materials were investigated in terms of density and molar volume in order to evaluate the influence of Fe₂O₃ incorporation on the structural arrangement of the glass network. The compositions belonging to the Na₂O–CaO–SiO₂–Fe₂O₃ quaternary system are illustrated in Figure 1a, while the macroscopic appearance of the obtained glass-ceramic samples is presented in Figure 1b. Samples S1–S3 were synthesized at 1350 °C, whereas sample S4 required a higher melting temperature of 1400 °C, which may be attributed to an increase in melt viscosity resulting from the combined effect of Fe₂O₃ enrichment and CaO depletion. All prepared samples exhibited an opaque appearance.

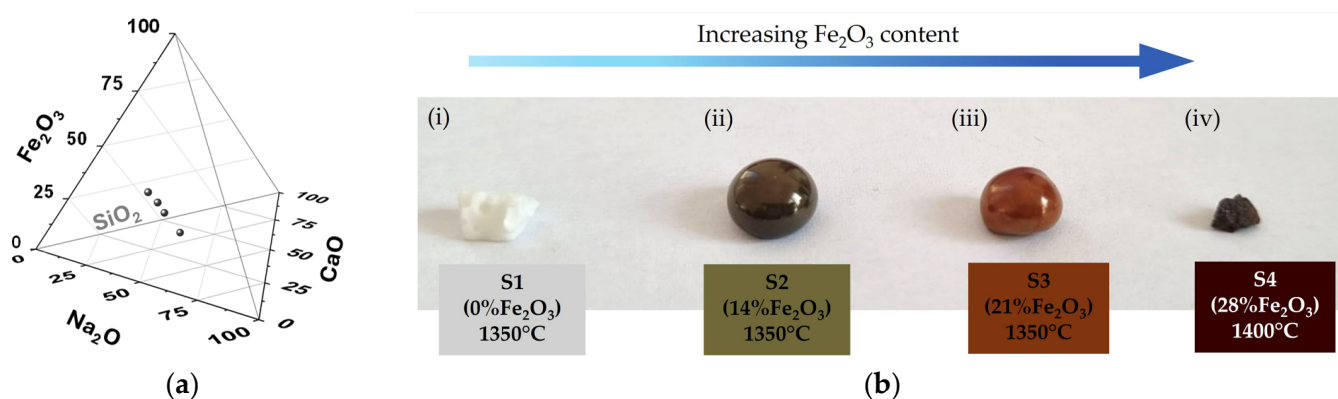


Figure 1. (a) Na₂O–CaO–SiO₂–Fe₂O₃ quaternary phase diagram; (b) macroscopic appearance of glass-ceramic samples with increasing Fe₂O₃ content.

However, in the literature, it is mentioned that the ferrous and ferric ions are localized in specific environments within glass structure, giving diluted glasses a blue (Fe²⁺), yellow (Fe³⁺), or green (mixed oxidation states) color [21]. Also, the progressive color evolution of the samples (Figure 1b), from white (S1) to dark brown (S2), reddish-brown (S3), and nearly black (S4) quantitatively follows the increase in optical absorption observed in the UV–VIS–NIR spectra. In technical glasses, both Fe²⁺ and Fe³⁺ are always present, resulting in an iron-green color. As the addition of iron increases, the color darkens (due to strong absorption) [22]. However, color alone cannot be considered evidence for the oxidation state distribution of iron.

The density and molar volume results (Table 1) provide important information regarding the structural evolution of the investigated glass-ceramic system with an increasing Fe₂O₃ content. In oxide glasses, density is closely related to atomic packing efficiency and the molecular weight of the constituent oxides, while the molar volume reflects the degree of structural compactness and the availability of free volume within the glass network [23,24].

Table 1. Density and Molar volume of the samples.

Samples Code	ρ (g/cm ³)	V _m (cm ³ /mol)
S1	2.77	21.13
S'1	2.49	23.53
S2	3.09	23.59
S'2	2.25	23.50
S3	3.56	22.56
S'3	2.84	28.28
S4	4.54	19.29

The density measurements of the as prepared and heat-treated materials were performed on different specimens of the same nominal composition.

The observed increase in density together with the decrease in molar volume suggests a more compact atomic packing. These changes are likely the combined result of the increasing Fe₂O₃ content and the corresponding reduction in CaO content, both of which affect the connectivity and packing of the glass network. The FTIR analysis further supports this interpretation by evidencing changes in the vibrational features of the silicate network.

The sample containing the highest Fe₂O₃ concentration (S4) exhibits the highest density value (4.54 g/cm³) together with a lower molar volume (19.29 cm³/mol), indicating the formation of a more compact and tightly packed structure. This behavior can be attributed to the high atomic mass of iron ions and to the increasing participation of Fe ions in octahedral coordination, which enhances structural packing [25,26]. In addition, the simultaneous decrease in CaO content, a major network modifier, may further contribute to increased network connectivity and reduced free volume, thereby supporting the observed densification [27].

For samples with intermediate Fe₂O₃ concentrations (S2 and S3), the decrease in density accompanied by relatively larger molar volumes suggests partial depolymerization and expansion of the silicate network. At these concentrations, Fe³⁺ ions may enter the glass network in tetrahedral coordination by partially replacing Si⁴⁺ ions, producing structural rearrangements and increasing the free volume of the system.

The annealed samples (S' series) generally exhibit lower density values and larger molar volumes compared to the as-quenched glasses-ceramic samples. This behavior may be associated with structural relaxation during thermal treatment, which reduces internal stresses and promotes local rearrangements within the glass network [25]. In some cases, heat treatment may also induce the formation of microcrystalline phases and structural heterogeneity, contributing to changes in the packing density.

Overall, the simultaneous variation of the density and molar volume suggests that Fe₂O₃ plays a dual structural role in the investigated glass-ceramic samples, acting both as a network former and as a network modifier depending on the concentration and iron oxidation state. These structural modifications strongly influence the thermal and optical properties of the investigated glass-ceramic materials.

3.2. Thermal Analyses

The thermal behavior of the investigated glass-ceramic samples was evaluated via DSC analysis (Figure 2), and the characteristic thermal parameters are summarized in Table 2. The glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), onset temperature (T_o), thermal stability parameter (ΔT), glass-forming

ability coefficient (K_{gl}), and stability factor (S) provide important information regarding the structural stability and crystallization tendency of the investigated materials. The Δ_{flux} corresponds to the heat-flow difference associated with the glass transition was determined directly from the DSC diagram. The thermal stability parameters were calculated according to the following equations [28,29]:

$$\Delta T = T_c - T_g$$

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c}$$

$$S = \frac{(T_c - T_o)(T_c - T_g)}{T_g}$$

where T_g , T_o , T_c , and T_m denote the glass transition, crystallization onset, crystallization peak, and melting temperatures, respectively.

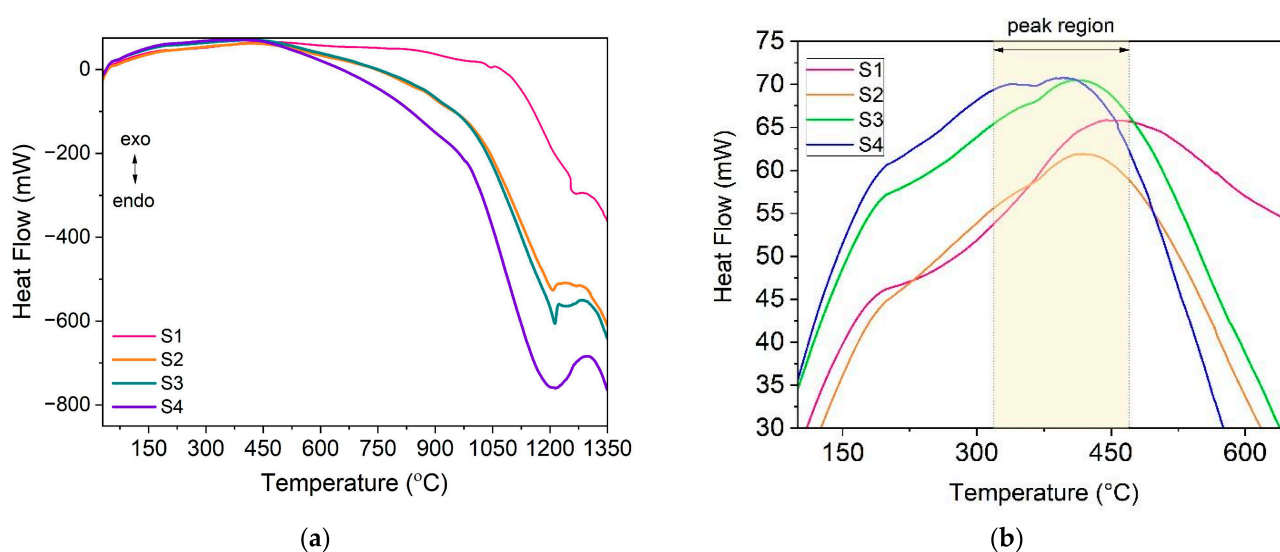


Figure 2. DSC curves of the investigated samples: (a) S1–S4 samples recorded up to 1350 °C; (b) enlarged DSC curves of the samples, highlighting thermal peaks in the 320–470 °C range.

Table 2. The DSC key parameters for the investigated samples.

Samples Code	Thermal Parameters							
	T_g (°C)	T_c (°C)	T_m (°C)	T_o (°C)	ΔT (°C)	Δ_{flux} (J/sg)	K_{gl}	S
S1	320	460	1046	290	140	0.3458	0.2389	74.375
S'1	319	421	1192	288	102	0.7312	0.1327	42.853
S2	362	420	1206	350	58	0.1226	0.0741	11.269
S'2	340	418	1207	319	79	0.2864	0.0999	23.123
S3	352	416	1213	345	64	0.1407	0.0805	13.007
S'3	327	392	1202	292	66	0.0108	0.0812	20.223
S4	351	401	1182	344	50	0.2371	0.0640	8.1624

The DSC results indicate that Fe_2O_3 incorporation strongly influences the thermal stability and crystallization behavior of the investigated samples. The glass transition temperature generally increases with an increasing Fe_2O_3 content, from 320 °C for the

reference sample S1 to values around 351–362 °C for iron-containing samples. This increase suggests that Fe ions contribute to strengthening the glass network by increasing network connectivity and restricting structural mobility. The observed behavior can be attributed not only to the incorporation of Fe ions, which may increase network connectivity through the formation of Fe-O structural units, but also to the simultaneous decrease in the CaO content. As a network modifier and fluxing agent, CaO is in the system, promoting the formation of non-bridging oxygens and partial disruption of the silicate network. Consequently, reducing the CaO concentration limits network depolymerization, leading to a more rigid structure and higher T_g values. This interpretation is consistent with the well-established role of CaO as a network modifier in silicate materials [27].

The crystallization temperature (T_c) exhibits a gradual decrease with an increasing Fe_2O_3 concentration, indicating that iron oxide promotes crystallization processes within the glass matrix. Sample S1 shows the highest T_c value (460 °C), whereas S4 presents the lowest crystallization temperature (401 °C). This behavior suggests that higher Fe_2O_3 concentrations facilitate nucleation and crystal growth due to the modifier role of iron ions at elevated concentrations.

The thermal stability parameter $\Delta T (=T_c - T_g)$, commonly used to evaluate glass stability against devitrification, decreases significantly from 140 °C for S1 to 50 °C for S4. Higher ΔT values indicate better resistance to crystallization during heating; therefore, the decrease in ΔT indicates that increasing the Fe_2O_3 content reduces the thermal stability of the glass-ceramics and increases their tendency toward crystallization.

The glass-forming ability parameter K_{gl} and the stability factor S also decrease with an increasing Fe_2O_3 concentration. The highest K_{gl} (0.2389) and S (74.375) values are observed for the Fe_2O_3 -free sample S1, confirming its superior glass-forming ability and structural stability. In contrast, sample S4 exhibits the lowest K_{gl} (0.0640) and S (8.1624), indicating reduced glass stability and enhanced crystallization tendency. These results suggest that iron oxide progressively modifies the silicate network and promotes the formation of glass-ceramic structures.

The annealed samples (S' series) exhibit variations in T_g , T_c , and Δ_{flux} compared to the as-quenched samples, reflecting structural relaxation and partial rearrangement of the network during heat treatment. In particular, for S'1 and S'2, the lower Δ_{flux} values for samples with higher Fe_2O_3 contents suggest reduced structural mobility.

Overall, the thermal analysis indicates that Fe_2O_3 plays a major role in controlling the structural organization and crystallization behavior of the Na_2O – CaO – SiO_2 glass-ceramic system. Increasing the iron oxide concentration enhances network rigidity but simultaneously promotes crystallization, favoring the formation of thermally stable glass-ceramic materials.

3.3. X-Ray Diffraction

The XRD patterns presented in Figure 3 reveal significant structural differences between the investigated samples as a function of the Fe_2O_3 concentration and thermal treatment. Structural analysis of the reference matrix (S1) confirmed the coexistence of multiple crystalline phases, dominated by calcium silicate phases (Ca_2SiO_4), ($\text{Ca}_3\text{Si}_2\text{O}_7$) and sodium silicate phases ($\text{Na}_6\text{Si}_2\text{O}_7$). These crystalline phases suggest partial crystallization of the soda–lime silicate system during cooling.

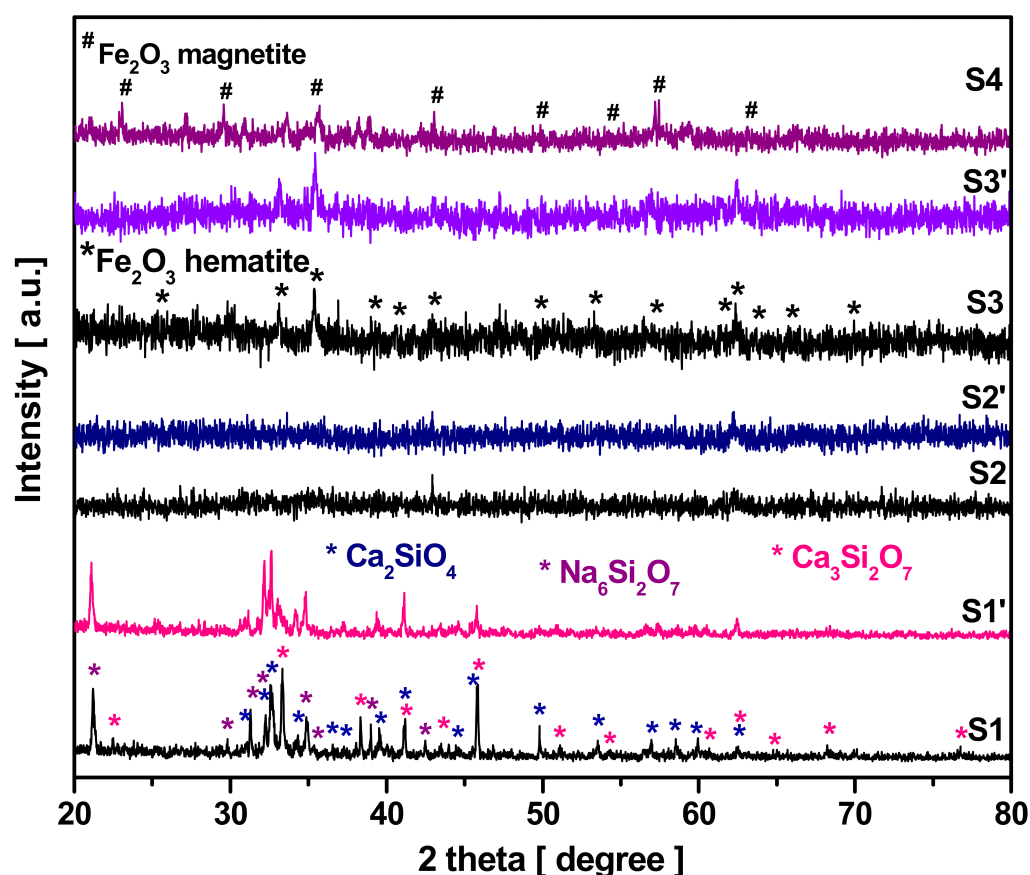


Figure 3. XRD patterns of the samples.

After thermal treatment, sample S'1 still preserves pronounced crystalline reflections, confirming that the heat treatment at 500 °C promotes further structural ordering and crystal growth within the material [30].

In contrast, for samples S2 and S'2, which contain intermediate Fe₂O₃ concentrations, the XRD patterns exhibited severe peak broadening and a substantial reduction in the relative intensity. Rather than indicating a true structural amorphization or a purely amorphous matrix transition—especially given the notable absence of characteristic diffuse amorphous halos—this signal attenuation is primarily attributed to strong iron-induced X-ray fluorescence under CuK α radiation. This phenomenon significantly elevates the background noise and drops the signal-to-noise ratio, effectively obscuring the underlying crystalline reflections. Consequently, the apparent loss of peak resolution masks the real crystallization state of these intermediate samples, which is highly dependent on the synergistic effects of the Fe₂O₃ content and subsequent thermal treatments.

While the base soda–lime–silicate system exhibit multiple diffraction peaks attributed to mixed sodium–calcium silicate phases, the Fe₂O₃-modified compositions show distinct structural features, indicating the influence of iron oxide on phase formation and crystallization behavior. Fe²⁺, with an ionic radius of 0.78 Å in octahedral coordination, is much closer in size to Ca²⁺ (1.00 Å) than to Fe³⁺ (0.49 Å in tetrahedral coordination). Consequently, the presence of Fe²⁺ promotes a network-modifying role, leading to depolymerization of the glass structure, unlike Fe³⁺, which can act as a network former.

The absence of sharp diffraction peaks after heat treatment suggests that 500 °C remains below the effective crystallization temperature for compositions S2 and S'2. The intermediate Fe₂O₃ concentration appears to increase the thermal stability of the glass network, delaying nucleation and suppressing crystal growth.

In contrast, samples S3 and S4 exhibit the appearance of additional diffraction peaks associated with iron oxide crystalline phases. In sample S3, the reflections marked with (*) are assigned to hematite ($\alpha\text{-Fe}_2\text{O}_3$), while in sample S4, the peaks marked with (#) correspond mainly to magnetite type phases (Fe_3O_4). The intensity and number of these peaks increase with an increasing Fe_2O_3 content, indicating enhanced crystallization and phase separation processes at higher iron concentrations.

The transition from hematite-rich reflections in S3 to magnetite reflections in S4 may suggest that increasing the Fe_2O_3 concentration modifies the local oxygen potential during melting and cooling. At higher iron loadings, the formation of mixed iron oxide phases reported in the literature is consistent with the possible coexistence of Fe^{2+} and Fe^{3+} ions. This observation is consistent with previous studies reporting that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio strongly governs the crystallization pathway of iron oxide phases in silicate glasses. After thermal treatment (S3'), the characteristic hematite diffraction peaks become significantly weaker, indicating a marked reduction in the detectable crystalline $\alpha\text{-Fe}_2\text{O}_3$ phase. This behavior suggests that the heat treatment modifies the iron oxide crystallization state, while the increased background caused by Fe fluorescence under $\text{CuK}\alpha$ radiation may also contribute to the reduced peak visibility.

The formation of hematite and magnetite phases indicate that iron oxide no longer remains fully incorporated within the silicate lattice at elevated concentrations but partially segregates into iron-rich crystalline domains. This behavior may be related to the coexistence of Fe^{2+} and Fe^{3+} ions and to local redox reactions occurring during melting and cooling [25,31].

Therefore, the increase in the diffraction peak intensity together with the appearance of new reflections indicates not only the formation of additional crystalline phases but also an increase in the crystallite fraction. The appearance of crystalline iron oxide phases at higher Fe_2O_3 contents suggests that the solubility limit of iron in the soda–lime silicate glass matrix is exceeded, leading to phase separation and precipitation of iron-rich crystalline domains.

Overall, the XRD results demonstrate that Fe_2O_3 plays a dual role in the soda–lime silicate glass. At higher concentrations, however, the solubility limit of iron in the silicate matrix is exceeded, resulting in phase separation and crystallization of iron oxide phases, first as hematite and subsequently as magnetite. These structural changes are expected to influence both the magnetic behavior and the physical properties of the glass-ceramic.

3.4. FT-IR Spectroscopy

Infrared spectroscopy (FT-IR) is used to investigate and identify the functional groups presented in the soda lime silicate system containing iron oxide. Figure 4a presents the FTIR spectra of the samples investigated in the range of $400\text{--}4000\text{ cm}^{-1}$.

The sketch of the polymeric $(\text{SiO}_4)_n$ network in silicate glass and their structural representation relevant to FTIR analysis with examples of the different conformations of tetrahedra, from isolated ($\text{NBO} = 4$, Q_0) to fully connected ($\text{NBO} = 0$, Q_4), is presented in Figure 4b. Selected FT-IR spectral bands and their assignment to vibrational modes of the selected characteristic groups in the investigated samples are listed in Table 3. The FTIR spectra of the soda–lime–silica glass-ceramic systems, with and without Fe_2O_3 , exhibit strong absorption bands in the $415\text{--}600\text{ cm}^{-1}$ region, which are primarily attributed to Si–O and Si–O–Si bending vibrations. For the Fe_2O_3 -containing samples, additional contributions from Fe–O-related vibrations may also be present in the higher-wavenumber portion of this region. In the $750\text{--}1250\text{ cm}^{-1}$, the asymmetric stretching vibrations of $[\text{SiO}_4]^-$ are tetrahedral with the various structural units Q_n . The 1189, 1090, 950, and 850 cm^{-1} are associated with $\text{Q}_4\text{--}[\text{SiO}_2]^0$, $\text{Q}_3\text{--}[\text{Si}_2\text{O}_5]^{2-}$, $\text{Q}_2\text{--}[\text{SiO}_3]^{2-}$, $\text{Q}_1\text{--}[\text{Si}_2\text{O}_7]^{6-}$

and Q_0 — $[\text{SiO}_4]^{4-}$, respectively [15,32,33]. These band assignments are consistent with a silicate network predominantly composed of SiO_4 tetrahedra [22].

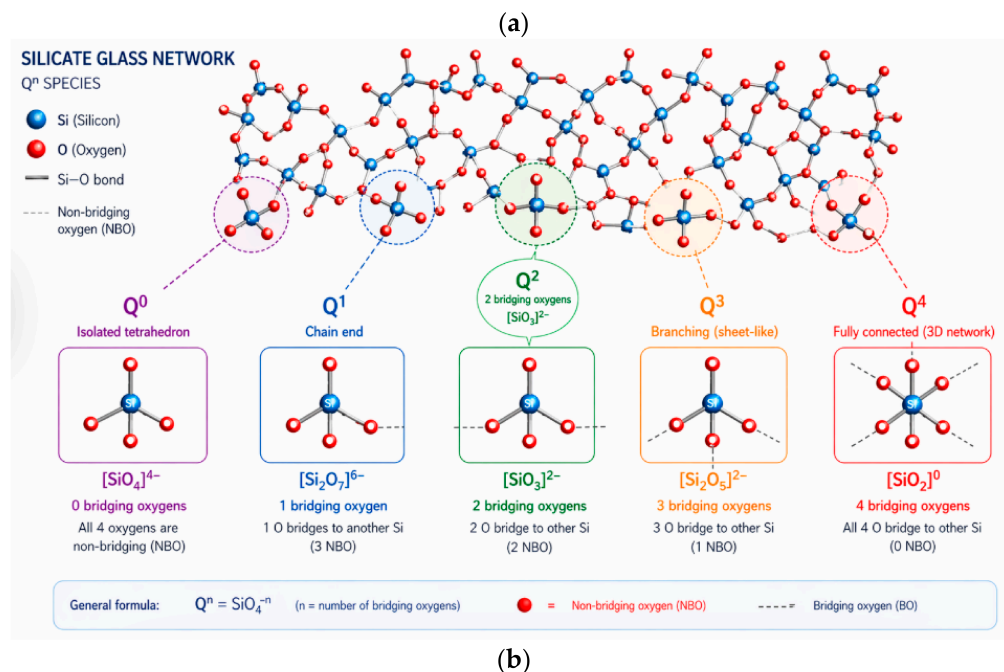
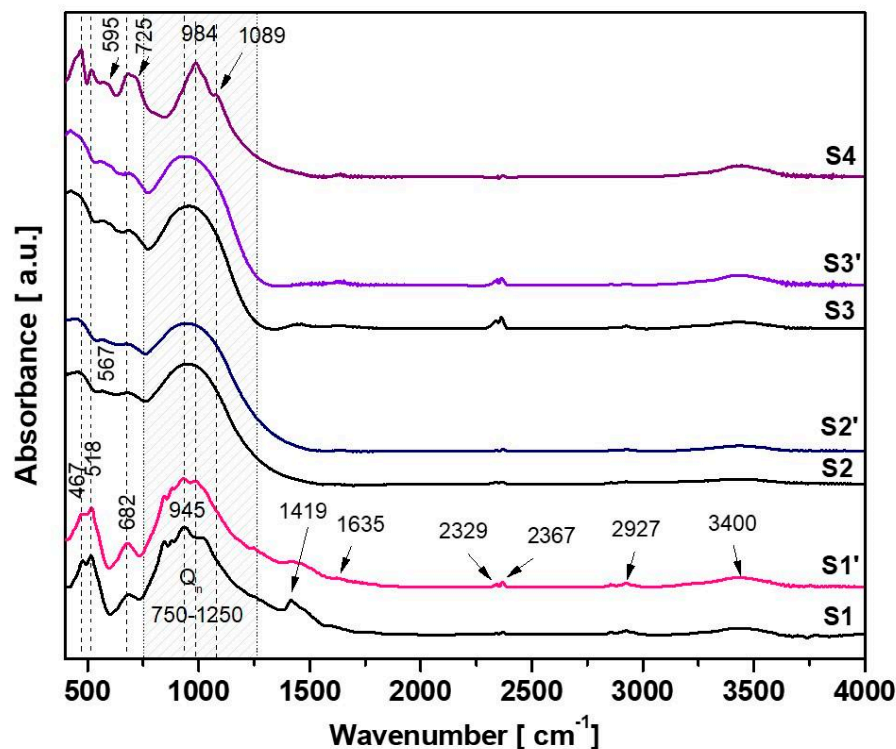


Figure 4. (a) FTIR absorption spectra of samples. (b) Distribution of Q^n species in silicate structure.

The band around 467 cm^{-1} is attributed to Si—O—Si bending vibrations, while the bands near 945 , 984 , and 1089 cm^{-1} correspond to Si—O stretching vibrations of non-bridging and bridging oxygen bonds. These bands indicate the presence of depolymerized silicate units, which is typical for soda–lime–silica glasses containing Na_2O and CaO as network modifiers [34].

Table 3. The FTIR vibrational frequencies and associated functional groups.

Wavenumber (cm ^{−1})	FTIR Bands
467	Si–O–Si bending vibrations
518, 682, 725	include contributions from γ -Ca ₂ SiO ₄ and β -CaSiO ₃ crystalline phase
567	Fe–O-related vibrations (reported for iron oxide-containing silicate materials)
596	Fe–O-related vibrations
750–500	region relating to the bending vibrations of SiO ₄
1419	asymmetric stretching vibrations of the CaO
1620	bending vibration of water molecules adsorbed on the surface
2848, 2927	stretching of C–H bonds
3400	relating to OH stretching vibrations

For the Fe₂O₃-containing samples, additional bands appear or become more evident in the low-wavenumber region. The absorption bands around 567 cm^{−1} and 596 cm^{−1} are assigned to Fe–O bending vibrations, associated with hematite- and magnetite-type iron oxide environments. Also, the Fe₂O₃ can be identified with two low absorption bands at ~468 cm^{−1} and 555 cm^{−1}. The bands at ~460 and ~570 are assigned to specific vibrations of Fe–O bonds [35]. Their presence suggests the incorporation of iron ions into the glass-ceramic structure and agrees with the XRD results, which indicate the formation of iron oxide crystalline phases at higher Fe₂O₃ contents.

At high temperatures, part of Fe³⁺ is reduced to Fe²⁺, as explained in the thermal analysis section. Thus, Fe²⁺ and Fe³⁺ usually coexist when Fe₂O₃ is present in the system. According to the literature, Fe²⁺ and Fe³⁺ may occupy tetrahedral and/or octahedral coordination sites in silicate structure, depending on the composition and thermal history) [36,37].

The bands observed at 518, 682, and 725 cm^{−1} may be related to calcium silicate crystalline phases, such as γ -Ca₂SiO₄ and β -CaSiO₃. This suggests partial crystallization of the soda–lime–silica matrix, especially after thermal treatment.

In the Fe-free sample S1, the silicate bands are more clearly defined, showing the typical structure of the soda–lime–silica network. With an increasing Fe₂O₃ content, the broadening and slight shifting of the bands in the 750–1250 cm^{−1} region indicates structural rearrangement of the silicate network. This behavior suggests that Fe³⁺ ions can enter the glass structure either as network formers in tetrahedral coordination or as network modifiers in octahedral coordination, depending on concentration.

The weak bands at 1419 cm^{−1} and 1635 cm^{−1} are assigned to carbonate group vibrations and adsorbed water molecules, respectively. The bands near 2927 cm^{−1} and the broad band around 3400 cm^{−1} correspond to C–H stretching and O–H stretching vibrations, indicating the presence of small amounts of surface-adsorbed species.

Overall, the FTIR results suggest that Fe₂O₃ incorporation influences the soda-lime-silica network by modifying the local silicate structure and introducing Fe–O-related structural units. The observed changes in band intensity, position, and broadening are consistent with structural rearrangements induced by increasing Fe₂O₃ content. The observed FTIR bands cannot be assigned uniquely to specific crystalline iron oxide phases. They may be also contributions from Fe–O structural units in the possible residual glass-ceramic matrix and/or iron-containing crystalline phases.

3.5. UV-Vis-NIR Spectroscopy

The UV-Vis-NIR absorption spectra, recorded in the wavelength range 200–2000 nm for the Na₂O-CaO-SiO₂ soda lime silicate glass-ceramic samples with Fe₂O₃ substitutions are presented in Figure 5a, while the corresponding Tauc plots used for the determination of the optical band gap are shown in Figure 5b. The spectra reveal broad and overlapping absorption bands, characteristic of transition on metal ions in the disordered silicate matrix. Table 4 presents the assignment of the characteristic UV-Vis-NIR absorption bands of the iron crystal field (d–d).

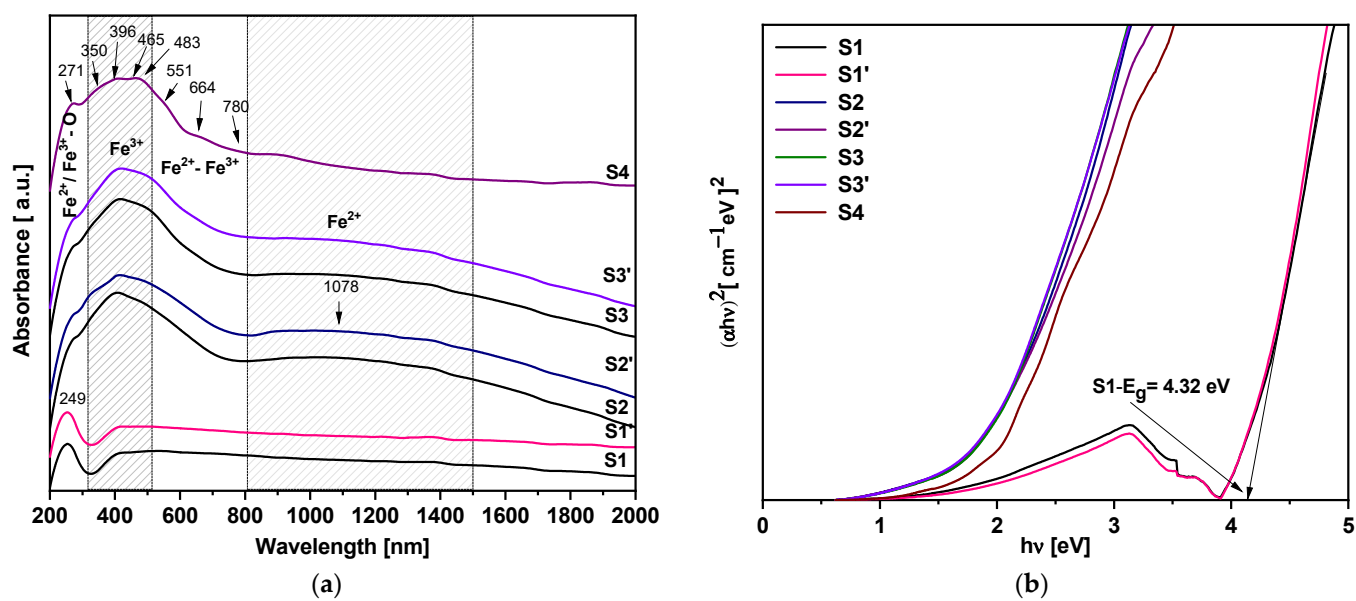


Figure 5. (a) UV-Vis-NIR spectra of investigated samples; (b) Tauc plot $(\alpha h\nu)^2$ versus $h\nu$ with linear extrapolation for the determination of the optical band gap (E_g).

Table 4. UV-VIS-NIR absorption bands of iron crystal field (d–d) transitions.

Ferrous—Fe ²⁺ (3d ⁶) range from 2500 to 526 nm
Ferric—Fe ³⁺ (3d ⁵) range from 526 to 350 nm
400–600 nm spin-forbidden d-d transitions of ferrous and ferric ions, with 4-, 5-, and 6-fold coordination states, in the spinel ligand field
<350 nm—oxygen-metal charge transfer bands (OMCT) due to both Fe ²⁺ and Fe ³⁺
350, 396, 465, 483 nm—Fe ³⁺ spin-forbidden transitions
551, 664, 780 nm—Fe ²⁺ Fe ³⁺ ion pairs (intervalence charge transfer, IV CT, transition)
1076 nm—5 T ₂ (D) → 5 E(D) transition for octahedral Fe ²⁺ ions in O _h sites in the glass network

The UV–Vis–NIR spectra show that Fe₂O₃ strongly influences the optical absorption behavior of the materials derived from the soda–lime–silica system. The absorption intensity increases progressively from S1 to S4, confirming the higher concentration of iron ions in the glass matrix. The Fe₂O₃-free sample S1 shows weak absorption, mainly in the UV region, while the Fe-containing samples present broad and intense absorption bands between 200 and 800 nm. The bands observed around 271, 350, 396, 465, and 483 nm are associated mainly with Fe³⁺ electronic transitions, especially spin-forbidden d–d transitions in tetrahedral and octahedral coordination environments [38,39]. The absorption features around 551, 664, and 780 nm can be assigned to Fe²⁺–Fe³⁺ ion-pair transitions and intervalence charge transfer (IVCT) transitions.

lence charge transfer processes. These bands indicate the coexistence of both Fe^{2+} and Fe^{3+} ions in the glass network [38,40]. The broad absorption in the visible region also explains the dark coloration and opacity of the iron-containing samples. In the literature, the broad absorption band around 1078 nm has frequently been attributed to crystal-field transitions associated with octahedrally coordinated Fe^{2+} ions in oxide glasses [41]. Accordingly, the weak band observed may be related to similar Fe^{2+} associated transitions. However, due to the broad and overlapping nature of absorption features in glass-ceramics, contributions from intervalence charge-transfer process and other overlapping electronic transitions cannot be excluded. Therefore, this band is tentatively assigned to Fe^{2+} -related transitions reported for oxide glasses, while recognizing that complementary spectroscopic techniques would be required to confirm the oxidation-state distribution. Therefore, this assignment should be regarded as tentative. The progressive increase in absorbance with an increasing Fe_2O_3 content, especially for S4, indicates enhanced electronic transitions and stronger light absorption and is consistent with the higher concentration of optically Fe-related absorbing species and the enhanced electronic absorption within the glass-ceramic matrix. According to the literature, the coexistence of Fe^{2+} and Fe^{3+} ions contribute to broad optical absorption and charge-transfer transitions in iron-containing glasses [21,22]. The optical behavior observed in the present samples is consistent with these previous reports, although the oxidation-state distribution was not directly determined in this work. The band gap energy values were determined from the Tauc plots $(\alpha h\nu)^2$ versus $f(h\nu)$ and are summarized in Table 5. The undoped sample (S1) exhibits the highest E_g value (4.32 eV). As the Fe_2O_3 content increases at the expense of CaO, the optical band gap decreases, reaching 1.62 eV for sample S4. This reduction in the optical band gap suggests that Fe incorporation introduces localized electronic states within the forbidden band, facilitating lower-energy electronic transitions, in agreement with previous studies on Fe_2O_3 -containing glass-ceramic systems [42,43]. The heat treatment at 500 °C did not affect the optical band gap of the iron-free sample (S1'), whereas the Fe-containing samples (S2' and S3') exhibited slightly lower E_g values than their corresponding parent glass-ceramic. This decrease may be attributed to structural rearrangement and/or partial crystallization, leading to additional localized defect states and further band-gap narrowing [44].

Table 5. Quantitative parameters extracted from the UV–Vis–NIR absorption spectra of the investigated glass-ceramic samples.

Sample	λ_{max} Wavelength (nm)	Calculated E_g (eV)	Integrated Absorbance (200–450 nm)	Integrated Absorbance (450–900 nm)	Integrated Absorbance (900–1200 nm)
S1	249	4.32	23.4	59.5	29.2
S1'	248	4.32	22.9	45.0	20.3
S2	400	1.81	146.1	231.1	121.4
S2'	406	1.67	136.6	224.9	118.2
S3	412	1.72	151.0	230.6	110.7
S3'	405	1.69	146.7	242.0	116.8
S4	396	1.61	124.4	151.0	40.0

To complement the qualitative interpretation of the UV–Vis–NIR spectra, quantitative optical parameters were extracted from the experimental absorption data. The wavelength of the dominant absorption maximum (λ_{max}), the calculated (E_g), together with the integrated absorbance calculated over three characteristic spectral regions (200–450, 450–900, and 900–1200 nm), are summarized in Table 5.

As summarized in Table 5, the dominant absorption maximum shifts from approximately 249 nm for the iron-free glass (S1) to 396–412 nm for the Fe₂O₃-containing samples, indicating that iron incorporation significantly modifies the electronic absorption profile of the glass matrix. The integrated absorbance also increases markedly in the 200–450 nm and 450–900 nm spectral regions with an increasing Fe₂O₃ content, reflecting the increasing contribution of iron-related electronic transitions. In contrast, the integrated absorbance in the 900–1200 nm region exhibits a different trend, particularly for sample P4, suggesting that the structural changes associated with the higher Fe₂O₃ content and thermal treatment influence the near-infrared absorption profile. However, due to the extensive overlap of crystal-field and charge-transfer transitions in iron-containing glasses, these changes cannot be unequivocally assigned to specific Fe²⁺ or Fe³⁺ species.

The evolution of the optical absorption spectra is consistent with the structural modifications evidenced by XRD, FTIR, and DSC. This behavior is accompanied by changes in the FTIR spectra, particularly in the 750–1250 cm^{−1} region, indicating modifications of the silicate network associated with iron incorporation. These structural changes are reflected in the optical response by the shift of the dominant absorption maximum from 249 nm for the iron-free glass to approximately 396–412 nm for the Fe-containing samples, together with the increase in the integrated absorbance in the UV–visible spectral regions. Moreover, the DSC results show a progressive decrease in the crystallization stability with an increasing Fe₂O₃ content, suggesting that iron modifies both the glass structure and its crystallization behavior. Overall, these observations demonstrate a clear correlation between the structural evolution and the optical properties of the glass-ceramics investigated.

4. Conclusions

A series glass-ceramics derived from the 16Na₂O–(44–x)CaO–40SiO₂:xFe₂O₃ (x = 0, 14, 21, and 28 wt.%) system were successfully prepared via the conventional melt-quenching method and subsequently characterized in terms of their structural, thermal, and optical properties. The influence of Fe₂O₃ incorporation, together with the corresponding decrease in CaO content, on these properties was investigated using density measurements, DSC, XRD, FTIR, and UV–Vis–NIR spectroscopy.

The results indicate that the compositional modifications significantly influence the glass network, crystallization behavior, and optical response of the investigated materials. Density and molar volume measurements, supported via FTIR analysis, suggest changes in the packing efficiency of the glass network. DSC and XRD analyses confirmed the formation of crystalline phases after heat treatment, while the crystallization behavior strongly depended on the Fe₂O₃/CaO ratio.

UVVis–NIR spectroscopy revealed progressively enhanced optical absorption with an increasing Fe₂O₃ content, which may be attributed to the presence of iron ions in different oxidation states. Such optical behavior may be advantageous for applications requiring efficient solar radiation absorption.

Author Contributions: Conceptualization, R.A.M. and M.Z.; methodology, R.A.M. and M.Z.; validation, R.A.M. and M.Z.; investigation, R.A.M., A.T. and M.Z.; resources, R.A.M. and M.Z.; data curation, R.A.M. and M.Z.; writing—original draft preparation, R.A.M.; writing—review and editing, R.A.M., A.T., O.R. and M.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the “Nucleu” Program within the National Research Development and Innovation Plan 2022–2027, Romania, carried out with the support of MEC, project no. 27N/03.01.2023, component project code PN 23 24 02 01, Project “Cluster inovativ pentru tehnologii avansate pilot în energii alternative—CITAT-E”, cod MySMIS 103720, ID P_35_468.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Vallese, L.; Javadi, H.; Badenes, B.; Urchueguia, J.F.; Lombardo, G.; Menegazzo, D.; Ure, Z.; Cesari, S.; Bottarelli, M.; Baccega, E.; et al. A comprehensive review of thermal energy storage technologies and their applications: Creation of a database. *Renew. Sustain. Energy Rev.* **2026**, *225*, 116133. [\[CrossRef\]](#)
- Sarbu, I.; Sebarchievici, C. A Comprehensive Review of Thermal Energy Storage. *Sustainability* **2018**, *1*, 191. [\[CrossRef\]](#)
- Faizan, M.; Alkaabi, A.K.; Nie, B.; Afgan, I. Thermal energy storage integration with nuclear power: A critical review. *J. Energy Storage* **2024**, *96*, 112577. [\[CrossRef\]](#)
- Kwasi-Effah, C.; Okpako, O. Comprehensive review of emerging trends in thermal energy storage mechanisms, materials and applications. *Front. Energy Res.* **2025**, *13*, 1651471. [\[CrossRef\]](#)
- Yang, Y.; Tang, Y.; Jiang, G.; Fang, G.; Xue, Y.; Tan, Z.; Zhang, X.; Pan, D. Advances in glass-ceramics raw material selection-performance modulation-application expression: A review. *Mater. Today* **2025**, *89*, 270–292. [\[CrossRef\]](#)
- Li, Z.-R.; Hu, N.; Fan, L.-W. Nanocomposite phase change materials for high-performance thermal energy storage: A critical review. *Energy Storage Mater.* **2023**, *55*, 727–753. [\[CrossRef\]](#)
- Li, S.; Chen, L.; Lu, J. Valorization of granite sludge into open-cell glass-ceramics: Correlating pore structure with mechanical and thermal properties. *J. Build. Eng.* **2026**, *123*, 115897. [\[CrossRef\]](#)
- Zhou, Y.; Yu, Z.; Xu, Z.; Gao, W.; Li, J.; Chen, L.; Yue, Y.; Kang, J. Effect of H₃BO₃ Content on the Crystallization Process, Foaming Behavior and Physical Properties of Foamed Glass-Ceramics Prepared from Waste Glass Fibers. *J. Wuhan Univ. Technol.-Mater. Sci. Ed.* **2026**, *41*, 54–63. [\[CrossRef\]](#)
- Savić, V.; Topalović, V.; Nikolić, J.; Djošić, M.; Matijašević, S.; Karamanov, A.; Jordanov, N.; Grujić, S. Synthesis and characterization of glass and glass-ceramics using industrial by-products. *J. Therm. Anal. Calorim.* **2026**, *151*, 7465–7479. [\[CrossRef\]](#)
- Xu, W.; Shen, K.; Tao, L. Selective Ion Migration and Kinetics Mechanisms of Crystallization on Microwave Heating Process from Bayan Obo Iron Slag Glass Ceramics. *Glass Phys. Chem.* **2025**, *51*, 520–533. [\[CrossRef\]](#)
- Bitay, E.; Csavdari, A. Some Unmodified Household Adsorbents for the Adsorption of Benzalkonium Chloride—A Kinetic and Thermodynamic Case Study for Commercially Available Paper. *Toxics* **2023**, *11*, 950. [\[CrossRef\]](#) [\[PubMed\]](#)
- Borges, R.; Oliveira, J.S.; Santos, A.C.; Marchi, J. From melt-derived to nanocomposite glasses: A brief history of magnetic bioactive glass-ceramics applied in magnetic hyperthermia. *J. Eur. Ceram. Soc.* **2026**, *46*, 118397. [\[CrossRef\]](#)
- Thomsen, L.; Jensen, L.R.; Yue, Y.; Østergaard, M.B. Crystallinity dependence of thermal and mechanical properties of glass-ceramic foams. *J. Eur. Ceram. Soc.* **2024**, *44*, 7936–7942. [\[CrossRef\]](#)
- Ebrahimum, M.M.; Abo-Mosallam, H.; Mahdy, E.A.; Aly, K.A. Improving properties of Na₂O–CaO–SiO₂ glass by CdO, Fe₂O₃ addition and its crystallization for sealing applications. *Ceram. Int.* **2024**, *50*, 10864–10872. [\[CrossRef\]](#)
- Zhi, L.; Guojun, M.; Dingli, Z.; Xiang, Z. Effect of Fe₂O₃ on the crystallization behavior, microstructure and properties of glass-ceramics prepared from the modified tailings after reduction of copper slag. *Mater. Today Commun.* **2022**, *31*, 103516. [\[CrossRef\]](#)
- Rogers, P.S. The initiation of crystal growth in glasses. *Mineral. Mag.* **1970**, *37*, 741–758. [\[CrossRef\]](#)
- Rada, V.; Ungureşan, M.-L.; Rednic, V.; Rada, S.; Lungu, F.; Culea, E. Zirconia Ceramics Doped with Ferrite for Solar Thermal Systems. *Nanomaterials* **2026**, *16*, 346. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhang, F.; Xiong, D.; Zhang, J.; Han, J.; Chen, D.; Wen, Z.; Fan, Z.; Chen, L.; Sun, T. Effect of Fe₂O₃ on the Structure, Physical Properties and Crystallization of CaO–Al₂O₃–SiO₂ Glass. *J. Wuhan Univ. Technol.-Mater. Sci. Ed.* **2024**, *39*, 954–961. [\[CrossRef\]](#)
- Abanades, S. A Review of Oxygen Carrier Materials and Related Thermochemical Redox Processes for Concentrating Solar Thermal Applications. *Materials* **2023**, *16*, 3582. [\[CrossRef\]](#) [\[PubMed\]](#)
- Evans, H.V.; Rossman, G.R. Fe²⁺/Fe³⁺ intervalence charge transfer and enhanced d-d absorption in mixed-valence iron minerals at elevated temperatures. *Am. Mineral.* **2026**, *111*, 324–334. [\[CrossRef\]](#)
- Vercamer, V.; Lelong, G.; Hijiya, H.; Kondo, Y.; Galois, L.; Calas, G. Diluted Fe³⁺ in silicate glasses: Structural effects of Fe-redox state and matrix composition. An optical absorption and X-band/Q-band EPR study. *J. Non-Cryst. Solids* **2015**, *428*, 138–145. [\[CrossRef\]](#)
- Zawada, A. The influence of redox state on the location of iron ions in the structure of silicate glass with high iron content. *J. Mol. Struct.* **2020**, *1206*, 127705. [\[CrossRef\]](#)
- Zagrai, M.; Suci, R.-C.; Gavrea, R.C.; Rednic, V. Evolution of the Radiation Shielding, Optical, and Luminescence Properties of PbO₂–SiO₂ Glass Systems and the Influence of Rare Earth Elements (Eu, Ce, Yb). *Appl. Sci.* **2025**, *15*, 864. [\[CrossRef\]](#)

24. Zagrai, M.; Macavei, S.G.; Gavrea, R.C.; Popa, A.; Dehelean, A.A.; Barbu-Tudoran, L.; Soran, M.-L. Evaluation of the physical, thermal and structural properties of copper-lead glass for efficient incorporation of MoO₃. *J. Alloys Compd.* **2023**, *968*, 172062. [\[CrossRef\]](#)
25. Tuheen, M.I.; Wilkins, M.C.; McCloy, J.; Du, J. The structures of iron silicate glasses with varying iron redox ratios from molecular dynamics simulations and EXAFS analysis. *J. Non-Cryst. Solids* **2024**, *624*, 122713. [\[CrossRef\]](#)
26. Cheremisina, E.; Zhang, Z.; de Bilbao, E.; Schenk, J. Density, viscosity and surface tension of high-silicate CaO–SiO₂ and CaO–SiO₂–Fe₂O₃ slags derived by aerodynamic levitation. The behavior of Fe³⁺ in high-silicate melts. *Ceram. Int.* **2023**, *49*, 4460–4472. [\[CrossRef\]](#)
27. Granados, L.; Morena, R.; Takamure, N.; Suga, T.; Huang, S.; McKenzie, D.R.; Ho-Baillie, A. Silicate glass-to-glass hermetic bonding for encapsulation of next-generation optoelectronics: A review. *Mater. Today* **2021**, *47*, 131–155. [\[CrossRef\]](#)
28. Saad, M.; Foulain, M. Glass Forming Ability Criterion. *Materials Sci. Forum* **1937**, *19*, 11–13. [\[CrossRef\]](#)
29. Annapurna, K. *Glasses and Glass-Ceramics: Advanced Processing and Applications (Advanced Structured Materials Book 178)*; Annapurna, K., Molla, A.R., Eds.; Springer: Singapore, 2022. [\[CrossRef\]](#)
30. Santoso, I.; Riihimäki, M.; Sibarani, D.; Taskinen, P.; Hupa, L.; Paek, M.-K.; Lindberg, D. Impact of recently discovered sodium calcium silicate solutions on the phase diagrams of relevance for glass-ceramics in the Na₂O–CaO–SiO₂ system. *J. Eur. Ceram. Soc.* **2022**, *42*, 2449–2463. [\[CrossRef\]](#)
31. Oskoui, P.R.; Rezvani, M. Structure and magnetic properties of SiO₂–FeO–CaO–Na₂O bioactive glass-ceramic system for magnetic fluid hyperthermia application. *Heliyon* **2023**, *9*, e18519. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Colomban, P.; Prinsloo, L. Optical Spectroscopy of Silicates and Glasses. In *Spectroscopic Properties of Inorganic and Organometallic Compounds*; RSC Publishing: Cambridge, UK, 2009. [\[CrossRef\]](#)
33. Zagrai, M.; Gavrea, R.C.; Macavei, S.; Dehelean, A.A.; Popa, A.; Loredana, M. Glass-Forming Ability, Chemical Durability, and Structural Properties of Lead Dioxide-Silicate Glass System. *Crystals* **2024**, *14*, 436. [\[CrossRef\]](#)
34. Zaid, M.; Sidek, H.; El-Mallawany, R.; Almasri, K.; Matori, K. Synthesis and characterization of samarium doped calcium soda–lime–silicate glass derived wollastonite glass–ceramics. *J. Mater. Res. Technol.* **2020**, *9*, 13153–13160. [\[CrossRef\]](#)
35. Toderaş, M.; Filip, S.; Ardelean, I. Structural study of the Fe₂O₃–B₂O₃–BaO glass system by FTIR spectroscopy. *J. Optoelectron. Adv. Mater.* **2006**, *8*, 1121–1123.
36. Mishra, R.K.; Avinashi, S.K.; Shweta, S.K.; Gautam, C. Synergistic Effect of Fe₂O₃ Doping on Physical, Structural, Optical, and Radiation Shielding Characteristics of the Glasses in a System (30–x)BaO–30TiO₂–40SiO₂–xFe₂O₃ (0 ≤ x ≤ 6) for Optoelectronic Applications. *J. Inorg. Organomet. Polym. Mater.* **2024**, *34*, 1379–1402. [\[CrossRef\]](#)
37. Yilmaz, S.; Ates, A.; Ercenk, E. Crystallization kinetics of basalt-based glass-ceramics for solid oxide fuel cell application. *J. Therm. Anal. Calorim.* **2018**, *134*, 291–295. [\[CrossRef\]](#)
38. Mysen, B.; Richet, P. *Silicate Glasses and Melts: Properties and Structure*; Elsevier: Amsterdam, The Netherlands, 2005.
39. Griscom, D. Electron spin resonance in glasses. *J. Non-Cryst. Solids* **1980**, *40*, 211–272. [\[CrossRef\]](#)
40. Amthauer, G.; Rossman, G.R. Mixed valence of iron in minerals with cation clusters. *Phys. Chem. Miner.* **1984**, *11*, 37–51. [\[CrossRef\]](#)
41. Burns, R.G. *Mineralogical Applications of Crystal Field Theory*, 2nd ed.; Cambridge University Press: Singapore, 1993.
42. Ghosh, B.K.; Biswas, D.; Ganguly, S.; Debnath, A.; Mandal, D.; Shaharukh, S.; Adhikari, S.; Mondal, R.; Kabi, S.; Das, A.S. Effect of the inclusion of Fe₂O₃ on the optical and electrical transport properties into sodium-zinc-phosphate quaternary glassy systems. *Mater. Today Commun.* **2024**, *38*, 107785. [\[CrossRef\]](#)
43. Sayyed, M.I.; Abdo, M.A.; Ali, H.E.; Sadeq, M.S. Fe₂O₃ within Na₂O–Al₂O₃–B₂O₃ glasses to study the structural and optical features changes. *Opt. Mater.* **2022**, *131*, 112419. [\[CrossRef\]](#)
44. Liu, T.; Huang, Q.; Liang, H.; Liu, P.; Luo, Z.; Zhu, L.; Lu, A. Effect of Fe₂O₃ doping on structure, physical-mechanical properties and luminescence performance of magnesium-aluminum-silicon based glass-ceramics. *Ceram. Int.* **2020**, *46*, 28851–28859. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.