

RESEARCH ARTICLE

YF₃-Regulated Crystallization and Stability in Gallate GlassesAo Shen^{1,2} | Yiguang Jiang² | Jiacheng Li² | Huidan Zeng¹ | Long Zhang²¹School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, China | ²Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai, China

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ABSTRACT

Gallate glasses hold significant promise for mid-infrared optical applications because of their low phonon energies and broad infrared transmission windows. However, the Ga₂O₃-CaO binary system suffers from poor glass-forming ability and high melting temperatures, making it difficult to obtain stable bulk glasses. In this study, YF₃-regulated 32Ga₂O₃-(68-x)CaO-xYF₃ (x = 0–10 mol%) gallate glasses were synthesized and investigated. The amount of bridging oxygen in the glass network decreases continuously with increase in the YF₃ content. Meanwhile, the glass stability first increases and then decreases. The glass achieves the best stability ($\Delta T = 138^\circ\text{C}$, $S = 5.71$, $H_r = 0.474$) when the YF₃ content is 8 mol% (GY8). The non-isothermal crystallization kinetics of the GY8 glass were studied based on the classical Johnson-Mehl-Avrami theory. The crystallization activation energies calculated by the Kissinger, Ozawa, and Augis-Bennett equations are in good agreement with each other, and the Avrami exponent calculated by the Matusita-Sakka and Augis-Bennett equations is approximately 3, indicating that the crystallization mechanism of the GY8 glass is either volume nucleation with two-dimensional growth, or three-dimensional growth from a fixed number of pre-existing nuclei. This system guides the design of glass composition and process optimization, thereby providing a theoretical foundation for the preparation of large-sized, highly stable glasses.

1 | Introduction

In recent years, the pressing demand for high-performance infrared optical materials in fields including space communication, biomedical imaging, and military guidance, has accelerated the development of novel mid-infrared (3–5 μm) transparent materials [1–5]. Among the various candidates, gallate glasses with Ga₂O₃ as the network former have attracted considerable attention because of their intrinsically low phonon energy, high glass transition temperature (T_g), and broad transmission window ranging from visible to mid-infrared wavelengths, demonstrating their potential application in optical windows, fibers, and lenses [6–8]. However, the practical use of gallate glasses is limited by high melting temperatures, poor glass-forming abilities, and low chemical stability [9–13].

To address these issues, the researchers have adopted various strategies to optimize and improve gallate glasses. For example, the introduction of Y₂O₃ [14] and Gd₂O₃ [15] into the Ga₂O₃-SrO-BaF₂ system effectively enhances the glass stability. Chung et al. [16] introduced La₂O₃ into a Ga₂O₃-BaO system, significantly broadening the glass-forming compositional range of Ga₂O₃ from 60–75 mol% to 30–70 mol%. These studies indicate that introducing cations with a high field strength is an effective strategy for improving the stability and glass-forming ability of gallate glasses. However, most of these studies have focused on Ga₂O₃-BaO or Ga₂O₃-SrO systems. By contrast, the Ga₂O₃-CaO system exhibits better chemical stability due to the smaller ionic radius (0.99 Å) and higher field strength (2.04 Å⁻²) of Ca²⁺ [17]; however, its glass-forming ability is very poor and melting temperatures are very high. Kokubo et al. [10, 18] reported that

$\text{Ga}_2\text{O}_3\text{-CaO-TiO}_2$ and $\text{Ga}_2\text{O}_3\text{-CaO-Ta}_2\text{O}_5$ glass systems require melting temperatures as high as 1550°C and possess very narrow or nonexistent glass-forming regions. Therefore, there is an urgent need to explore efficient stabilizers suitable for the $\text{Ga}_2\text{O}_3\text{-CaO}$ system to enhance its glass-forming ability while preserving its chemical stability.

Fluorides play a unique role in glass preparation and property optimization. First, they act as effective fluxes, lowering the melting temperature of the glass, which is crucial for practical glass preparation. Second, the introduction of low-phonon-energy fluorides helps reduce the phonon energy of the glass system and extend the infrared transmission edge [19]. Currently, fluorides introduced into gallate glasses are primarily divalent (PbF_2 and BaF_2). Yu et al. [20] substituted PbO with PbF_2 in an Er^{3+} -doped $18\text{Ga}_2\text{O}_3\text{-}25\text{Bi}_2\text{O}_3\text{-(}57\text{-}x\text{)PbO}$ glass system, reducing the maximum phonon energy from 680 to 550 cm^{-1} and enhancing the mid-infrared luminescence efficiency. Han et al. [21] introduced $10\text{ mol}\%$ BaF_2 into a $25\text{Ga}_2\text{O}_3\text{-}36\text{Bi}_2\text{O}_3\text{-}29\text{GeO}_2$ glass system, increasing the thermal stability, while also reducing the OH^- absorption coefficient and the maximum phonon energy. However, studies on the introduction of trivalent fluorides into gallate glasses are rare [22–24], with only brief mentions of AlF_3 , GaF_3 , and YF_3 , and systematic investigations are still lacking.

In this study, we select a $\text{Ga}_2\text{O}_3\text{-CaO}$ binary glass system and introduce YF_3 to optimize the glass composition. We systematically investigate glass stability and crystallization kinetics behavior. The crystallization activation energy and crystallization mechanism of the glass are obtained, which guides the glass composition design and process optimization, providing a theoretical foundation for preparing large-sized, high-quality glasses.

2 | Experimental Details

2.1 | Sample Preparation

The molar composition of the glass was $32\text{Ga}_2\text{O}_3\text{-(}68\text{-}x\text{)CaO-}x\text{YF}_3$ ($x = 0, 2, 4, 6, 8$, and 10 , denoted as GY0 to GY10). Gallium oxide ($\text{Ga}_2\text{O}_3 \geq 99.99\%$) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Calcium carbonate ($\text{CaCO}_3 \geq 99.0\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd. Yttrium fluoride ($\text{YF}_3 \geq 99.9\%$) was purchased from Shanghai Taiyang Technology Co., Ltd. All the chemicals were used directly without further purification. The glasses were prepared using the melt-quenching method. A total of 50 g of well-mixed batch materials was placed in a platinum crucible, covered with a lid, and melted at 1400°C – 1450°C for 1 h . The homogeneous melt was poured onto a stainless-steel plate and immediately transferred to a preheated muffle furnace, where it was annealed for 2 h at a temperature which is approximately equal to T_g to eliminate internal stress. The annealing temperatures for GY0–GY10 were 715°C , 710°C , 690°C , 680°C , 650°C , and 640°C , respectively. The annealed glass was subjected to a crystallization heat treatment. For the heat treatment, a $10 \times 10 \times 1\text{ mm}^3$ GY8 glass piece was placed in a furnace preheated to 650°C , heated to 810°C at the rate of 5°C/min , held for 5 min for heat treatment, and then allowed to cool along with the furnace.

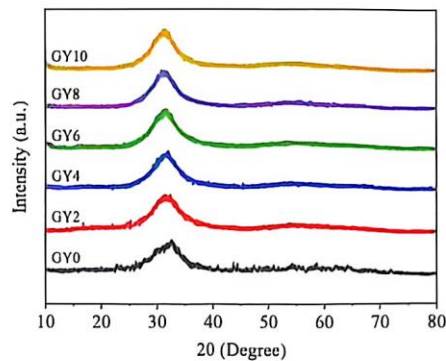


FIGURE 1 | XRD patterns of as-quenched GY0–GY10 samples.

2.2 | Characterization

Differential thermal analysis (DTA) was performed using a synchronous thermal analyzer (STA 2500 Regulus, NETZSCH, Germany) under a pure N_2 atmosphere. The measurement temperature range was 400°C – 1300°C , with a heating rate of 10°C/min . The sample mass was $20 \pm 1\text{ mg}$, and the particle size was $100\text{--}120\text{ mesh}$. For non-isothermal crystallization kinetics, DTA measurements were performed at heating rates of $10, 15, 20, 25$, and 30°C/min and a temperature range of 700°C – 950°C .

The as-quenched GY0–GY10 specimens, and the crystalline phases precipitated from the GY8 glass after heat treatment were measured using X-ray diffractometer (XRD) (Empyrean, PANalytical B.V., the Netherlands) over a scanning angle range of $10^\circ\text{--}80^\circ$ at a scanning speed of $8^\circ/\text{min}$. To identify the crystalline phases, the obtained XRD patterns were compared with JCPDS standard cards using software (Jade 6.0).

The Raman spectra of the samples in the range of $200\text{--}1000\text{ cm}^{-1}$ at 25°C were recorded using a microscope-laser Raman spectrometer (LabRam HR 800) with a laser beam having a wavelength of 633 nm to excite the specimen.

3 | Results

3.1 | Glass Stability

To confirm the amorphous nature of the as-quenched glasses prior to thermal analysis, XRD measurements were performed on all GY0–GY10 samples. As shown in Figure 1, the XRD patterns of all as-quenched samples exhibit only a larger amorphous hump at the range of $20^\circ\text{--}40^\circ$, without any sharp diffraction peaks corresponding to crystalline phases. This observation indicates that all samples are fully amorphous after melt quenching.

Figure 2 shows the DTA curves of samples GY0–GY10, and the characteristic temperatures (T_g , T_x , T_p , T_m) are listed in Table 1. The glass transition temperature T_g , onset crystallization temperature T_x , and melting temperature T_m were determined using the

TABLE 1 | Characteristic temperatures and glass stability parameters ΔT , S , H_r of samples at a heating rate of $10^\circ\text{C}/\text{min}$.

Sample	T_g ($\pm 2^\circ\text{C}$)	T_x ($\pm 2^\circ\text{C}$)	T_p ($\pm 2^\circ\text{C}$)	T_m ($\pm 2^\circ\text{C}$)	ΔT ($\pm 2^\circ\text{C}$)	S	H_r
GY0	720	824	840	1147	104	2.31	0.322
GY2	716	820	842	1150	104	3.2	0.315
GY4	692	813	839	1146	121	4.55	0.363
GY6	680	809	838	1138	129	5.50	0.392
GY8	652	790	817	1081	138	5.71	0.474
GY10	642	746	766	1079	104	3.24	0.312

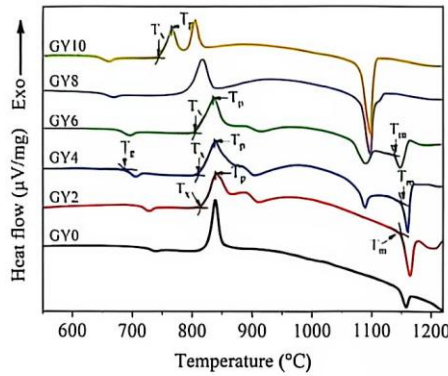


FIGURE 2 | DTA curves of samples GY0-GY10.

tangent method. T_p is the peak crystallization temperature. As shown in Figure 1, with the progressive substitution of CaO by YF_3 , all the characteristic temperatures show a decreasing trend. T_g decreases from 720°C (GY0) to 642°C (GY10), T_x decreases from 824°C to 746°C , T_p decreases from 840°C to 766°C , and T_m decreases from 1147°C to 1079°C .

Regarding the peak shapes in the DTA curves, the GY0 sample exhibits one crystallization peak and one melting peak. Samples GY2, GY4, and GY6 all display two crystallization peaks, with the intensity of the first peak being significantly higher than that of the second, while two melting peaks appear in the high-temperature region. The GY8 sample exhibits one crystallization peak and one melting peak. Although the GY10 sample has two crystallization peaks, only one melting peak is observed, which is relatively intense and is likely to have resulted from the overlap of the melting peaks of the two crystalline phases.

Dietzel first proposed the commonly used glass stability parameter ΔT ($\Delta T = T_x - T_g$) in 1968. Saad and Poulain [25] proposed another criterion S , defined as $S = (T_x - T_p)(T_p - T_g)/T_g$. Hruby [26] proposed the glass stability parameter H_r , which depends on the melting temperature T_m and is defined as $H_r = (T_x - T_g)/(T_m - T_g)$. Based on the measured values of T_g , T_x and T_m , the values ΔT , S , and H_r of each sample were calculated to evaluate their thermal stability, and the results are shown in

Table 1. With increasing YF_3 content, the ΔT , S , H_r values first increase and then decrease, reaching their respective maxima for the GY8 sample (8 mol% YF_3), with $\Delta T = 138^\circ\text{C}$, $S = 5.71$, and $H_r = 0.474$. Moreover, the DTA curve of GY8 sample shows only a single relatively weak crystallization peak. Therefore, we consider GY8 to have the highest glass stability. This result is consistent with the experimental observation that GY8 forms a transparent bulk glass more readily during melting.

3.2 | Non-isothermal Crystallization Kinetics

Various non-isothermal crystallization kinetic analysis methods have been derived based on the classical Johnson-Mehl-Avrami theory, including the Kissinger equation (KE) [27], Ozawa equation (OE) [28], Augis-Bennett (AB) equation [29], and Matusita-Sakka (MS) equation [30]. For the GY8 glass sample, which exhibited the best glass stability, we employed non-isothermal kinetic methods to investigate the crystallization kinetics and to calculate the crystallization activation energy and Avrami exponent.

The KE [27] assumes that the crystallization process follows first-order reaction kinetics and is expressed as:

$$\ln \left(\frac{T_p^2}{\beta} \right) = \frac{E}{RT_p} + \ln \left(\frac{E}{R} \right) - \ln v \quad (1)$$

where, β is the heating rate, R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T_p is the crystallization peak temperature, v is the frequency factor, and E is the crystallization activation energy.

The OE [28] is often used to determine the activation energy of solid-state reactions and is expressed as:

$$\ln(\beta) = -\frac{E}{RT_p} + \ln v \quad (2)$$

The AB equation [29], a modification of the Kissinger method, can be used to evaluate complex multiphase solid-state reactions and is expressed as:

$$\ln \left(\frac{T_p}{\beta} \right) = \frac{E}{RT_p} + \ln K_0 \quad (3)$$

where, K_0 is the pre-exponential factor.

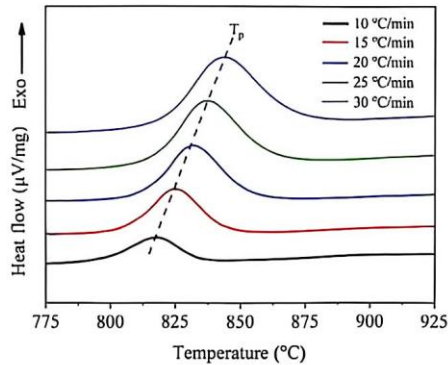


FIGURE 3 | DTA curves of sample GY8 at heating rates of 10, 15, 20, 25, and 30 °C/min.

Figure 3 shows the DTA curves of GY8 samples heated at heating rates of 10, 15, 20, 25, and 30 °C/min. As the heating rate increases, the glass transition and peak crystallization temperatures also increase. This is primarily because atomic migration cannot keep up with the changes in free volume caused by the increasing heating rate; therefore, the system requires a higher temperature to transition from the supercooled liquid state to the relaxed state, leading to a shift in T_g and T_p to higher temperatures [31].

Plots of $\ln(T_p^2/\beta)$, $\ln\beta$, and $\ln(T_p/\beta)$ versus $1000/T$ were generated for sample GY8. The data points were fitted by linear regression using the least-squares method and the corresponding activation energy E was calculated from the slopes of these lines. Figure 4 shows the linear fits obtained for sample GY8 using the KE, OE, and AB equations. The E values obtained from the KE fit, OE fit, and AB fit are 398.16 kJ/mol, 408.22 kJ/mol, and 402.81 kJ/mol, respectively. The crystallization activation energies calculated by the three methods are very similar (relative deviation of the range $\leq 3.00\%$).

To further elucidate the nucleation and growth mechanisms during glass crystallization, determining the Avrami exponent n is considered an effective approach for understanding the nature of the crystallization process [32, 33]. The classical MS equation [30] was used to calculate the Avrami exponent n of a sample:

$$\ln[-\ln(1-x)] = -n \ln\beta - 1.052 \frac{mE_c}{RT} + \text{constant} \quad (4)$$

where, x is the crystallized volume fraction, n is the Avrami exponent, m is the dimensionality of the crystal growth, and E_c is the crystallization activation energy. The crystallized volume fraction, x , is obtained from the DTA curve and calculated using the following formula [14]:

$$x = \frac{A_T}{A} \quad (5)$$

where, A is the total area of the exothermic peak from the onset temperature T_i to the end temperature T_f and A_T is the partial

area from T_i to an intermediate temperature T , as illustrated in Figure 5a. Figure 5b shows the relationship between the crystallized volume fraction x and the temperature T . The slope of the curve reflects the crystallization rate of GY8 at a given heating rate. All the x - T curves exhibit a typical “S-shaped” sigmoidal relationship. This can be attributed to the slow atomic diffusion in the initial stages of crystallization ($x < 0.2$). As the temperature increases, more energy is supplied, atomic migration accelerates, and the number of nuclei increases, marking the start of the rapid crystallization stage ($x = 0.2$ – 0.8), where the volume fraction of the crystalline phase increases sharply. Near the end of crystallization ($x = 0.8$ – 1.0), the growing grains make contact and impinge upon each other, hindering further atomic diffusion [31, 33]. Consequently, the grains gradually coarsen, and crystallization tends toward completion.

A plot of $\ln[-\ln(1-x)]$ versus $\ln\beta$ is shown in Figure 5c. The data points were fitted by linear regression using the least-squares method, and the slope of the line gives $-n$. Six temperatures (817 °C, 820 °C, 823 °C, 826 °C, 829 °C, and 832 °C) were selected for the calculation, and the average Avrami exponent n obtained was 2.99, approximately equal to 3.

Using the known crystallization activation energy E , the Avrami exponent n can be calculated using the AB formula [29]:

$$n = \frac{2.5}{\Delta T_{FWHM}} \times \frac{RT_p^2}{E} \quad (6)$$

where, ΔT_{FWHM} is the full width at half maximum of the crystallization peak, E is the crystallization activation energy calculated using the AB method, and T_p is the peak crystallization temperature. Following the approach described in Ref. [29], a DTA curve at a heating rate of 10 °C/min was used for the n -value calculation. Here, $T_p = 1090.15$ K, $\Delta T_{FWHM} = 20.56$ K, and $E = 402.81$ kJ/mol, yielding $n = 2.98$, also approximately equal to 3.

The n values calculated using the MS equation is 2.99, and that calculated by the AB equation is 2.98. Both are approximately 3. The Avrami exponent (n) is related to the growth mechanism (b) and the dimensionality of the crystal growth (m) by the following relationship [34, 35]:

$$n = a + m \cdot b \quad (7)$$

where, a is the nucleation rate, b is the growth mechanism, and m is the dimensionality of the crystal growth. $a = 0$ and $a = 1$ correspond to a zero-nucleation rate and a constant nucleation rate, respectively; $a > 1$ and $a < 1$ correspond to increasing and decreasing nucleation rates, respectively. $b = 1.0$ corresponds to an interface-controlled process, and $b = 0.5$ corresponds to a diffusion-controlled process. For sample GY8, $n \approx 3$. Combining this with Equation (7), we can deduce either $a = 1$, $m = 2$, and $b = 1$, or $a = 0$, $m = 3$, and $b = 1$. Therefore, the crystallization mechanism of the GY8 glass (100–120 mesh powder particles) is either volume nucleation at a constant rate, followed by two-dimensional interface-controlled growth, or fixed number of pre-existing nuclei (zero-nucleation rate), followed by three-dimensional interface-controlled growth.

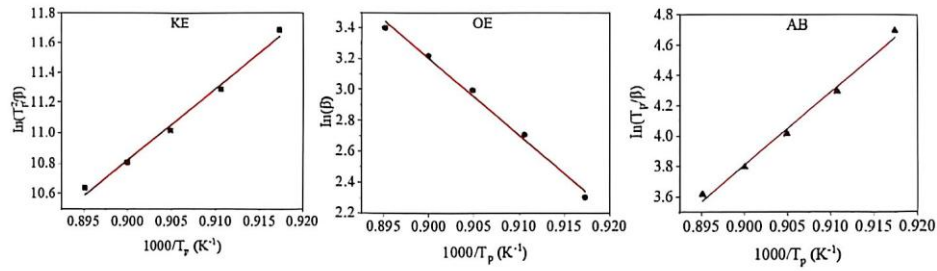


FIGURE 4 | Linear fitting curves for crystallization activation energy calculated using the Kissinger, Ozawa, and AB methods.

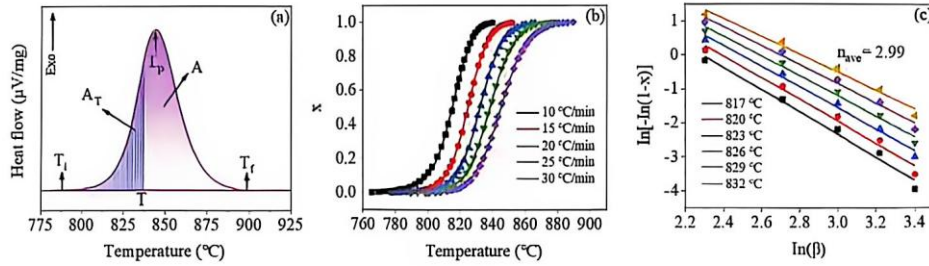


FIGURE 5 | Calculation of the Avrami exponent using the MS equation: (a) schematic for crystallized volume fraction calculation; (b) plot of x vs. T ; (c) plot of $\ln[-\ln(1-x)]$ vs. $\ln\beta$.

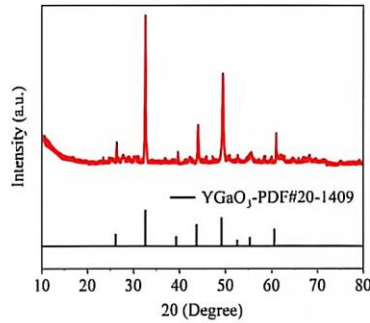


FIGURE 6 | XRD pattern of sample GY8 after heat treatment.

3.3 | XRD

Figure 6 shows the XRD pattern of GY8 after heat treatment at 810°C for 5 min. All the diffraction peaks of the sample are in good agreement with the standard diffraction data for YGaO_3 (JCPDS No. 20-1409), and no other crystalline phases are detected. This is consistent with the DTA results showing only one crystallization peak, indicating that the GY8 sample exhibits a crystallization peak at 820°C and a melting peak at 1080°C, corresponding to the crystallization and melting of the YGaO_3 phase within the glass.

3.4 | Raman Spectroscopy

Raman spectroscopy was used for the preliminary structural study of the GY0–GY10 glass samples. Figure 7a shows the normalized Raman spectra of samples with different YF_3 contents. Three distinct peaks are observed. The peak observed at approximately 510 cm^{-1} is assigned to the bending vibration of the bond (bridge oxygen, BO) in the $[\text{GaO}_4]$ tetrahedra [36, 37]. The peak located at 680 cm^{-1} is assigned to bond (non-bridging oxygen, NBO) stretching vibrations [38]. The peak observed at around 300 cm^{-1} is generally assigned to the vibrational mode of the glass network-modifying cations (MO, where M is Y or Ca) [39, 40]. As the YF_3 content increases, the intensity of the peak observed at around 510 cm^{-1} decreases significantly, indicating a decrease in the number of Ga–O–Ga (BO) bonds.

To reveal the variation in the relative proportions of MO, BO, and NBO in the glass network more intuitively, we performed Gaussian fitting on the Raman characteristic peaks of the GY0–GY10 samples and conducted a quantitative analysis by calculating the areas of the fitted peaks. Figure 7b shows the fitting results for GY6 sample, where three characteristic peaks are resolved and assigned to MO, BO, and NBO. The relative contents of the three components in each sample are shown in Figure 7c. The relative BO content of the undoped sample (GY0) is 34%. As the YF_3 content increases, the BO content gradually decreases to 25% for GY10, whereas the NBO content fluctuates between 56% and 59%, and the MO content increases from 8% (GY0) to 16% (GY10).

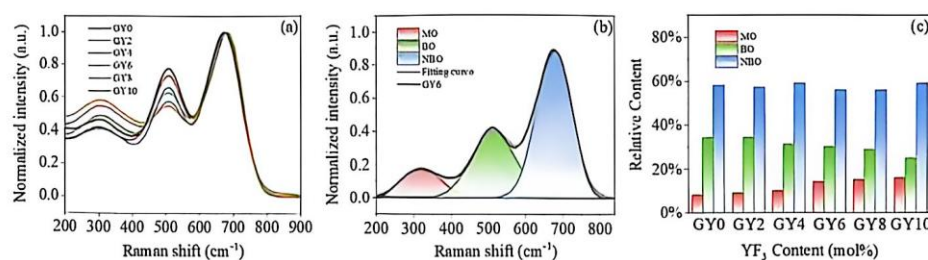


FIGURE 7 | Structural characterization of samples GY0-GY10: (a) Raman spectra; (b) peak fitting of Raman peaks for GY6; (c) relative content of MO, BO, and NBO.

Additionally, the BO/NBO ratio decreases from 0.59 in GY0 to 0.52 in GY8, and then decreases sharply to 0.42. These trends indicate that the introduction of YF_3 significantly promotes the depolymerization of the glass network.

4 | Discussion

As YF_3 gradually replaces CaO , the characteristic temperatures (T_g , T_x , T_p , T_m) show an overall decreasing trend. This phenomenon can be attributed to the depolymerization effect of the fluoride ions on the glass network structure. The depolymerization effect of F^- ions transforms some of the bridging oxygen linkages (Ga-O-Ga) in the glass structure into Ga-F and O-Ga-O^- , breaking the network and reducing the degree of polymerization [41]. The Raman results in Figure 7c confirm this, showing a decrease in the Ga-O-Ga(BO) content from 34% (GY0) to 25% (GY10), indicating a looser glass network structure. The weakening of the network structure allows structural relaxation and viscous flow to occur at lower temperatures; hence, T_g systematically decreases with increasing YF_3 content. Concurrently, network breakage reduces melt viscosity, leading to a decrease in T_m .

In contrast to the changes in the characteristic temperatures, the effect of YF_3 on glass stability is concentration-dependent. The glass stability parameters (ΔT , S , H_g) initially increase and then decrease, reaching an optimum at GY8 ($x = 8$ mol%), with $\Delta T = 138^\circ\text{C}$, $S = 5.71$, and $H_g = 0.474$. This variation arises owing to two competing effects: (i) the depolymerizing effect of F^- ions, which reduces glass stability, and (ii) the stabilizing effect of Y^{3+} ions, which may occupy interstitial positions in the network. At low YF_3 contents, the potential stabilizing effect of Y^{3+} dominates, enhancing glass stability. When 2–8 mol% of YF_3 is added, the introduced F^- causes partial depolymerization of the network; however, the Y^{3+} ions may occupy the network interstices and bond with the three NBOs to maintain charge neutrality. This hypothesis is made by analogy with the well-established behavior of alkali ions in silicate glass systems [41], where Na^+ ions reside in interstitial sites and act as network breakers. This analogy is reasonable because both silicate and gallate glasses are built on tetrahedral network structures (Si-O-Si and Ga-O-Ga , respectively), with cations located in interstitial sites interacting with non-bridging oxygens. Given that Y^{3+} carries three positive charges, it is plausible that it coordinates with three

NBOs to maintain local charge neutrality. Due to their higher field strength (Y^{3+} : ionic radius $r = 0.89 \text{ \AA}$, field strength $Z/r^2 = 3.76 \text{ \AA}^{-2}$; Ca^{2+} : $r = 0.99 \text{ \AA}$, $Z/r^2 = 2.04 \text{ \AA}^{-2}$) [17], the Y^{3+} ions may increase the compactness of the glass network, making the glass structure more stable, thereby increasing glass stability. In addition, the Y-O bond energy (209.01 kJ/mol) is higher than that of Ca-O (133.76 kJ/mol) [42], which further suggests that Y^{3+} incorporation may enhance local network compactness. This localized strengthening effect can partially offset the overall network depolymerization caused by F^- , allowing the glass to maintain a low melting viscosity while retaining relatively high network compactness. Hence, the glass stability improves steadily, as evidenced by the increases in ΔT (from 104°C for GY2 to 138°C for GY8), S (from 3.2 to 5.71), and H_g (from 0.315 to 0.474). An excessively high YF_3 content causes the depolymerizing effect of F^- to prevail which when compounded by the possible Y^{3+} -induced crystallization decreases glass stability. When the YF_3 content reaches 10 mol%, the depolymerizing effect of F^- becomes dominant. Excess F^- continuously breaks the BO bonds, generating a large number of Ga-F bonds. Simultaneously, the increased concentration of Y^{3+} ions combined with their high polarizing power may lead to clustering, inducing crystallization. At this point, the glass network is very depolymerized and becomes “fragmented” significantly increasing atomic mobility. During DTA heating, this highly activated structure is readily rearranged, leading to crystallization. This is confirmed by the appearance of two crystallization peaks in the DTA curve of GY10. Hence, the glass stability decreases significantly, as evidenced by the decreases in ΔT (from 138°C for GY8 to 104°C for GY10), S (from 5.71 to 3.24), and H_g (from 0.474 to 0.312).

This YF_3 concentration-dependent regulation of glass stability is comparable to findings for other gallate glass systems. For instance, the $\text{Ga}_2\text{O}_3\text{-SrO-BaF}_2\text{-Y}_2\text{O}_3$ system [14] reported by Cui et al. also showed an initial increase followed by a decrease in glass stability with increasing Y_2O_3 content. However, in that study, the glass stability began to decline at 6 mol% Y_2O_3 , whereas in the present study, a decline occurred at 8 mol% YF_3 . Cui et al. reported a crystallization activation energy of 266 kJ/mol for their glass ($32\text{Ga}_2\text{O}_3\text{-52SrO-6Y}_2\text{O}_3\text{-10BaF}_2$), whereas the value calculated in this work ($32\text{Ga}_2\text{O}_3\text{-60CaO-8YF}_3$) ranged from 398.16 to 408.22 kJ/mol. This difference primarily stems from the different crystallization mechanisms; in the study by Cui et al. the glass crystallized as the SrY_2O_4 phase via surface nucleation and one-dimensional growth, whereas the glass in this study

crystallized as the YGaO_3 phase via either volume nucleation with two-dimensional growth, or three-dimensional growth from a fixed number of pre-existing nuclei. Although both crystallize as yttrate phases (Y^{3+} has the highest field strength and strongly attracts O^{2-}), the differences in the specific crystalline phase and growth mode collectively account for the difference in the crystallization activation energy.

Raman spectroscopy further confirms the network-depolymerizing effect of F^- from a structural perspective. As shown in Figure 7, with an increase in the YF_3 content, the intensity of the Ga–O–Ga (BO) vibrational peak continuously weakens, and the relative BO content decreases from 34% (GY0) to 25% (GY10). The BO/NBO ratio decreases from 0.59 in GY0 to 0.42 in GY10. This trend directly reflects the effect of F^- in breaking the BO bonds and generating Ga–F and O–Ga–O $^-$ linkages in the network. Cui et al. reported that the introduction of Y^{3+} could increase the BO content in a glass network [14]. However, in the present system, a decrease in the BO content is observed, indicating that the effect of Y^{3+} on increasing the BO content is masked by the depolymerizing effect of F^- . This can also be understood from the perspective of ion incorporation in the nominal composition: for each 1 mol% of YF_3 introduced, 1 mol% of Y^{3+} and 3 mol% of F^- are introduced. Clearly, the amount of F^- introduced is greater. Therefore, although Y^{3+} can increase the BO content, the higher proportion of F^- dominates the overall network depolymerization, explaining why the BO content continuously decreases in this system.

5 | Conclusion

In this study, the regulation effects of YF_3 on thermal stability, crystallization kinetics, and network structure of $32\text{CaO}_3\text{--}(68\text{--}x)\text{CaO--}x\text{YF}_3$ ($x = 0\text{--}10$ mol%) glasses were studied. With the gradual substitution of CaO with YF_3 , the amount of bridging oxygen in the network structure decreased continuously from 34% to 25%, which was attributed to the depolymerizing effect of F^- ions on the glass network. Meanwhile, the glass stability parameters ΔT , S and H , showed a trend of first increasing and then decreasing, and the glass achieved the best stability when the YF_3 content was 8 mol% ($\Delta T = 138^\circ\text{C}$, $S = 5.71$, $H = 0.474$), where the stabilizing effect of Y^{3+} and the depolymerizing effect of F^- achieved the best balance. Upon heat treatment, the GY8 sample crystallized into the YGaO_3 phase, and the crystallization mechanism was determined to be either constant-rate volume nucleation followed by two-dimensional interface-controlled growth, or three-dimensional growth from a fixed number of pre-existing nuclei. This YF_3 -containing gallate glass shows potential for mid-infrared applications, warranting further investigation of its optical and mechanical properties.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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