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Influence of dopants on the crystallization of borosilicate glass

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Abstract

The effects of TiO_2 nucleating agent and CeO_2, ZrO_2, La_2O_3 and Y_2O_3 network modifiers on crystallization and structure of borosilicate glasses were systematically investigated. It was found that the nucleating Ti^{4+} ions entered $[TiO_6]$ octahedron, participated in network formation and promoted glass crystallization, while the network modifiers induced α-quartz formation, favoring its crystallization as major crystal phase, which positively affected thermal expansion coefficient of the glass–ceramics. Network modifiers allowed strengthening glass network and conduced α-quartz-like structure, which was helpful for α-quartz crystallization.

Keywords: D. Glass–ceramics; Network modifier; Structure

1. Introduction

Borosilicate glasses are well-known due to their variety of technological applications like sealing agent for sodium–sulfur battery, optical glasses, ovenwares, nuclear waste materials and in the electronics industry [1,2]. Most borosilicate glasses are phase separable, with formation of a chemically durable silica-rich and a less durable borate rich phase [3]. Since crystallization enthalpy of cristobalite is only -8.2 kJ/mol [4] and structure of amorphous SiO_2 is “cristobalite like” [5], borosilicate glasses easily precipitate cristobalite. However, cristobalite is thought as an unfavorable transformation product in terms of its thermal expansion behavior. Cristobalite transforms from α- to β-cristobalite around 200 °C. This transformation causes a large volume change, sometimes causes microcrack formation during cooling, which destroys the mechanical strength of the final products. Thus, it is desirable to avoid cristobalite crystallization in borosilicate glasses [6]. Rieck and Stevels reported that quartz formed from impure fused silica by heating 1200 °C [5]. Five kinds of dopants ($MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$, $MnCO_3$) were found to be effective in causing amorphous silica acid to be transformed to quartz. Takeuchi and coworkers explored the mechanism of quartz formation in silica gel and silica glass mixed with various substances as additives [7]. They found that quartz formation was closely related to the presence of a metal silicate. It was assumed that the silicate promoted quartz nucleation. Moreover, they showed that Li_2CO_3 produced the largest amount of quartz ($94 \pm 4\%$) among all the additives and it also had the lowest onset temperature of quartz formation. However, these dopants could not avoid cristobalite formation. Although Al_2O_3 is a good dopant to avoid cristobalite formation [8,9], it can increase glass viscosity significantly and restrict application of borosilicate glasses.

The objective of this paper is to look for capable agents to avoid cristobalite formation in borosilicate glasses. TiO_2 mainly as a nucleating agent and large radii and high field intensity Ce^{4+}, Zr^{4+}, La^{3+} and Y^{3+} ions mainly as network modifiers were chosen. Their influences on crystallization and structure of borosilicate glasses were systematically investigated.

2. Experimental

2.1. Glass composition and preparation

The compositions of the parent glass and doped glasses are listed in Table 1. Appropriate mixtures of analytical grade SiO_2, Al_2O_3, H_3BO_3, Na_2CO_3, K_2CO_3, TiO_2, CeO_2, ZrO_2, La_2O_3 and

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Table 1
.Compositions of the studied glasses.

No.	Compositions of the glasses (wt.%)									
	SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	TiO_2	CeO_2	ZrO_2	La_2O_3	Y_2O_3
0	69.8	3.2	18.0	5.0	4.0	0	0	0	0	0
1	65.8	3.2	18.0	5.0	4.0	4.0	0	0	0	0
2	65.8	3.2	18.0	5.0	4.0	3.8	0.2	0	0	0
3	65.8	3.2	18.0	5.0	4.0	3.8	0	0.2	0	0
4	65.8	3.2	18.0	5.0	4.0	3.8	0	0	0.2	0
5	65.8	3.2	18.0	5.0	4.0	3.8	0	0	0	0.2
6	69.6	3.2	18.0	5.0	4.0	0	0.2	0	0	0
7	69.6	3.2	18.0	5.0	4.0	0	0	0.2	0	0
8	69.6	3.2	18.0	5.0	4.0	0	0	0	0.2	0
9	69.6	3.2	18.0	5.0	4.0	0	0	0	0	0.2

Y_2O_3 were mixed and heated to melt in an electric furnace. Then the glass melts were poured into cooled water. The obtained glass frits were further ground.

2.2. Formation of the glass–ceramics

A differential scanning calorimeter (DSC, Netzsch STA 409PC, Waldkaiburg, Germany) was employed. The measurements were carried out in the temperature range of 50–1000 °C at a heating rate of 10 °C/min. The crystallization temperature was obtained by the DSC. The glasses were converted to glass–ceramics by heating at 800 °C, 850 °C and 900 °C, respectively.

2.3. Evaluation of glass–ceramics properties

The crystal phases in glass–ceramics were determined by X-ray diffraction (XRD) analysis (Rigaku RAD-C, Japan) at room temperature using Cu Kα radiation. All the instrument settings were maintained identical to observe the integral peak area precisely. Fourier transform infrared spectroscopy (FTIR, BRUKER TENSOR 27, Germany) was used to analyse structure evolution of glasses as a function of the dopants. Samples for the FTIR measurements were prepared in the form of KBr pellets. The microstructure of glass–ceramics was observed by scanning electron microscopy (JSM-6700F, Japan) on polished and HF solution etched samples. The thermal expansion coefficient of glass–ceramics was measured with a dilatometer (NETZSCH DIL 402C, Germany) from room temperature to 700 °C at a heating rate of 5 °C/min.

3. Results and discussion

3.1. Crystallization behavior

Fig. 1 shows the XRD patterns of the glass–ceramics co-doped with nucleating agent TiO_2 and network modifiers after heat treatment at 800 °C and 900 °C for 2 h. As seen in Fig. 1, the parent glass heat treatment at 800 °C for 2 h displayed amorphous feature, and it precipitated only α-cristobalite when heated at 900 °C for 2 h. As shown in Fig. 1(a), the co-doped glasses precipitated not only α-cristobalite but also α-quartz and rutile when heated at 800 °C for 2 h. In particular, the major crystal phase was α-quartz instead of α-cristobalite in glasses co-doped with TiO_2/CeO_2 and TiO_2/Y_2O_3, respectively. All doped glasses precipitated a small amount of rutile after treatment at 800 °C for 2 h. The amount of rutile in co-doped glass–ceramics was higher than that in glass–ceramics doped with only TiO_2. As shown in Fig. 1(b), almost all α-quartz in doped glass–ceramics was transformed into α-cristobalite as temperature increased to 900 °C.

Fig. 2 shows the integral area of the maximum intensity of α-quartz and α-cristobalite in doped glasses when heated at 800 °C for 2 h. As seen, sample 1 (doped with only TiO_2) had the minimum amount of α-quartz and maximum amount of α-cristobalite. The addition of modifiers significantly avoided α-cristobalite formation, and simultaneously induced α-quartz formation. Among all modifiers, CeO_2 and Y_2O_3 afforded glass–ceramics lowest α-cristobalite amount, and highest α-quartz amount.

It was indicated that nucleating agent accelerated glass crystallization, while co-doping with nucleating agent and network modifiers promoted α-quartz formation.

It has been found early that only certain ions are capable of promoting α-quartz formation [5]. Such ions have ionic radii between 0.075 nm and 0.11 nm and they might serve as germs for α-quartz-like structure formation, which grows at the expenses of glass matrix. The ionic radii of Ti^{4+}, Ce^{4+}, Zr^{4+}, La^{3+} and Y^{3+} are 0.074 nm, 0.092 nm, 0.084 nm 0.131 nm, and 0.089 nm, respectively [10–12]. Although the ionic radii of Ti^{4+} and La^{3+} are beyond the range of 0.075–0.11 nm, doping with TiO_2 and La_2O_3 induced α-quartz precipitation. It is worthwhile to note that the maximum interstices of α-cristobalite and α-quartz are 0.17 nm and 0.096 nm, respectively. Based on FTIR spectrum analysis, doping with small amount of such ions could strengthen glass network and make glass to be α-quartz-like instead of α-cristobalite-like, no matter if the ionic radius is in the range of 0.075–0.11 nm or not. The reason is that minor amount of such ions can enter and strengthen the gap of glass network.

In order to further clarify the influence of network modifiers on glass crystallization, a series of glasses doped with network modifiers but without nucleating agent as listed in Table 1 were investigated by heating them at 800 °C, 850 °C and 900 °C for 2 h.

XRD results showed doped glasses to be almost amorphous when heated at 800 °C for 2 h, whereas, crystallization occurs

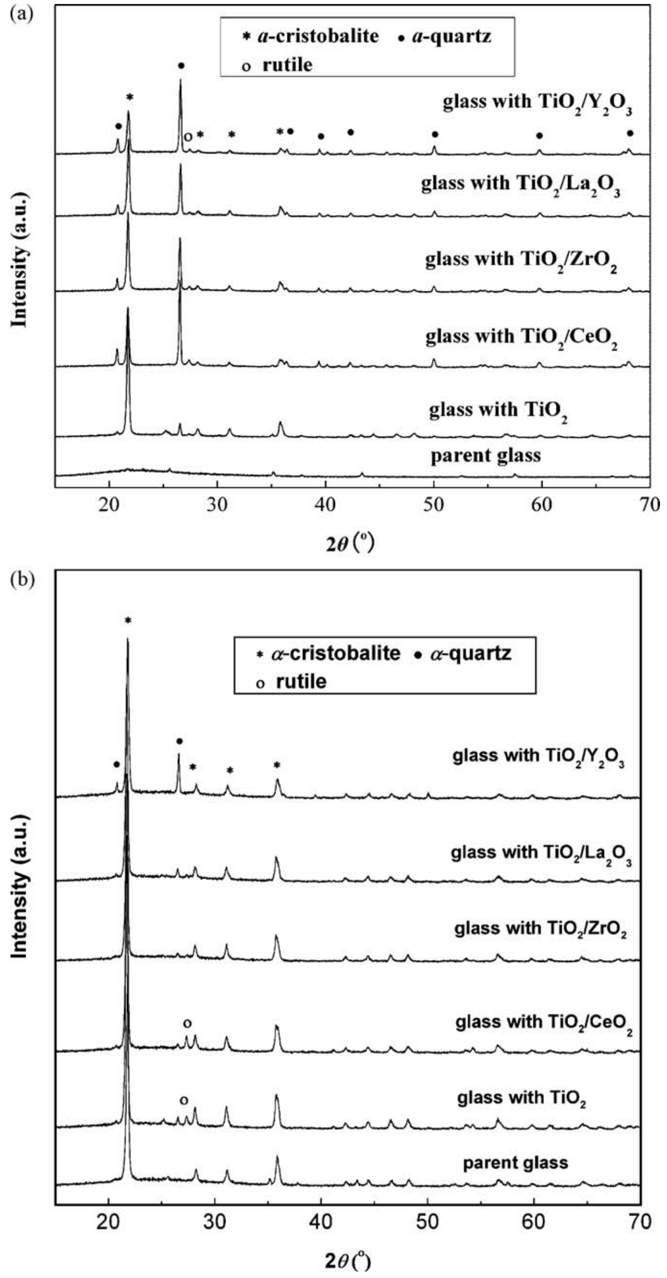

Fig. 1. XRD patterns of the glasses with various dopants and heat treated (a) at 800 °C for 2 h and (b) at 900 °C for 2 h.

after heat treatment at 850 °C for 2 h. α-cristobalite was major crystal phase in glass doped with CeO_2 heated at 850 °C for 2 h, whereas, α-quartz became major crystal phase in glasses doped with ZrO_2, La_2O_3, and Y_2O heated at 850 °C for 2 h. Increase of heating temperature correspondingly increased amount of α-quartz which was major crystal phase in all doped glasses except the one doped with ZrO_2.

The amorphous phase amount was relatively high in all glasses doped with only network modifiers heated at 850 °C and 900 °C for 2 h. Network modifiers appear not to increase the level of crystallization, but to promote α-quartz crystallization. Network modifiers inhibited glass crystallization by strengthening its network, which agrees with FTIR analysis results.

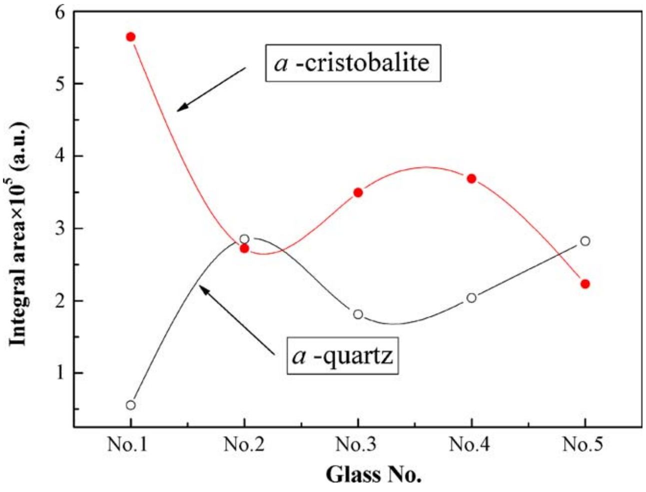

Fig. 2. Integral area of the maximum intensity of α-quartz and α-cristobalite in the glasses co-doped with nucleating agent and network modifiers heated at 800 °C for 2 h.

3.2. FTIR spectra

Fig. 3 shows the FTIR spectra of various glasses and glass–ceramics. As observed, each spectrum is composed of a broad band and several peaks. The band at about 460 cm^{-1} on

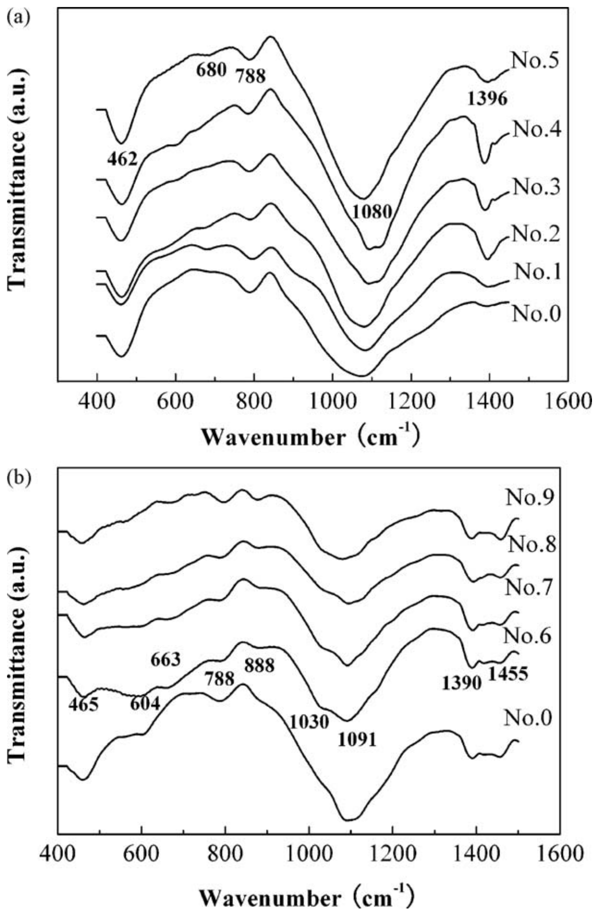

Fig. 3. FTIR spectra of the glasses at room temperature: (a) parent glass and glasses co-doped with nucleating agent and network modifiers; (b) parent glass and glasses doped with only network modifiers.

the spectra of both series of co-doped glasses could be attributed to bending vibrations of Si–O–Si bond in [SiO_4] tetrahedron, and it was not sensitive to change of the dopants. The strong broad band located at about 1084 cm^{-1} was attributed to contributions of Si–O–Si bond in [SiO_4] tetrahedron. The 600–850 cm^{-1} band was attributed to bending vibration of [BO_3] unit, while 1200–1500 cm^{-1} band related to stretching vibration of [BO_3] unit [13]. The band at about 790 cm^{-1} was considered as overlapped contributions of vibration of [BO_3] unit and [AlO_4] tetrahedron. The band at about 1397 cm^{-1} was attributed to stretching vibration of [BO_3] unit.

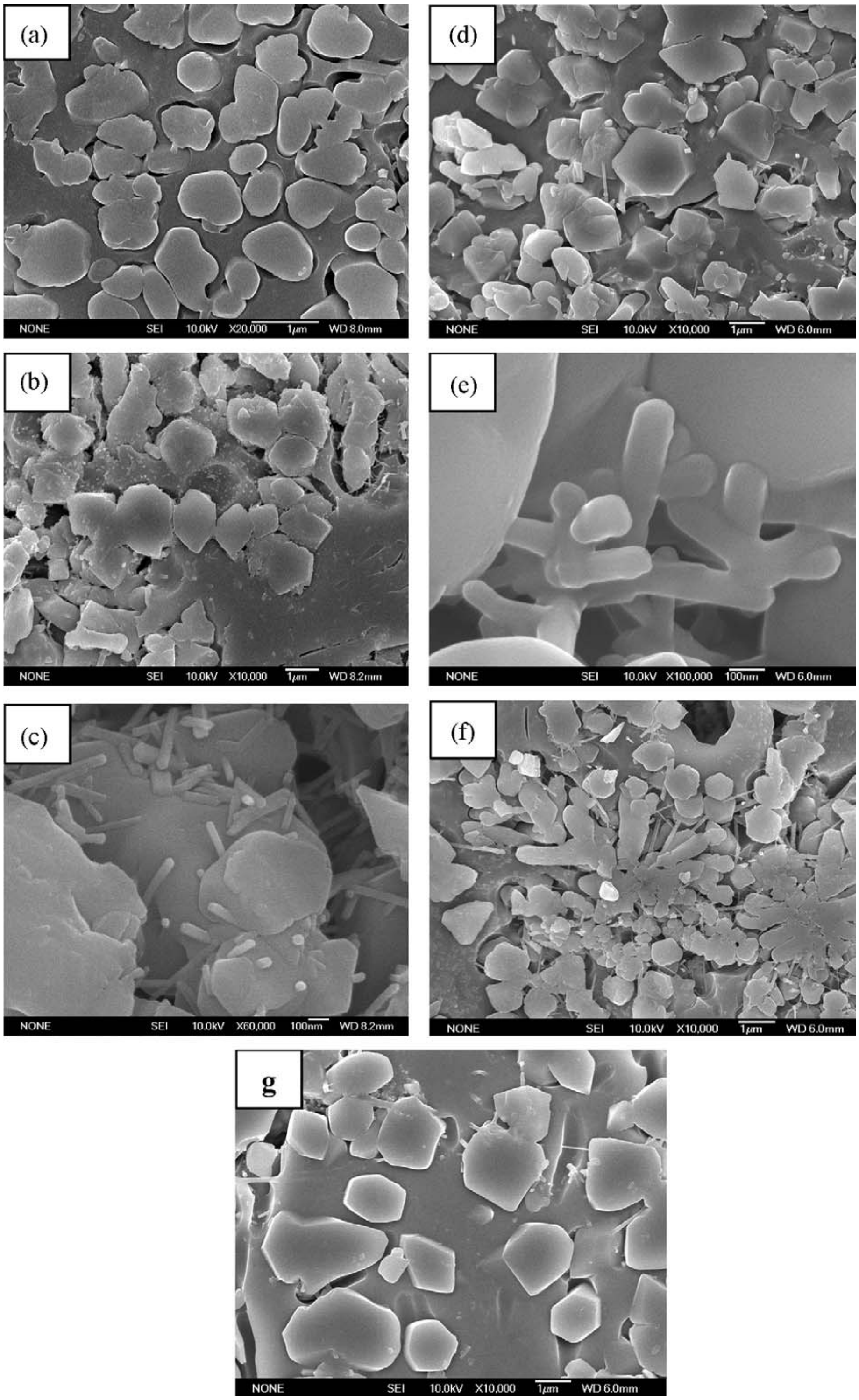

Fig. 4. Microstructure of the glasses co-doped with nucleating agent and network modifiers heated at 800 °C for 2 h. (a) With only TiO_2, (b) with TiO_2/CeO_2, (c) high-resolution micrographs of (b), (d) with TiO_2/ZrO_2, (e) high-resolution micrographs of (d), (f) with TiO_2/La_2O_3 and (g) with TiO_2/Y_2O_3.

Furthermore, as seen in Fig. 3(a), a band at about 680 cm^{-1} appeared in the glasses doped with TiO_2 was close to the band due to vibration of $[TiO_6]$ group reported by Kokubo et al. [14]. Ei-alaily and Mohamed ever found the band at about 660 cm^{-1} owing to vibration of $[TiO_4]$ group [15]. In the present paper, the relative variation of the intensity of the band at about 1397 cm^{-1} of the glasses doped with TiO_2 is larger than for that the parent glass. It was suggested that the amount of $[BO_3]$ unit is higher in TiO_2 doped glasses than that in the parent glass. The band at about 1084 cm^{-1} of the TiO_2 doped glasses was much sharper than that in the parent glass, indicating that the $[SiO_4]$ tetrahedron was more tight in structure and the amount of non-bridging oxygen decreased after TiO_2 doping. The decreased non-bridging oxygen was mainly consumed by $[TiO_6]$ octahedron formation. Therefore, the band at about 680 cm^{-1} could be attributed to vibration of $[TiO_6]$ group in the investigated systems.

The presence of $[TiO_6]$ group indicated the existence of non-bridging oxygen in the investigated glasses even if the mole ratio of $(Na_2O + K_2O)/(Al_2O_3 + B_2O_3)$ was below 1. The band at about 1080 cm^{-1} was sharper in the glasses doped with TiO_2 than that in the parent glass and much sharper in the co-doped glasses, especially in samples 2 and 5, which indicated that the doping of TiO_2, CeO_2, ZrO_2, La_2O_3, and Y_2O_3 strengthened glass network, especially the co-doping of TiO_2/CeO_2 or TiO_2/Y_2O_3.

Fig. 3(b) shows the FTIR spectra of the glasses doped with only network modifiers. Comparing them with that of the parent glass, we can find new bands at about 663 cm^{-1}, 888 cm^{-1} and 1030 cm^{-1}. The band at about 663 cm^{-1} consisted of overlapped contributions of vibration of $[BO_3]$ and $[BO_4]$ units [16]. The 888 cm^{-1} band could be attributed to vibration of $[BO_4]$ tetrahedron [17]. The band as a shoulder at about 1030 cm^{-1} could be assigned to vibration of B–O–Si links [18]. These new vibration bands arising in the doped glasses indicated the strengthening effect by the dopants.

3.3. Microstructure

Fig. 4 shows the morphology of glasses co-doped with nucleating agent and network modifiers heated at 800 °C for 2 h. All doped glasses precipitated hexagonal-like α-quartz and α-cristobalite with well-developed microstructure. In addition, a randomly distributed rod-like rutile phase was found in co-doped glasses. As seen in Fig. 4(a), the glass with only TiO_2 precipitated a bit of rod-like rutile, whereas, amount was so slight that it was hard to observe it in the SEM photos. The glass with TiO_2 and CeO_2 precipitated a large amount of rod-like and fine rutile phase Fig. 4(b) and (c). The glass co-doped with pairs of TiO_2/ZrO_2 precipitated a large amount of fine rutile Fig. 4(e). The glass with TiO_2 and La_2O_3 precipitated a large amount of rod-like and large rutile phase Fig. 4(f).

The SEM observations were consistent with the XRD results. Doping with network modifiers promoted hexagonal-like α-quartz formation with a well-developed microstructure and a rod-like rutile phase formation.

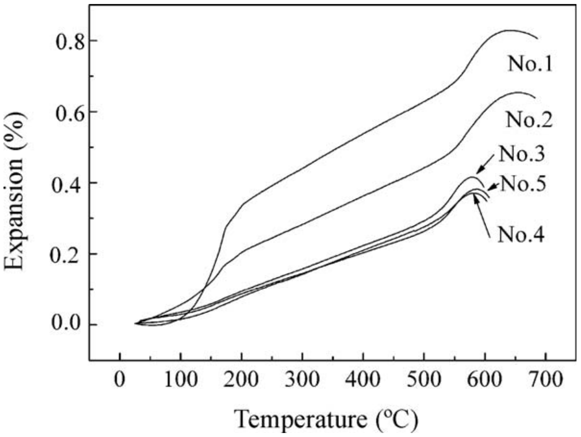

Fig. 5. Thermal expansion curves of the glasses co-doped with nucleating agent and network modifiers heated at 800 °C for 2 h.

3.4. Thermal expansion

Fig. 5 shows the thermal expansion curves of the glasses co-doped with nucleating agent and network modifiers heated at 800 °C for 2 h. The thermal expansion coefficients (TECs) of sample 1 (doped with only TiO_2) and sample 2 (doped with TiO_2 and CeO_2) were relatively large. However, the glass–ceramics doped with TiO_2/ZrO_2, TiO_2/La_2O_3 or TiO_2/Y_2O_3 (samples 3, 4, 5) had relatively small TECs. As known, the TECs of glass–ceramics are primarily dependent on crystallized phase and residual amorphous phase. As seen in Fig. 2, samples 1 and 2 precipitated higher amount of crystallized phases than those of samples 3, 4 and 5, which resulted in larger TECs of samples 1 and 2. The thermal expansion curves of samples 3, 4 and 5 were similar to that of amorphous glass, indicating their relatively high amount of amorphous phase.

4. Conclusions

The influence of TiO_2 as nucleating agent and of some network modifiers such as CeO_2, ZrO_2, La_2O_3 and Y_2O_3 on the crystallization and structure of borosilicate glasses was studied. The nucleating agent was effective in promoting glass crystallization. The network modifiers induced α-quartz formation as major crystal phase at the expense of α-cristobalite formation, which could affect the thermal expansion coefficient of glass–ceramics significantly. The α-quartz formation was apparently unrelated with ionic radii of dopants. The network modifiers strengthened glass network and made its structure α-quartz-like, which consequently promoted α-quartz crystallization.

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