Quantitative analysis of crystalline and remaining glass phases in CaO–B$_2$O$_3$–SiO$_2$ ternary system glass ceramics

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ABSTRACT

Based on Rietveld method of X-ray techniques and volume additivity rule, a new method was developed to quantitatively analyze the phase composition of CaO–B$_2$O$_3$–SiO$_2$ ternary system glass ceramics. Lattice parameters, densities and relative weight fractions of crystalline phases in CaO–B$_2$O$_3$–SiO$_2$ ternary system were obtained by X-ray diffraction (XRD) refinement. According to the relative weight fraction of crystalline phases and densities of various components, the volume additivity rule was revealed by calculating the absolute weight fraction of crystalline phases of CaO–B$_2$O$_3$–SiO$_2$ glass ceramics. In addition, molar contents of the oxides in the remaining glass can also be determined by this method. Comparing this method with internal standard method, it is found that the maximum deviations of the crystallinity and the absolute weight fraction of crystalline phases are less than 2.6% and 2.9%, respectively. As a result, quantitative evaluation of CaO–B$_2$O$_3$–SiO$_2$ ternary system glass ceramics can be achieved using this method.

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1. Introduction

CaO–B$_2$O$_3$–SiO$_2$ ternary system glass ceramics have become an attractive material technology for electronic packaging applications due to their significant advantages, such as low sintering temperature, low dielectric constant, low cost and good compatibility with Si substrates [1–5]. From the material processing point of view, CaO–B$_2$O$_3$–SiO$_2$ ternary system is a glass ceramic composite, which can be densified at sintering temperatures <900 °C. It is known that the physical characteristics of the resulting glass ceramic composites, such as the dielectric constant, thermal expansion, and mechanical strength, are mainly determined by the amount of crystalline and glass phases. Thus, quantitative analysis on the crystalline and glass phases of the composites after sintering is of utmost importance to study the dielectric, thermal, and other properties of CaO–B$_2$O$_3$–SiO$_2$ glass ceramics. Meanwhile, it is necessary to investigate on the crystallization kinetics, the conversion mechanism of glass ceramic in the manufacturing process.

The approaches using the qualitative analysis of the glass ceramics, such as internal standard addition, external standard addition, *K*-value method and incremental calculation have been widely reported [6–8]. These works require a certain amount of standard samples. Also, there are very great efforts requirement in the selection and preparation of standard sample. Therefore, free-standard methods of quantitative phase analysis have been explored in ceramics industries and other areas [9–11]. In all the free-standard methods, Rietveld refinement is still widely applied for samples only containing pure crystalline phases, which provided information not only about the lattice parameters but also about their morphologies [12]. Nevertheless, most of them are not directly applicable for materials containing amorphous phase, because of difficulties in obtaining Bragg reflection data of amorphous phase. As for CaO–B$_2$O$_3$–SiO$_2$ ternary system, it is difficult to determine quantitatively the absolute amounts of crystalline and remaining oxides due to the complex phase compositions by the above-mentioned methods.

In the present study, as an extension of earlier quantitative studies [13,14], an available method based on the Rietveld refinement of X-ray techniques was used to analyze quantitatively the relative weight fraction and densities of crystalline phases. According to these above data, it is possible to determine quantitatively the absolute weight fraction of crystalline phases and also the oxides molar content in the remaining glass using volume additivity rule.

2. Experimental

2.1. Sample preparation

The CaO–B$_2$O$_3$–SiO$_2$ glass ceramic samples were prepared by high temperature melting process. Analytical purity materials of quartz (SiO$_2$), boric acid (H$_3$BO$_3$) and calcium carbonate (CaCO$_3$) were used as the starting materials. According to a cer-

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Table 1
Composition of the original powders.

Oxide	SiO_2	CaO	B_2O_3	ZrO_2
Composition before/after considering mass loss (wt%)	45.95/42.13	42.07/38.58	11.68/10.71	0.30/0.275
Mol content before/after considering mass loss (mol)	0.76/0.70	0.75/0.69	0.17/0.156	0.0025/0.0023

tain ratio, as listed in Table 1, a mixture formula for original oxides was placed in a barrelled mill. The milling medium was isopropanol, and the milling was continuously performed for 72 h. The resulting suspension was collected, evaporated, and dried at 80 °C. An 8 wt% acrylic emulsion was then added to the dried mixture. The mixture was carefully ground, and then pressed at 20 MPa into tablets with a diameter of 23.7 mm and thickness of 1.0 mm. The tablets were then baked at 850 °C and at normal atmospheric pressure with a heating rate of 5 °C/min and 10 °C/min for samples A1 and A2, respectively. After normally cooling down, samples were manually ground in an agate mortar into powders with a particles size of less than 10 μm, and then filtrated with a 200 mesh sieve.

2.2. Measurements and calculation

An X-ray powder diffractometer (X'Pert PRO MPD, Philips) with a Cu Kα ($\lambda = 1.54056$) radiation was used to estimate the crystalline phases of all the samples. For all investigations, the angular range 2θ was 20–80°, with a step width of 0.02°. A copper tube was operated at 40 kV and 40 mA. The density of samples was determined according to the Archimedes principle. The qualitative analysis of the phases was performed using MAUD (material analysis using diffraction) 2.046 software. Thermogravimetry analysis (Beifen PCT-IA) was used to evaluate the mass loss that occurs during the synthesis and sintering processes.

According to the X-ray diffraction theory, any crystalline phase has a unique set of diffraction peaks and corresponding diffraction intensity. The diffraction intensity y_i of i-phase in a multi-phase system can be expressed as,

$$y_i = I_0 \frac{\lambda^3 e^4}{64\pi R m_e^2 c^4} \frac{V_i}{v^2} \left| F_{(hkl)} \right|^2 P_{(hkl)} \varphi(\theta) \frac{e^{-2M}}{2\mu} \tag{1}$$

where I_0 is the incident light beam intensity, λ the X-ray wavelengths, R goniometric radius, c the speed of light, e the electron charge, m_e the mass of an electronic quality, V_i the i-phase volume, v the unit cell volume, $F_{(hkl)}$ the structural factor, $P_{(hkl)}$ the multiplicity factor, φ the angle factor, e^{-2M} the temperature coefficient, and μ the sample absorption.

Similarly, the diffraction peak intensity of crystalline phase is a function of its content. Based on Eq. (1), if the i-phase diffraction intensity is y_i and the j-phase diffraction intensity is y_j, we can obtain

$$\frac{y_i}{y_j} = \frac{\left| (PF^2/v^2)\varphi(\theta)e^{-2M} \right|_i}{\left| (PF^2/v^2)\varphi(\theta)e^{-2M} \right|_j} \frac{V_i}{V_j} = \frac{\left| (PF^2/v^2)\varphi(\theta)e^{-2M} \right|_i}{\left| (PF^2/v^2)\varphi(\theta)e^{-2M} \right|_j} \frac{w_i/\rho_i}{w_j/\rho_j}$$

$$= \frac{\left| (PF^2/v^2)\varphi(\theta)e^{-2M} \right|_i}{\left| (PF^2/v^2)\varphi(\theta)e^{-2M} \right|_j} \frac{\rho_j}{\rho_i} \frac{w_i}{w_j} = \frac{K_i}{K_j} \frac{W_i}{W_j} = K_j^i \frac{w_i}{w_j} \tag{2}$$

$$K_j = \left| \frac{PF^2}{v^2} \varphi(\theta)e^{-2M} \right|_i \rho_i, \quad K_i = \left| \frac{PF^2}{v^2} \varphi(\theta)e^{-2M} \right|_i \rho_j$$

where w_i and w_j are the relative weight fraction of the i-phase and the j-phase, and ρ_i and ρ_j are the corresponding densities, respectively. By the XRD technology, the weight fraction of each crystalline in the multi-phase ceramics can be determined

$$w_p = \frac{y_p}{K_p \sum_{j=1}^n \left(y_j/K_p^j \right)} \tag{3}$$

w_p represents the relative weight fraction of phase p in a mixture of n crystalline phases (not including the remaining glass). For Rietveld-based quantitative analysis of a crystalline substance, w_p is corrected using the equation

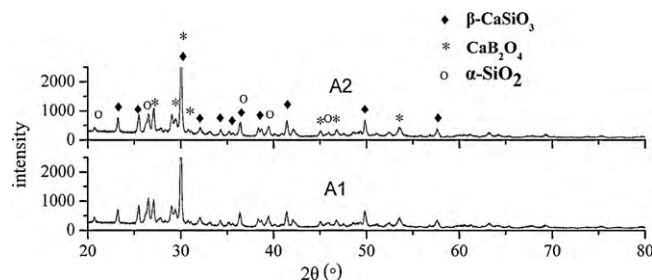$$w_p = \frac{S_p v_p Z_p M_p}{\sum_n S_p v_p Z_p M_p} \tag{4}$$

Fig. 1. The XRD patterns of samples A1 and A2.

where S is the Rietveld scale factor, Z the number of formula units per unit cell, M the mass of the formula unit, and v the unit cell volume. The accuracy of the fitting results by Rietveld method is usually determined with residual value of figure-of-merit (R), which defined such an equation as

$$R = \sum_p \frac{1}{y_p(\text{obs})} [y_p(\text{obs}) - y_p(\text{calc})] \to \min \tag{5}$$

where $y_p(\text{obs})$ is the measured profile at the pth step, and $y_p(\text{calc})$ the calculated profile.

3. Results and discussion

3.1. Analysis of the relative weight fraction of the crystalline phases via the Rietveld refinement

From the XRD results of samples A0 and A1 (in Fig. 1), we can find that the crystalline wollastonite (β-$CaSiO_3$) is the major phase, and CaB_2O_4 and α-SiO_2 are the minor phases. Based on the parameters of β-$CaSiO_3$, CaB_2O_4, α-SiO_2 phases from ICSD [15], Rietveld refining was made by MAUD software. The refining results of densities and relative weight fraction of crystalline phases are shown in Table 2. As an indication of Rietveld refinement quality, the difference plot for the observed and calculated patterns for the sample A1 is shown in Fig. 2. The refining errors of Rw and Sig are 5.09% and 0.61, respectively, which is reliable (Rw < 15%, Sig < 2.0).

3.2. Quantitative analysis of the crystalline phases and residual glass by volume additivity rule

Original powders are amorphous materials, which do not show defined Bragg reflections (in Fig. 3). Therefore, it is not possible to quantify them like a crystalline phase by the Rietveld method. To do so, volume additivity rule has to be used. The specific volume of CaO–B_2O_3–SiO_2 samples can be expressed as

$$\frac{W_{gc}}{\rho_{gc}} = \frac{W_c}{\rho_c} + \frac{W_g}{\rho_g} = \frac{W_{c1}}{\rho_{c1}} + \frac{W_{c2}}{\rho_{c2}} + \frac{W_{c3}}{\rho_{c3}} + \frac{W_g}{\rho_g} \tag{6}$$
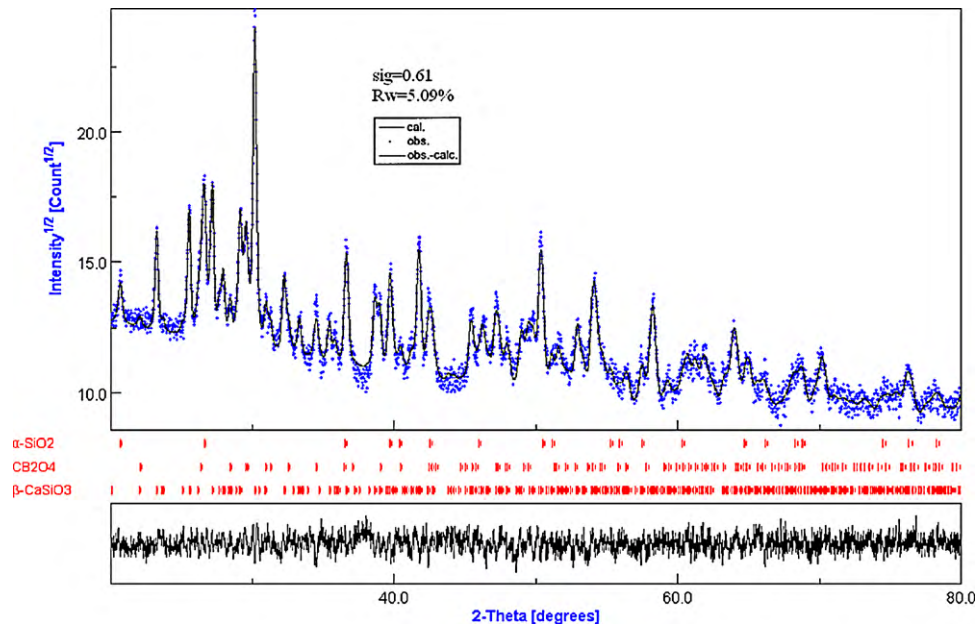
Table 2
Lattice parameters, densities and relative weight fraction of crystalline phases.

Crystal phase	Experimental and fitting density (g/cm³)	Experimental and fitting lattice parameters (Å)			Relative weight fraction (wt%)	
		a	b	c	A1	A2
β-$CaSiO_3$	2.91/3.00	7.90/7.83	7.29/7.22	7.08/7.00	62.9	61.9
CaB_2O_4	2.72/2.79	6.21/6.06	11.60/11.42	4.29/4.29	25.1	24.5
α-SiO_2	2.65/2.86	4.91/4.87	4.91/4.87	5.41/5.10	12.0	13.6

Fig. 2. The XRD refinement result of typical sample A1.

where W_{gc}, W_g, W_c, W_{c1}, W_{c2}, W_{c3} are the absolute weight fraction of CaO–B$_2$O$_3$–SiO$_2$ glass ceramics, remaining glass, crystalline phases, β-CaSiO$_3$, CaB$_2$O$_4$, α-SiO$_2$, respectively. And ρ_{gc}, ρ_g, ρ_c, ρ_{c1}, ρ_{c2}, ρ_{c3} are the corresponding density. ρ_{c1}, ρ_{c2}, ρ_{c3} can be obtained by the Rietveld refinement (in Table 2).

Provided that the weight of CaO–B$_2$O$_3$–SiO$_2$ glass ceramics is 100 g, the oxide mole contents in the residual glass can be calculated by Gan's method [16]

$$\rho_g = \frac{100(1 - f_c^W)}{n_{io}v_{io}} \qquad (7)$$

$$v_{io} = \frac{M_{io}}{\rho_{io}} \qquad (8)$$

where f_c^W is the weight fraction of the crystalline phases (also called crystallinity) in composites; n_{io} and v_{io} the molar content and molar volume (cm^3/mol) of various oxides in the remaining glass, M_{io} the molecular mass per formula unit, and ρ_{io} the density of the i-phase oxide. According to Eq. (6), the volume of oxide phases in the remaining glass can be determined. Ideally, n_{io} can be acquired by the molar content in original materials (in Table 1) sub-

tracting that of the corresponding crystalline phase. Fig. 4 shows that there existed total weight loss (about 16.3% including 8.0% acrylic emulsion) during sintering processes. Therefore, the weight loss of original powders was about 8.3%. Assumed the same weight loss occurs at each component of original powders during sintering processes, n_{io} can be similarly obtained by the molar content after considering the mass loss (in Table 1) subtracting that of the corresponding crystalline phase. ρ_g can be expressed as a function of variable f_c^W. The absolute weight fraction of crystalline phases can be calculated by $f_c^w w_i$ (i = 1, 2, 3).

The measured densities (ρ_{gc}) of samples A1 and A2 were 2.56 g/cm^3 and 2.54 g/cm^3, respectively. According to the original formula (shown in Table 1) and the relative weight fraction of β-CaSiO$_3$, CaB$_2$O$_4$, and α-SiO$_2$ (shown in Table 2), Eq. (4) can be described as follow

$$\frac{100}{\rho_{gc}} = \frac{100f_c^w w_1}{\rho_{c1}} + \frac{100f_c^w w_2}{\rho_{c2}} + \frac{100f_c^w w_3}{\rho_{c3}} + \frac{100(1 - f_c^W)}{\rho_g} \qquad (9)$$

where w_1, w_2 and w_3 are the relative weight amount of β-CaSiO$_3$, CaB$_2$O$_4$ and α-SiO$_2$, respectively, which is given in Table 2. By solving Eq. (7), the crystallinities of samples A1 and A2 are shown in
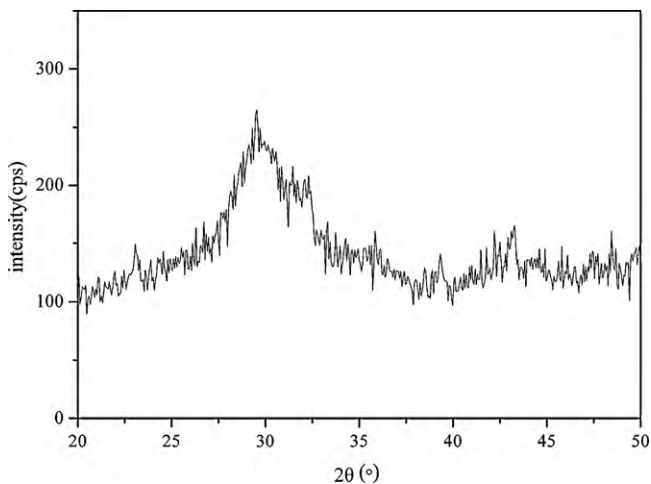

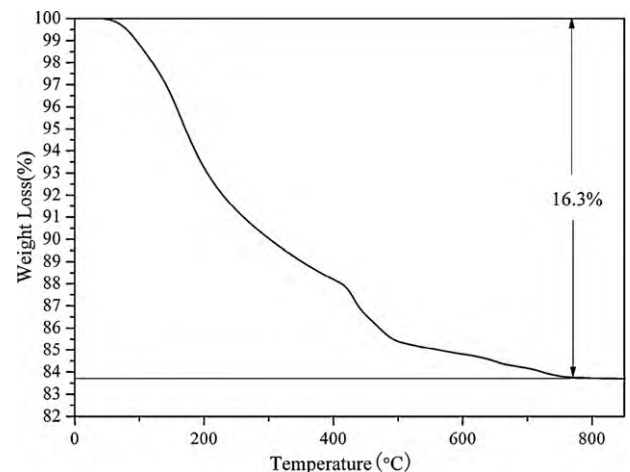**Fig. 3.** The XRD pattern of original powder for sample A1.

Fig. 4. The weight loss of typical sample A1 during the sintering processes.

Table 3
Crystallinities and mass fraction of each phase in glass ceramic samples.

Crystal phase		Crystallinity	β-CaSiO$_3$	CaB$_2$O$_4$	α-SiO$_2$
A1	This method 1 (wt%)	58.3	36.7	14.6	7.0
	Internal standard method 1 (wt%)	56.8	35.7	14.3	6.8
	Error	2.6%	2.8%	2.1%	2.9%
A2	This method (wt%)	59.1	36.6	14.5	8.0
	Internal standard method (wt%)	58.4	36.2	14.3	7.9
	Error	1.2%	2.8%	1.4%	1.3%

Table 4
Molecule amounts (n_{io}) and volume (V_{io}) of oxide in remained glass of glass ceramic sample A1.

Oxide	SiO$_2$	CaO	B$_2$O$_3$	ZrO$_2$
n_{io} (mol)	0.45	0.31	0.05	0.003
V_{io} (cm^3/mo1)	25.90	16.89	37.63	21.06

Table 3. Compared this method with internal standard method, the maximum deviations of the crystallinities and each crystalline phase are less than 2.6% and 2.9%, respectively. Even so, there are still other three error sources which are not be considered (the mass loss that certainly occurs during the synthesis, the relative weight fraction of crystalline phases and densities of the various phases in the CaO–B$_2$O$_3$–SiO$_2$ ternary system) when estimating the accuracy of the quantitative analysis.

By Eqs. (5) and (6), the mo1ar content and the molar volume of each oxide in sample A1 were illustrated in Table 4, which indicated that CaO and SiO$_2$ were the major oxides in the remaining glass. The results of sample A2 were omitted due to its same calculated method.

4. Conclusions

The relative weight fractions and densities of the crystalline phases in CaO–B$_2$O$_3$–SiO$_2$ ternary system were determined by Rietveld method. Both relative weight fractions of crystalline phases and densities of all phases are used to construct a table.

So the volumes of all the phases including glass ceramics can be calculated. Using volume additivity rule, the absolute amounts of crystalline and molar contents of oxides in remaining glass are obtained by analyzing the crystallinities and densities of various phases. The presented method can be applied to quantitative analyze the phases of multi-component materials that contain crystalline and amorphous phases, i.e., glass ceramics.

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