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journal homepage: www.elsevier.com/locate/jnoncrsolInvestigation of the structure evolution process in sol–gel derived CaO–B₂O₃–SiO₂ glass ceramicsMin Wang^a, Ruzhong Zuo^{a,*}, Jiao Jin^a, Shi Su^a, Jiwei Zhai^b^a Institute of Electro Ceramics and Devices, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China^b Functional Materials Research Laboratory, Tongji University, Shanghai 200092, China

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ABSTRACT

A sol–gel method was used to prepare CaO–B₂O₃–SiO₂ (CBS) glass powder for making low-temperature cofired ceramics. This paper was focused on the mechanism of hydrolysis and polymerization and also on the structural evolution of xerogel at various temperatures. The xerogel was transformed into glass ceramics containing CaSiO₃ and CaB₂O₄ crystalline phases through nucleation and crystallization processes. The results indicated that the xerogel exhibits [BO₄] or [SiO₄] based three-dimensional network structure whose interstices Ca ions fill in, which becomes more orderly and stable after heat treatments. The CBS glass ceramics through controlled crystallization have a potential as electronic packaging materials.

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1. Introduction

CaO–B₂O₃–SiO₂ (CBS) glass ceramics with a wollastonite-type main crystalline phase have to date achieved industrial application in electronic package fields [1,2] because they have excellent electrical properties and can co-fire with base metals. Although many attempts were made to study on its preparation method, sintering behavior, and crystallization kinetics and so on [2–6], yet it seems that deep studies are still necessary as argued below. A melt-quenching technique was recognized as a conventional way to prepare CBS glass powder. However, this method needs a high sintering temperature to obtain CBS melt so that oxides with low-melting points, such as B₂O₃, tend to volatilize away. It thus becomes difficult to get desired compositions [7]. A sol–gel route has been tried in recent years to prepare CBS glass powder; however it was investigated from the point of view of powder processing [3]. How chemical bonds react during the sol and gel formation and how the sol–gel structure evolves and is further adjusted during heat treatment were rarely reported about the CBS system. Uhlmann et al. [8] ever investigated the difference between sol–gel derived glass and melt-quenching glass and made a conclusion that sol–gel derived glass treated at high temperature shows essentially identical crystallization behavior to that of conventional glass.

A uniform and transparent CBS xerogel was synthesized by a sol–gel soft method at a relatively low temperature. The emphasis of this study was then put on the chemical reaction process from sol to gel

and the crystallization behavior during heat treatment. This method avoids the loss of chemical compositions for a solid-state mixed oxide route or a melt-quenching method. In addition, glass powders obtained by the sol–gel technique will be more uniform in compositional distribution. The powder compact of the heat treated xerogel has a tendency to convert to a glass ceramic if the nucleation temperature and sintering temperature are appropriately controlled. This feature could make CBS become potential materials for microelectronic packages.

2. Experimental

The material with a composition of 40 wt.% CaO, 20 wt.% B₂O₃ and 40 wt.% SiO₂ was synthesized by using raw materials: calcium carbonate (CaCO₃, ≥99.0%), boracic acid (H₃BO₃, ≥99.0%), tetraethyl orthosilicate (TEOS, analytically pure), anhydrous ethyl alcohol (EtOH, ≥99.7%), nitric acid (HNO₃, 65–68%), and ammonia (NH₃ H₂O, 25–28%). At first, calcium nitrate solution was gained through the reaction of CaCO₃ with HNO₃ and the pH value needs to be controlled. Then, TEOS dissolved in EtOH is added in a suitable amount of deionized water. The mixture of the former and the later solutions are stirred at 80 °C, and finally H₃BO₃ was added slowly. The three compounds were mixed together and form a transparent liquid. At this time, The pH value was adjusted to be ~2 by use of NH₃ H₂O and a molar ratio of H₂O:TEOS was controlled at 20:1 by adding some deionized water.

The pH value was measured by using a pH meter (FE20, METTLER TOLEDO, Switzerland). The structure evolution of sol and gel, and xerogel after heat treatment at different temperatures was analyzed by Fourier Transform Infrared Spectroscopy (FT-IR, Spectrum 400,

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PerkinElmer, USA). Thermo-gravimetry (TG) and differential scanning calorimetry (DSC) analyses of the as-prepared gel were carried out by using a simultaneous thermal analyzer (STA409C, Netzsch, Germany). The phase structure of CBS powder was characterized by an X-ray diffractometer (XRD, D/Max-RB, Rigaku, Japan). The dielectric properties at 1 MHz of the as-sintered glass ceramics were measured at room temperature by an LCR meter (Agilent E4980A, USA).

3. Results

Fig. 1 shows the infrared absorption characteristics of CBS sol and gel. The sample was prepared into disks by means of the KBr method under high pressure and tested in the scope between 4000 cm^{-1} and 400 cm^{-1} . The intensity of peaks may be related to the sample preparation, while the position of peaks hardly changes. So we control that the volume ratio of KBr to CBS is 100:1 to keep the consistency of all measurements. It can be seen that there are no obvious differences between sol and gel, except for an absorption peak at 946 cm^{-1} that can be considered as the symmetric stretching of B–O bonds. This peak intensity declines slightly as the sol transforms into the gel. Besides, it seems that B–O–Si chains are not developed because the absorption peaks do not appear at 670 cm^{-1} and 915 cm^{-1} [9]. The absorption peak at 480 cm^{-1} proves that Ca^{2+} has been dispersed evenly in the sol–gel system. J. Livage [10] yielded a similar conclusion in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system.

Fig. 2 indicates the FT-IR spectra of pre- and post-heat treated CBS powders at different temperatures. The functional groups are confirmed by vibration bands which will lie in a specific range of standard spectroscopy or nearby [11]. A small shift in a range of 5 cm^{-1} may happen for different measurements. The vibration band at 2432 cm^{-1} is assigned to asymmetric stretching of $-\text{CH}_2-$. The noticeable absorption bands at 3450 cm^{-1} and 1640 cm^{-1} correspond to the stretching and bending of O–H in $[\text{SiO}_4]$ or $[\text{BO}_3]$ groups. The region of $1438\text{--}1384\text{ cm}^{-1}$ accords with the superposition of Si–O–Si in $[\text{SiO}_4]$ and B–O–B in $[\text{BO}_3]$, which moves to the low wavenumber with the increase of heat-treatment temperature. The band at 1110 cm^{-1} is obvious and strong as the powder is heat treated below $400\text{ }^\circ\text{C}$, and becomes broad as the heat-treatment temperature increases above $500\text{ }^\circ\text{C}$, and finally merges with a band at 915 cm^{-1} at $700\text{ }^\circ\text{C}$. The absorption peaks at 827 cm^{-1} and 745 cm^{-1} correspond to in-of-plane and out-of-plane bending of Si–O–H bond, respectively. The peaks locating at 600 cm^{-1} are due to the bending vibration of B–O–B in the $[\text{BO}_3]$ group, which disappears after heat treatment at $500\text{ }^\circ\text{C}$. The characteristic frequency of the coupling of Ca–O bending vibration and Si–O–Si stretching vibration is detected at 480 cm^{-1} .

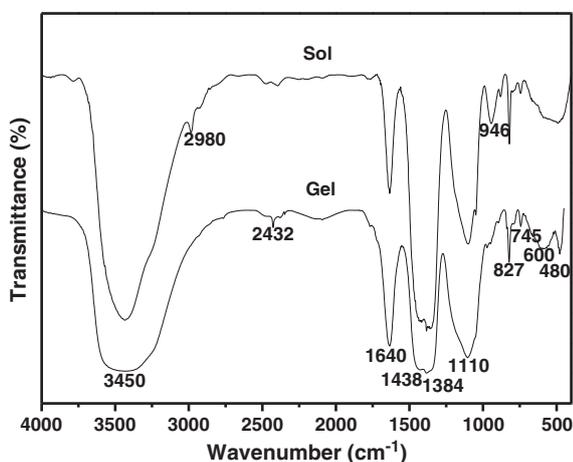


Fig. 1. FT-IR spectra of $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ sol and gel.

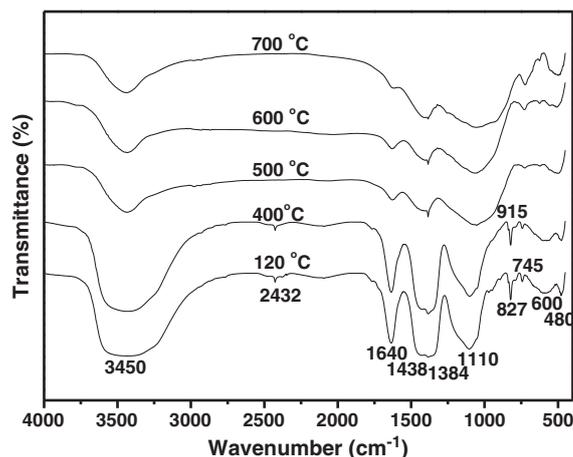


Fig. 2. FT-IR spectra of pre- and post-heat treated $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ powders.

TG and DSC curves of the CBS gel are shown in Fig. 3. The peaks may be slightly different with changing the heating rate. The small peak at $\sim 30\text{ }^\circ\text{C}$ is caused by the hot air flow in the beginning of heating. There is a small weight loss at temperatures up to $400\text{ }^\circ\text{C}$ and a sharp weight loss during $400\text{--}600\text{ }^\circ\text{C}$. No large weight loss can be seen after $600\text{ }^\circ\text{C}$ in TG curves. In DSC curves, there are three endothermic peaks at $\sim 78\text{ }^\circ\text{C}$, $\sim 553\text{ }^\circ\text{C}$, and $\sim 640\text{ }^\circ\text{C}$, and two exothermic peaks at $\sim 740\text{ }^\circ\text{C}$ and $\sim 875\text{ }^\circ\text{C}$.

In order to have a good comparison, powders obtained from one experiment were sintered at different temperatures for XRD examinations. The XRD patterns of CBS gel powders calcined at different temperatures are shown in Fig. 4. The amorphous phases at $120\text{ }^\circ\text{C}$ give an indication of the formation of homogeneous network in gel. The powders calcined below $400\text{ }^\circ\text{C}$ exhibit similar patterns to amorphous phases. When the calcination temperature rises to $550\text{ }^\circ\text{C}$ or $600\text{ }^\circ\text{C}$, the characteristic diffraction peaks of calcium silicate (PDF#45-0156) begin to appear. The xerogel is transformed into glass ceramic after nucleation at $680\text{ }^\circ\text{C}$ and crystallization at $800\text{--}900\text{ }^\circ\text{C}$ and its XRD patterns are shown in Fig. 5. The main phases of CBS glass ceramic are wollastonite (CaSiO_3 , PDF#42-0550) and calcium borate (CaB_2O_4 , PDF#32-0155). Semi-quantitative analysis of XRD results indicates that the molar ratio of the above two crystal phases is 7:3 at $850\text{ }^\circ\text{C}$.

Fig. 6 displays the dielectric properties of the CBS glass ceramic sintered at different temperatures. The data of dielectric properties were recorded one time after 30 s. The dielectric constant ϵ increases gradually with the sintering temperature, which indicates that glass

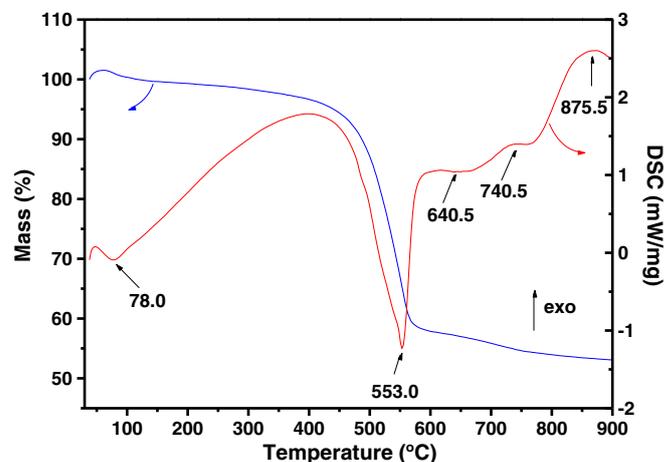


Fig. 3. TG-DSC curves of the $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ gel.

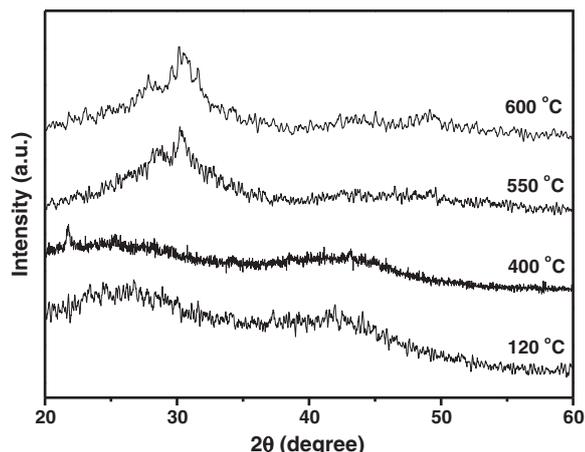


Fig. 4. XRD patterns of CaO-B₂O₃-SiO₂ powders calcined at different temperatures.

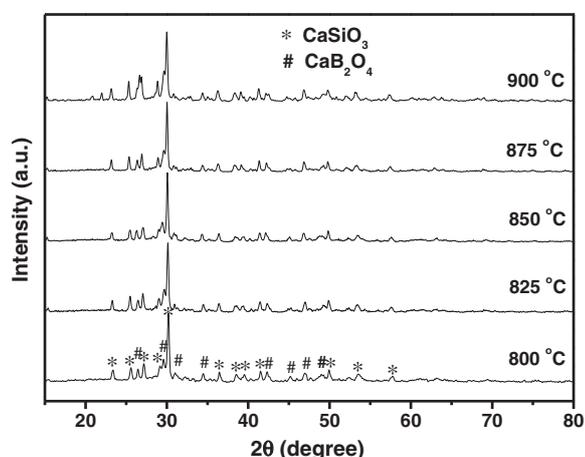


Fig. 5. XRD pattern of xerogel after heat treatment at different temperature.

4. Discussion

The formation of various compounds in sol-gel and the transformation of network in the solution can be deduced as follows. We can infer from Fig. 1 that Si-O and B-O chains become cross-linked in the course of sol-gel transformation whereas B-O-Si bonds haven't formed, probably because of the unstability of B-O-Si bonds that are prone to hydrolyze and alcoholize. Thus boracic acid exists in the form of [B(OH)₃OH]⁻ in the mixed solvent of EtOH and H₂O. Besides, as an electrophilic reagent, boracic acid is prone to adduct the -OH from H₂O molecules. The conjugation between the isolated electron pair in O atoms of the -OH group and empty p orbit in boron atoms can release H ions and further accelerate the hydrolysis of TEOS. In the acidic solution, one side of TEOS is attacked by H ions so that the electron cloud moves closer to the -OR group, forming a preferable leaving group. The augment of interspace generates the electrophilicity of Si atoms at the other side, attacked by H₂O that is of electronegativity. Therefore, TEOS becomes a transition state with pentacoordinate [12] whose electric charge diverts and induces hydrolysis ultimately. In the system of high H₂O/TEOS (R ≥ 20), the speed of hydrolysis is faster than that of polymerization. In this situation, more hydrolysates exist as Si(OR)₂(OH)₂ in the sol-gel process. As the polymerization goes, gel is finally achieved with the combination of short chains toward many dimensions. Therefore, the gel should be composed of TEOS, (Si(OR)_x(OH)_{4-x}) and free Ca²⁺, NO₃⁻ and BO₃³⁻.

In regard to the structure evolution of xerogel with heat-treatment temperature, we can deduce the following information from Fig. 2. The vibration band at 2432 cm⁻¹ fades away with increasing heat-treatment temperature, indicating that the organic residue has been completely removed. The absorption peak at 3450 cm⁻¹ and 1640 cm⁻¹ becomes weakened with increasing temperature, meaning that the gel is still polymerizing during heat treatment and that the xerogel is active and needs to be stored under a dry and sealed condition. The band at 1110 cm⁻¹ merges with a band at 915 cm⁻¹ at 700 °C, indicating the formation of Si-O-B bond [9]. The Si-O-Si stretching vibration band tends to be combined with the B-O-B bond located at 600 cm⁻¹ above 500 °C, also indicating that Si-O-B bond has been formed. In a word, the network of Si, B and O enlarges gradually and the structure is more compact with the increase of heat-treatment temperature.

In Fig. 3, a small weight loss at temperatures up to 400 °C is due to the elimination of the residues of TEOS hydrolysis. There is a gentle endothermic peak at ~78 °C, which is owing to the evaporation of remaining water, ethanol and ammonia. The large endothermic peaks at ~553 °C are mainly attributed to the thermal decomposition of calcium nitrate. After 600 °C, the thermal decomposition of CBS gel is completed. Therefore, the broad endothermic peak at ~640 °C corresponds to glass transition temperature (T_g), while the exothermic peaks at ~740 °C and ~875 °C are attributed to the formation of two kinds of crystal phases in glass powder. The temperature difference up to ~100 °C between T_g and the first crystalline temperature makes it possible to transform amorphous xerogel into crystallites through a controllable heat treatment. The presence of two crystallization peaks indicates a strong capability of crystallizing and the temperature difference between two peaks demonstrates that the physics properties of CBS powder are adjustable.

During the change from the amorphous phase to the microcrystal phase in Fig. 4, the xerogel forms the network and begins to change at ~550 °C or higher, which is consistent to the analysis of TG-DSC. In order to eliminate all the organic matter as well as to avoid crystallization at this stage, we set 600 °C as the calcination temperature, because the more crystalline phase the glass powder contains, the higher its T_g is.

We compared as-prepared powders to those by the solid-state reaction method [6] and detect that there is not cristobalite or quartz

ceramic becomes dense with more crystal precipitate. Afterwards the ε value does not change much until 900 °C, owing to an increase in the content of CaB₂O₄ in glass ceramic. As far as the dielectric loss tanδ is concerned, it is higher at a lower sintering temperature such as 800 °C, and it decreases gradually as the sintering temperature is higher than 850 °C.

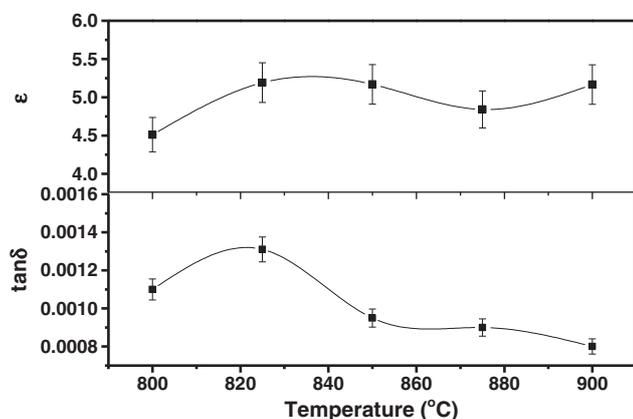


Fig. 6. Dielectric properties of CaO-B₂O₃-SiO₂ samples sintered at different temperatures.

phase in CBS glass ceramic prepared by the sol–gel technique in Fig. 5. It is probably because powder prepared by sol–gel route is more uniform in the microscopic field, which results in a smaller space among molecules adjusted during crystallization. More Si atoms tend to participate in the formation of CaSiO_3 . It can be also seen that the crystallization peak of CaB_2O_4 becomes more obvious with the increase of sintering temperature, accompanying a decrease of the ratio of $\text{CaSiO}_3/\text{CaB}_2\text{O}_4$ crystalline phases. It illuminates that the crystal growth temperature of CaB_2O_4 is higher than that of CaSiO_3 . That is the reason why there are two endothermic peaks at $\sim 740^\circ\text{C}$ and $\sim 875^\circ\text{C}$, respectively in TG-DSC curves. Moreover, it is indicated that the sintering temperature window of CaSiO_3 is narrow, such that it may re-dissolve into the glass phase if the sintering temperature is too high. As a result of this, the dielectric properties of glass ceramics will be influenced.

The dielectric constant ϵ_r is mainly determined by the amount of crystals and the connectivity between glass and ceramic of the CBS glass ceramic and fits the mixing rule of dielectrics as expressed by Maxwell–Wagner's equation. When the sintering temperature is 800°C , it is too low to make the crystals fully grow. While the sintering temperature is up to 900°C , the increase of the CaB_2O_4 content thus leads to the increase of ϵ_r . The dielectric loss $\tan\delta$ is higher at a low sintering temperature, which is lower than the optimum temperature for the crystal growth but higher than the softening temperature of glass phases, leading to a loose structure with a low content of crystal phases. As the sintering temperature is higher than 850°C , the crystal phase content and density increase so that the dielectric loss is reduced gradually. In summary, the CBS glass ceramic sintered at 850°C has a good dielectric performance, which can be considered as a potential electronic packaging material that can co-fire with base metals such as Ag at low temperatures.

5. Conclusions

The CBS glass powder was synthesized via a sol–gel route and its chemical reaction mechanism, structure evolution and crystallization

process were investigated in this study. The evolution of sol to gel relies on the hydrolysis and polymerization of TEOS such that Si–O and B–O could be uniformly dispersed. The as-prepared powder exhibits amorphous network structure with steady Si–O and B–O bonds after heat treatment at 600°C , in which Ca^{2+} is distributed. The xerogel powder of the CBS system exhibits a strong crystallization capability and can form glass ceramics through proper nucleation and crystallization processes. The main phases in CBS glass ceramic are CaSiO_3 and CaB_2O_4 , which have made the as-sintered CBS glass ceramic have excellent dielectric properties.

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