

# Sol-gel derived CaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass/CaSiO<sub>3</sub> ceramic composites: processing and electrical properties

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**Abstract** The CaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass/CaSiO<sub>3</sub> ceramic (CBS/CS) composites were fabricated via sol-gel processing routes. Their densification behavior, structures and dielectric properties were investigated. The precursors of CBS glass and CS ceramic filler were firstly obtained via individual soft chemical route and then mixed together in various proportions. The results indicated that the structures of CBS/CS composites are characteristic of CS and CaB<sub>2</sub>O<sub>4</sub> (CB) ceramic phases distributed in the matrix of glass phase at 800–950 °C. The CS ceramic phase not only acts as fillers, but nuclei for the crystallization of CBS glass as well such that the CS content exhibits an effect on the densification and dielectric properties of the composites. The CBS/CS composites with 10% CS sintered at 850 °C own dielectric properties of  $\epsilon_r < 5$  and  $\tan\delta = 6.4 \times 10^{-4}$  at 1 MHz.

## 1 Introduction

Low temperature co-fired ceramics (LTCC) technology has been so far widely used, showing such advantages as low cost, space-saving and high density [1–3]. The modules manufactured by LTCC technology could be embedded with passive-components and 3-D micro-circuit connection [4]. The development and application of LTCC technology should simultaneously take the material, design, processing and equipment into consideration. As far as the material system is concerned, the low sintering temperature, low

dielectric constant  $\epsilon_r$  and low dielectric loss  $\tan\delta$  are the most important parameters. Accordingly, glass/ceramic composite systems and crystallizable glass systems have been commercially applied [5]. Typical examples are Pb–B–Si–O glass/Al<sub>2</sub>O<sub>3</sub> ceramic system developed by DuPont [6] and Ca–B–Si–O crystallizable wollastonite by Ferro [7]. Researches on these systems have been carried out by many research groups [8–10].

However, the above two systems have their own disadvantages. For instance, the wetting properties between glass and ceramic phases should be carefully considered at the start of selecting suitable materials, although each material has a few choices in a glass/ceramic composite. For a crystallizable glass system, an increase in the degree of crystallization for the purpose to improve dielectric properties should be vital because residual glass phase may disorder the structure and as a result degrade the dielectric properties [10]. In order to counterbalance the disadvantage of the two systems, we decided to take CaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (CBS) crystallizable glass filled with CaSiO<sub>3</sub> (CS) ceramic which is actually the main crystal phase in crystallizable CBS glass for better wetting property and easier crystallization.

The melt-quenching technique was used a traditional way to make glass powder. However, this method needs a rather high temperature such that raw oxides with low-melting points, such as B<sub>2</sub>O<sub>3</sub>, tend to volatilize [11]. In contrast, the sol-gel route enables the glass powder to be synthesized at a low temperature. However, an identical crystallization behavior of gel-derived glass to that by a traditional way can be achieved [12]. In this study, the precursors of the CBS glass and CS ceramic were separately prepared by sol-gel processing and transformed into glass or ceramic by individual appropriate heat treatment scheme. The glass or ceramic powders should be finer in size and more uniformly mixed than the fused-glass

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powder [13]. The effect of CS ceramic addition on the sintering behavior and dielectric properties of CBS crystallizable glass were investigated in detail.

## 2 Experimental

The sol–gel method was used to prepare the precursors of CBS glass and CS ceramics. High-purity calcium carbonate ( $\text{CaCO}_3$ ,  $\geq 99.0\%$ ), boracic acid ( $\text{H}_3\text{BO}_3$ ,  $\geq 99.0\%$ ), tetraethyl orthosilicate (TEOS, analytically pure), anhydrous ethyl alcohol ( $\text{EtOH}$ ,  $\geq 99.7\%$ ), nitric acid ( $\text{HNO}_3$ , 65–68%), and ammonia ( $\text{NH}_3\cdot\text{H}_2\text{O}$ , 25–28%) were used as raw materials. At first, the CBS gel was prepared according to the following procedures: Calcium nitrate solution was gained through the reaction of  $\text{CaCO}_3$  with  $\text{HNO}_3$  with a control of the pH value. TEOS solution was prepared by adding a suitable amount of  $\text{EtOH}$  as well as some distilled water.  $\text{H}_3\text{BO}_3$  was added into the mixture of the above two solutions and simultaneously stirred at  $80^\circ\text{C}$  until a transparent liquid was formed. In the meantime, pH value was adjusted to be  $\sim 2$  by using  $\text{NH}_3\cdot\text{H}_2\text{O}$  and the molar ratio of  $\text{H}_2\text{O}$ : TEOS was controlled at 20:1 by adding some more deionized water. With a gradual increase of the viscosity, the solution lost its fluidity and changed to gel ultimately. The similar processing was used to prepare the CS gel, except that  $\text{H}_3\text{BO}_3$  was not required. The CBS gel needed to be heat treated at  $600^\circ\text{C}$  in order to completely remove unwanted groups and form stable glass phase, whereas the purpose of heat treatment for CS gel is not only to remove organic substances, but also to form crystalline phases. Subsequently, CS ceramic powder was mixed with the CBS glass powder with mass fraction of 0, 5, 10, 20 and 40% of CS, respectively. The mixed powder compacts nucleated at  $680^\circ\text{C}$  for 3 h and then crystallized at  $800$ – $950^\circ\text{C}$  for 2 h in air. The conditions for heat treatment were determined by means of thermal analysis. Fired-on silver paste was used as electrodes for the measurement of electrical properties.

Thermo-gravimetry (TG) and differential scanning calorimetry (DSC) analysis of the as-prepared gels was carried out by using a simultaneous thermal analyzer (STA409C, Netzsch, Germany). The phase structures of the as-prepared powder after calcination and the as-sintered samples were characterized by an X-ray diffractometer (D/Max-RB, Rigaku, Japan). The densities of the sintered samples were measured by the Archimedes method. The microstructure of the sintered samples was observed using a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). The dielectric properties at 1 MHz of the as-sintered glass/ceramic composites were measured at room temperature by an Impedance Analyzer (HP4194A Impedance/Gain-Phase Analyzer, USA).

## 3 Results and discussion

The TG and DSC curves of the CBS and CS gels were shown in Fig. 1. No obvious differences can be observed between TG curves of the two gels. Taking the CS gel as an example, a small weight loss at temperatures up to  $400^\circ\text{C}$  is due to the elimination of the residues of TEOS. A large mass loss during  $400$ – $600^\circ\text{C}$  was ascribed to the combustion of nitrate, organic groups and so on. No significant weight loss can be seen after  $600^\circ\text{C}$  in TG curves, indicating that most of organic matters in gel have been decomposed before  $600^\circ\text{C}$ . In DSC curves of CS gel, a gentle endothermic peak at  $71.5^\circ\text{C}$  is due to the evaporation of remaining water, ethanol and ammonia, and a large endothermic peak at  $\sim 563.6^\circ\text{C}$  corresponds to a large mass change during  $400$ – $600^\circ\text{C}$  in TG curves. A visible endothermic peak at  $667.1^\circ\text{C}$  probably results from the initial crystallization between  $\text{CaO}$  and  $\text{SiO}_2$  [14]. Similar weight loss and peaks can be detected in the TG and DSC curves of CBS, except for a broad endothermic peak at  $\sim 640.5^\circ\text{C}$  corresponding to the glass transition temperature and two exothermic peaks at  $\sim 740.5^\circ\text{C}$  and  $\sim 875.5^\circ\text{C}$  corresponding to the formation of two kinds of crystal phases in glass powder. Therefore, the CS crystal

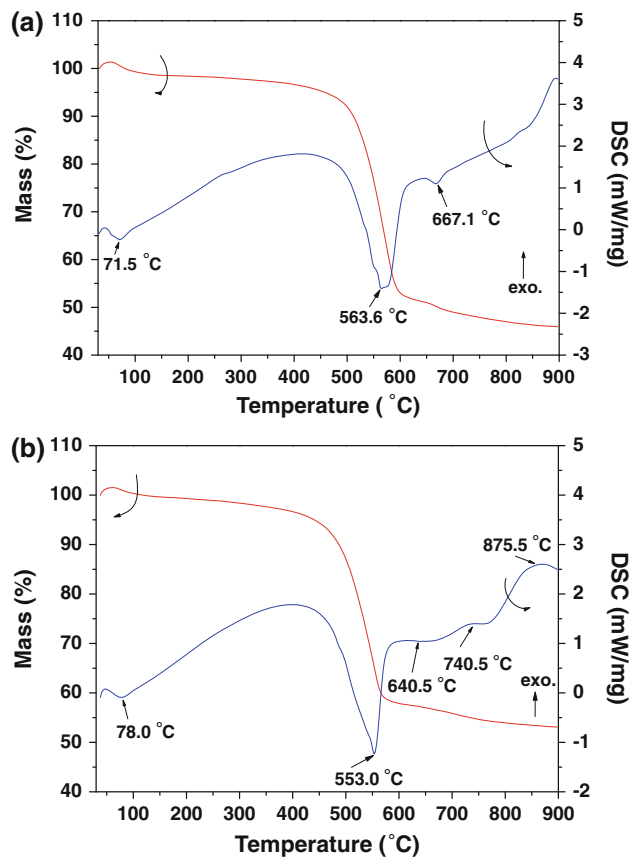
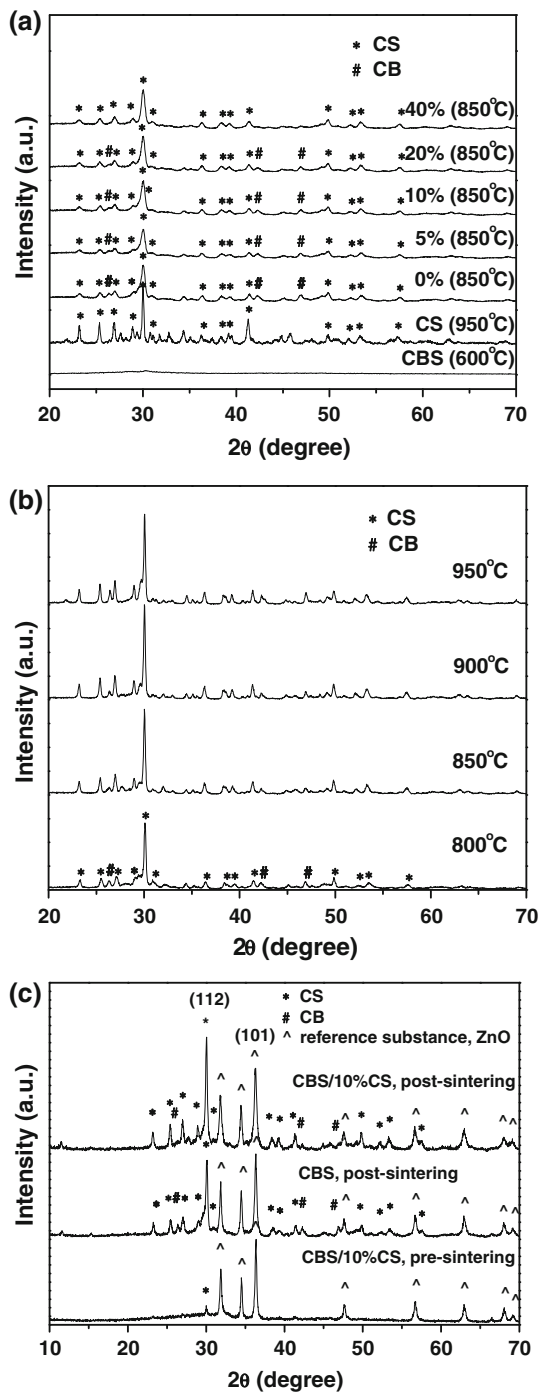


Fig. 1 TG-DSC curves of a CBS gel and b CS gel

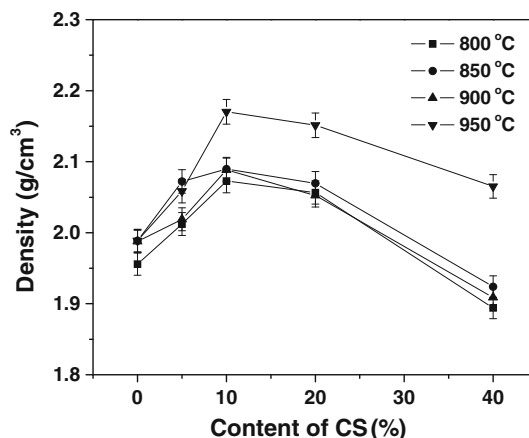
phase and CBS glass can be obtained from their respective gels by controlling appropriate heat treatment temperature.

Figure 2a indicates the XRD patterns of the CBS powder, CS powder, and the CBS/CS mixtures. It can be seen that the CBS powder is amorphous after heat treatment at

600 °C for 4 h and the CS powder exhibits a typical wollastonite (CS, PDF#42-0550) structure after heat-treatment at 950 °C. The main phases of pure CBS powder consist of wollastonite (PDF#42-0550) and calcium borate (CB, PDF#32-0155). The similar phase structure of CS and CBS powders after heat treatment hints that the added CS can merge harmoniously with the one crystallized from the CBS xerogel. With the increase of the CS fraction in the sample, the peak corresponding to the CB phase fades away gradually and the relative intensity of CS increases. With regard to the XRD patterns of CBS + 10% CS samples sintered at different temperatures as shown in Fig. 2b, the intensity of diffraction peaks of CS was strengthened with increasing the sintering temperature, which means an improved crystallization to a certain extent. However, a small amount of crystal phases can re-dissolve into the glass phase at 950 °C such that the peak intensity slightly decreases. In order to testify that the addition of CS can improve the crystallization ability of CBS glass, a simple experiment was designed as shown in Fig. 2c. Three samples of post-sintered CBS, post-sintered CBS/10%CS, and pre-sintered CBS/10%CS were examined by XRD for comparison, in which the same content of the reference substance ZnO was added thereafter. The additional increment of (112) peak intensity of CS ( $I_3 = 1.363$ , the intensity of (101) peak for ZnO was considered as an unity.) in the as-sintered CBS/10%CS sample in comparison to the sum of the (112) peak intensities in the other two samples ( $I_1 = 0.924$  and  $I_2 = 0.224$  for the CBS and CBS/10%CS samples as-prepared, respectively) could be semi-quantitatively accounted as an indication of the increased crystallization of CBS glass ( $I_3 > I_1 + I_2$ ). It is thus concluded that most of CS crystals come from the crystallization of CBS glass. Moreover, the addition of CS in the composite also acts as nuclei to promote the additional crystallization of CBS glass.



**Fig. 2** XRD patterns of **a** CBS and CS gel powders calcined at different temperatures and CBS/CS samples sintered at 850 °C, **b** CBS/10%CS samples sintered at various temperatures, and **c** pre-sintered CBS/10%CS, post-sintered CBS and post-sintered CBS/10%CS samples

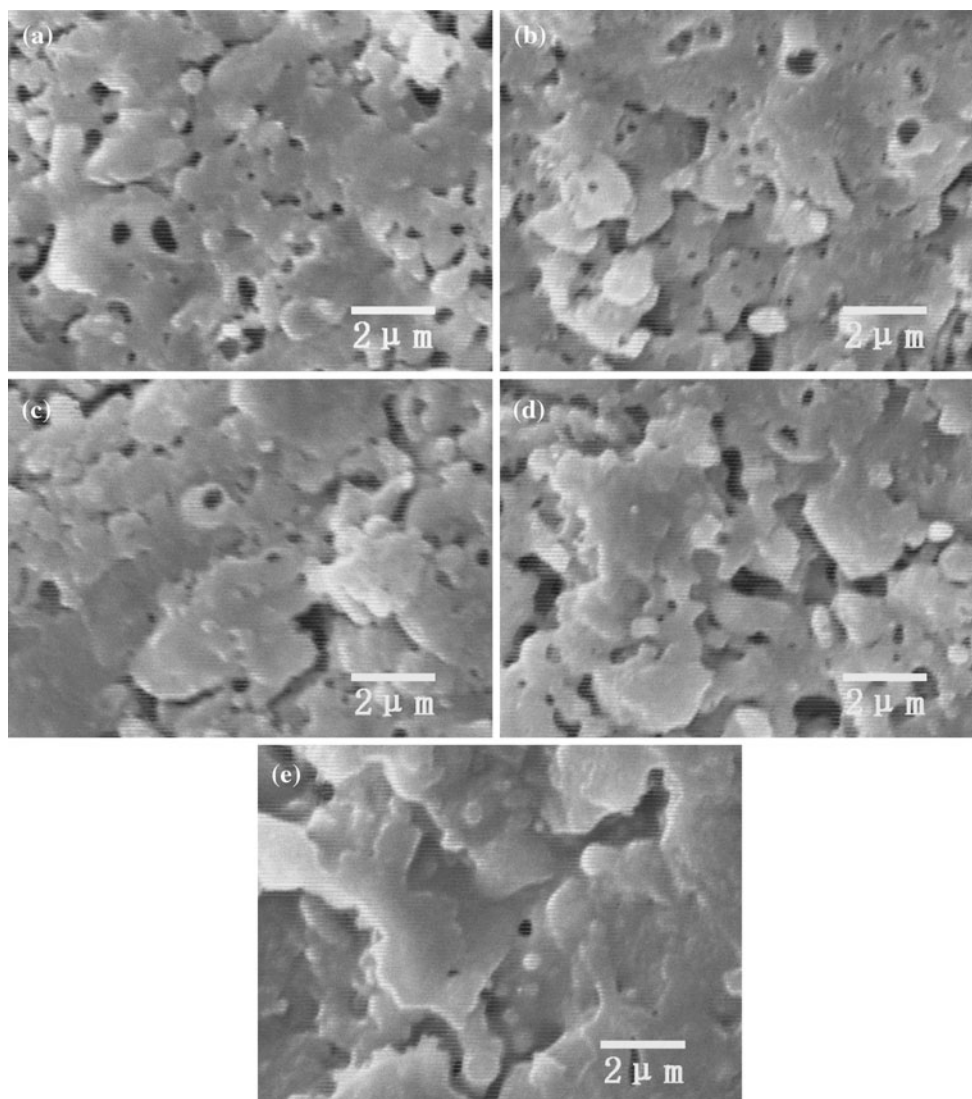


**Fig. 3** Densification behavior of CBS/CS samples as a function of the CS content

Figure 3 shows the densities of the CBS/CS samples as a function of sintering temperature. It can be seen that the pure CBS sample (without sintering aids such as ZnO) owns a similar density to that reported by other researchers [15, 16]. As the sintering temperature was changed within the range of 800–900 °C, there is no significant change in the density for samples with various CS contents. While the sintering temperature rises to 950 °C, the sample density increases significantly especially for the sample with more than 5% CS, but the samples begin to adhere with each other after sintering, hinting that the optimum sintering temperature is exceeded. Moreover, the density of the CBS/CS samples slightly increases as the CS content is increased within the range of 5–10% but it tends to decrease as the CS content gets more. A relatively high sintering temperature is needed for the sample with higher

content of CS, probably because of higher sintering temperature of pure CS ceramic itself [17], which acts as the skeleton in the glass network and changes the sintering mechanism from viscous sintering to a liquid-phase sintering as larger amount of ceramic phases were added [18]. However, the sintering mechanism of CBS glass is not significantly influenced as only a small amount of CS is added. On the contrary, it can act as nuclei to promote the crystallization of CBS glass, as discussed above. Moreover, CS and CBS powders were homogeneously mixed in an appropriate proportion so that the CS/CBS samples could be well sintered at relatively low temperature than the CBS crystallizable glass [15].

The SEM morphology on the surface of the samples with different CS contents sintered at 850 °C for 2 h is shown in Fig. 4. It can be seen that the crystalline phase is



**Fig. 4** SEM morphology of the CBS glass/CS ceramic composites with different contents of CS sintered at 850 °C for 2 h: **a** 0%, **b** 5%, **c** 10%, **d** 20% and **e** 40%

enwrapped by low-melting-point glass and a small amount of pores are included. Considering the viscous sintering mechanism, pores could be eliminated along the grain boundary to the surface of the samples, which explains why some surface pores can be seen. Zhou [10] and Chen [16] also discovered pores in CBS system after sintering. With regard to the sample with 40% CS, the optimum densification can not be reached at 850 °C in spite of better connection structure, which corresponds to the analysis of densification.

The dielectric properties of the CBS/CS samples sintered at different temperature were plotted as a function of the CS content, as shown in Fig. 5. The dielectric constant values  $\epsilon_r$  are mainly determined by the amount of crystals and the connectivity between glass and ceramic as the sample density is similar. The results fit the mixing rule of dielectrics as expressed by the Polder-Van Santen model [19]. The relationship between the  $\epsilon_r$  value and the sintering temperature reveals the same trends as that between the density and the sintering temperature. Therefore, the  $\epsilon_r$  values of the CBS/CS composites increase gradually with

slightly increasing the amount of CS additive, which is mainly due to the enhanced densification and more amount of CS crystals. As for dielectric loss  $\tan\delta$ , it decreases slightly when the content of CS additive is below 10%, but rises distinctly as the CS content further increases owing to the enhanced extrinsic dielectric loss from a large porosity. With regard to the influence of sintering temperature, it affords a tiny change to the  $\epsilon_r$  value between 800 and 900 °C because of the enhanced crystallization ability and densification, while a sharp increase of  $\epsilon_r$  at 950 °C results from higher densities. The minimum value  $6.4 \times 10^{-4}$  of  $\tan\delta$  appears in the sample with 10% CS sintered at 850 °C. When the sintering temperature is 800 °C, it is too low to make the crystals fully grow. While the sintering temperature is too high, the formed crystals might re-dissolve into the glass. In a word, the composition and sintering parameters of the CBS/CS composites could be adjusted to a certain extent. However, the composite density should be further improved in future in order to satisfy the application requirement of LTCC.

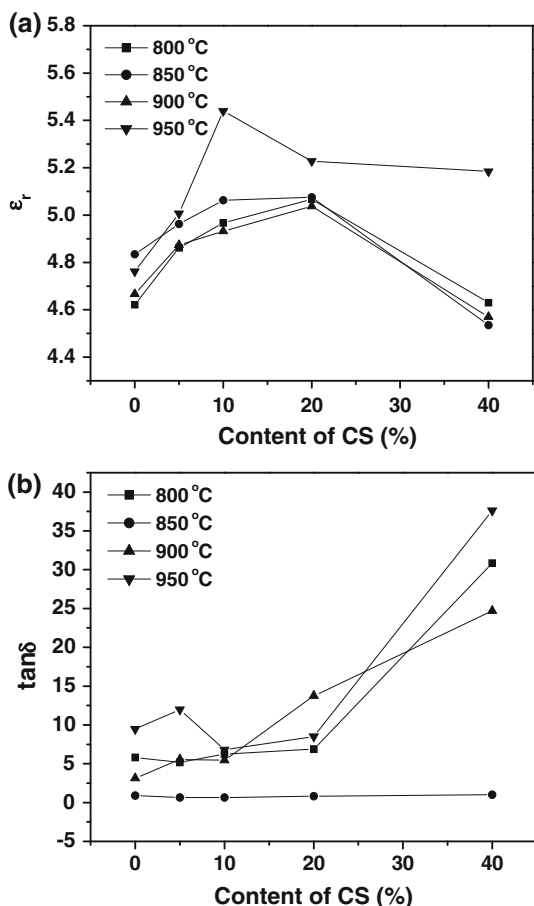
#### 4 Conclusions

The sintering behavior and dielectric properties of the CBS glass/CS ceramic composites were investigated with a focus on the role that CS played in CBS system. Their precursors were prepared via sol–gel soft chemical routes. The results show that the densification, microstructure and dielectric properties of the composite samples are dependent on the content of the CS ceramic filler. The addition of the CS ceramic filler simultaneously promotes the crystallization of the CBS glass, thus influencing the final dielectric properties. The composites with 10% CS sintered at 850 °C show acceptable dielectric properties of  $\epsilon_r \leq 5$  and  $\tan\delta \sim 6.4 \times 10^{-4}$  at 1 MHz.

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**Fig. 5** Dielectric constant **a** and loss  $\tan\delta$  **b** at 1 MHz of CBS/CS composites as a function of sintering temperature and the CS content

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