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Effect Of B₂O₃ And P₂O₅ on Fluorosilicic Mica Glass-Ceramic Sintering Process**S. Wu, X. Lv, M. Zhang, Y.-J. Chen^{*)}, R.-N. Zhao**

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Abstract:

To study the effect of B₂O₃ and P₂O₅ on fluorosilicic mica glass-ceramic sintering process, six sets of K₂O-MgO-SiO₂-F glasses were prepared by using B₂O₃ and P₂O₅ as sintering aid, respectively. Green bodies of the glass powder were formed by gel casting and sintered at 800, 850, 900, 950, 1000°C for 6 hours, respectively. The sintering and crystallization behavior were studied by thermal shrinkage, X-ray diffraction and SEM. The results showed that the shrinkage rate of the glass with 2wt% B₂O₃ and P₂O₅ was highest, while the rate of the glass with 5wt% P₂O₅ was lowest. An additional crystal other than fluorosilicic mica was precipitated in the glass ceramics generated by sintering of glass powder. The present results confirmed that the glass powder of pure K₂O-MgO-SiO₂-F system had poor sinterability, while glass powder with minor addition of P₂O₅ and/or B₂O₃ showed good sinterability. This result was also verified by SEM.

Keywords: Fluorosilicic Mica, Sinterability, P₂O₅, B₂O₃**1. Introduction**

Fluoromica glass ceramics are widely used in the dental field because of their high esthetics, good mechanical properties and excellent machinability [1-4]. The main crystalline phase in fluoromica glass ceramics is either fluorophlogopite or fluorosilicic mica [5].

There are two methods to produce glass ceramics. The first one is the "melt-casting method", [6-8] where glass bulks are formed by melt-casting technique and then heat-treated to form glass ceramics. The second one is the "sintering method", [9,10] i.e. the glass articles are fabricated from pulverized glass powders by conventional ceramic-shaping techniques and then sintered to form glass ceramics. Compared with the first method, the latter permits manufacturing of small quantities of products with complex shapes, as favored by the dentist very much. Vita is the most notable dental glass ceramics fabricated by sintering. However, it seems that the effect of various additives on the above-mentioned characteristics of sintered mica glass-ceramics has been discussed in only several papers [11,12].

In this paper, efforts had been made on the understanding of the effect of B₂O₃ and P₂O₅ on the sintering of fluorosilicic mica glass ceramics.

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2. Experimental procedures

2.1. Composition preparation

The composition in weight percent of the base glass (glass B₀P₀) was SiO₂ 56%, MgO 17%, MgF₂ 12%, K₂O 11%, ZrO₂ 4%. Based on this, different amounts of B₂O₃ and/or P₂O₅ were added to modify the sinterability of the base composition. Detailed compositions are listed in Tab.I. All the raw materials were of reagent grade, from Sinopharm Chemical Reagent Beijing Co., Ltd. Batches were firstly melted for 2h in alumina crucibles in an electric furnace at 1500°C, and then quenched in deionized water to form frit. The frit was ground and screened with a 100-mesh sieve.

Tab. I. Nominal compositions of the glasses with respect to the base composition in wt%

	B ₀ P ₂	B ₀ P ₅	B ₂ P ₂	B ₂ P ₅
B ₂ O ₃	0	0	2%	2%
P ₂ O ₅	2%	5%	2%	5%

The green bodies of glass powders are fabricated by gel-casting. [13] Glass powders, organic monomers (methacrylamide, MAM), cross-linker (N-N'-methylene bisacrylamide, MBAM), dispersants (Duramax D3019 Rohm, Hass Corp.) and deionized water were ball milled for 4 hours to form slurries. Then slurries were cast into cylindrical glass moulds using ammonium persulfate (APS) and tetramethylethyl enediamine (TEMED) as initiator and catalyst, respectively. The moulds were 10~15mm in diameter and 30~40mm in length. After being dried at 100 °C for 6h, the green bodies were sintered at different temperatures for different soaking times, while the heating rates were held constant, 10K/min. The densities of the dried powder compacts are around 60% of theoretical ones.

2.2. Analysis methods

The resulting particle size of the glass powders were measured with a particle size analyzer (SHIMADZU, SA-CP3), and the measurement result is illustrated in Fig.1. The diameters of the cylindrical bodies before and after sintering were measured by a vernier caliper. The density of sintered glass ceramics was determined by the Archimedes method.

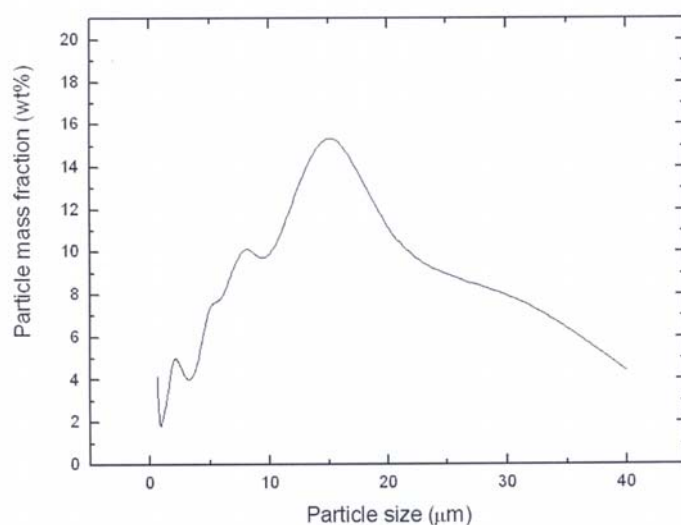


Fig. 1. The particle size distribution of the glass powders after milling for 4h with deionized water

The crystallization temperature of the glasses was determined by differential thermal analysis (DTA) (Setaram TGDTA 92. X-Ray ($\text{CuK}\alpha$) Powder Diffraction (RIGAKU, D/max-RB,) was employed to identify the crystalline phases precipitated in the powder compacts during sintering. The microstructure was analyzed under scanning electron microscope (ESEM, Philips,JSM-6301,).

3. Results and discussions

The relationships between the linear shrinkage rate and sintering temperature for various compositions are illustrated in Fig.2. The increase of P_2O_5 content led to the decrease of the sinterability, while 2wt% addition of B_2O_3 highly promoted the densification process. This phenomenon was also verified in Fig.3. At each temperature point between 900 °C and 1000 °C, B_2P_2 glass showed better sinterability than B_2P_5 glass. The bulk density of B_2P_2 sintered at 1000 °C for 8h was $2.54 \pm 0.01 \text{ g/cm}^3$ while density of base glass heat-treated at 1000 °C for 8h was $2.72 \pm 0.01 \text{ g/cm}^3$. According to XRD curves, the mica crystalline volume content in the B_2P_2 and base glass heat-treated were calculated. The results showed that the former (38.1%) was higher than the latter (26.5%). It can be elucidated that P_2O_5 could be incorporated into the glass network and improved the phase separation in glass.

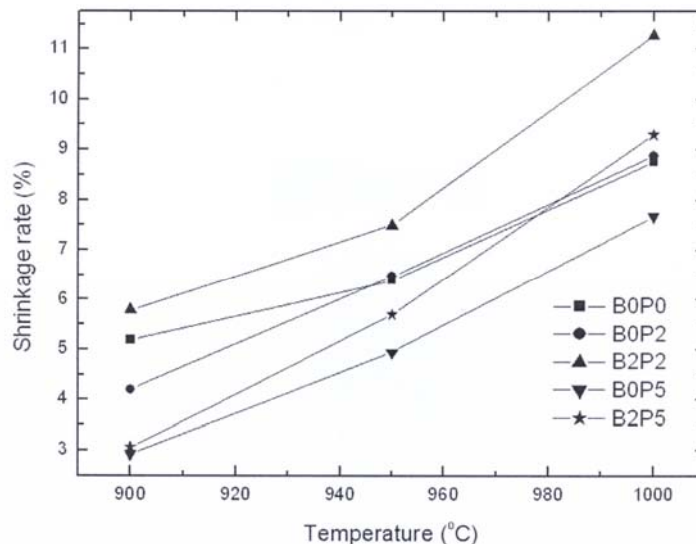


Fig. 2 The shrinkage rate vs. temperature of all the glass powder compacts

Both B_2O_3 and P_2O_5 could be incorporated into the glass network and lower the viscosity of the glass. The opposite effect on the sintering of this glass system might be attributed to their different effect on the temperature interval between T_g (glass transition temperature) and T_0 (onset crystallization temperature). Some researchers had proposed that a high value of $(T_g - T_0)$ favored the sintering of glass powders because the densification of glass sintering was of viscous flow mechanism. [14] As illustrated in Fig.4, the value of $(T_g - T_0)$ in the DTA curve of B_0P_0 glass was about 100 °C, apparently bigger than 44 °C of B_0P_2 glass. Fig 3 shows that sinterability of glass was decreased by the addition of more P_2O_5 . There were two typical DTA curves of fluoromica glass, one observed by Eftekhari [11] had no any clear crystallisation peak, the other, illustrated in Fig.4 and Wood, [15] had a clear crystallisation peak. Eftekhari added B_2O_3 , PbO and P_2O_5 to the composition of the base glass to modify the glass sinterability, and the result showed that sinterability of glass was improved by the addition of more B_2O_3 (11.16 wt %) but it degraded the machinability. According to our

results, addition of a small amount of P_2O_5 might improve the effect of B_2O_3 on fluoromica glass sintering process.

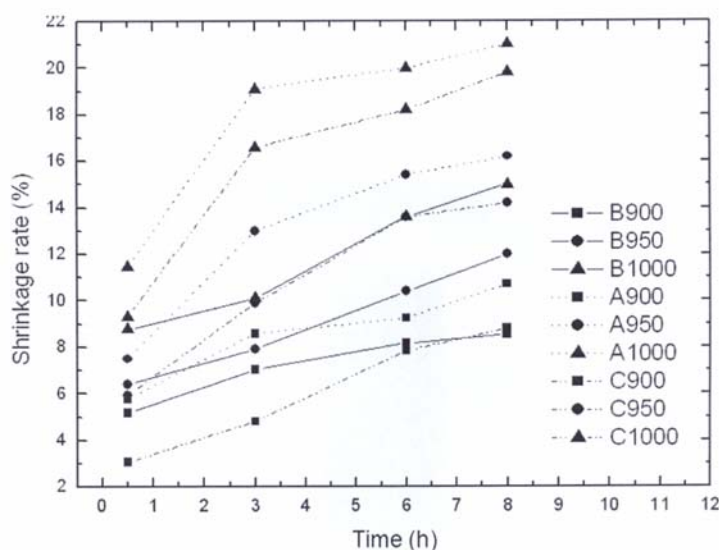


Fig. 3 The shrinkage rate vs. time of three glass powder compacts (A- B_2P_2 ; B- B_0P_0 ; C- B_2P_5)

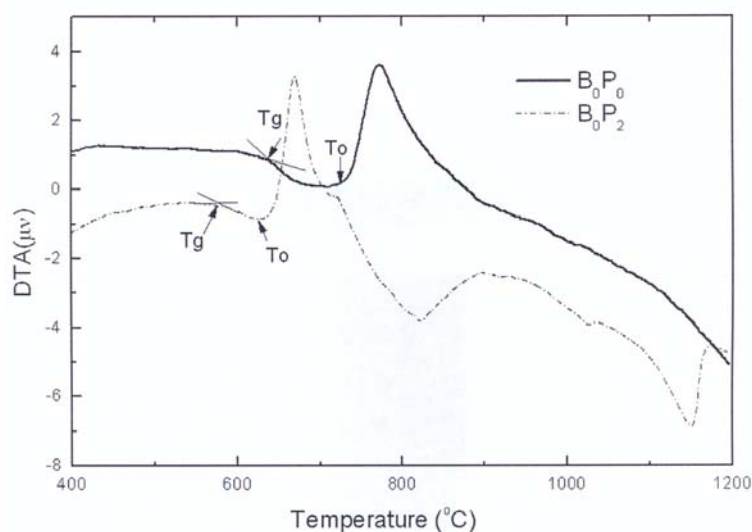


Fig. 4 DTA curves for the glass powder

Typical microstructures of sintered B_0P_0 and B_2P_2 powder compacts held at 1020 °C for 6h are illustrated in Fig.5. The B_2P_2 sample was nearly fully sintered and almost all the fine pores were eliminated. The remaining large pores (Fig.5a) can be attributed to the volumetric contraction because of crystallization and the release of gases dissolved in the glass network. The boundaries of original glass powders were largely disappeared. Crystalline phases precipitated not only within the original glass powders, but also among the boundaries (Fig.5b). However, various sizes of pores dispersed homogeneously in the sintered B_0P_0 bodies (Fig.5c), and the sintering necks among original particles were not obvious (Fig.5d).

Compared with the heat-treated bulks fabricated by the “melt-casting” method of the same composition, an additional crystalline phase other than fluorosilicic mica ($K_2Mg_{2.5}Si_4O_{10}F_2$), clino-enstatite ($MgSiO_3$), precipitated in the B_0P_0 powder compact during

sintering process (Fig.6).

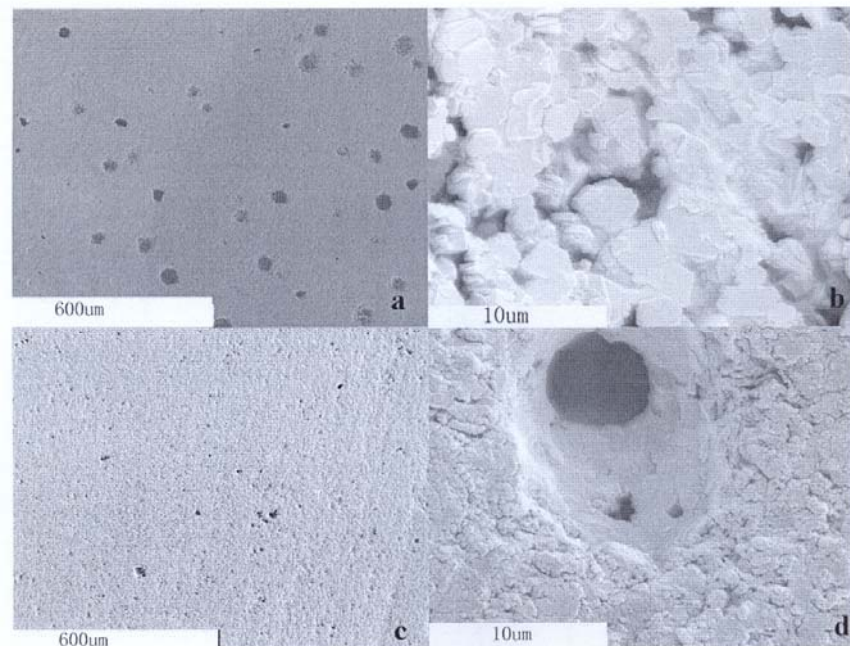


Fig. 5 The microstructure of fracture surface of glass compacts holding at 1020°C for 6hs. (a,b: B₂P₂; c,d: B₀P₀).

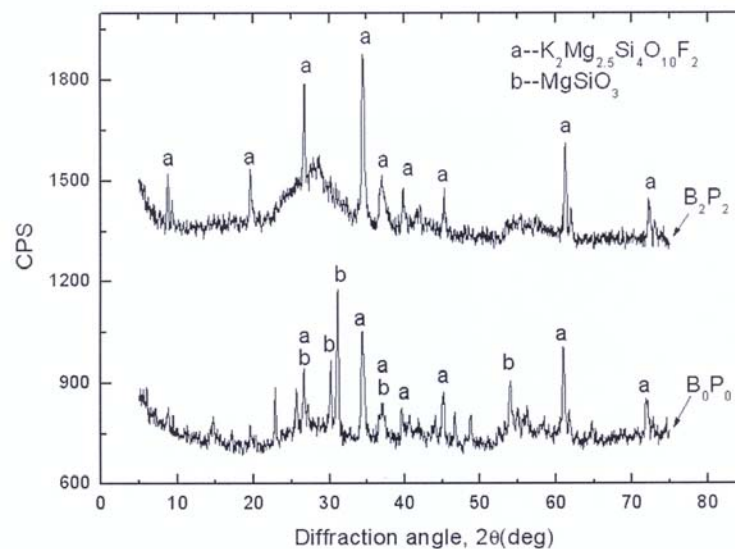


Fig. 6 XRD patterns showing an additional phase formed in the B₀P₀ compacts (T=1020°C, holding time is 6 h)

However, only $K_2Mg_{2.5}Si_4O_{10}F_2$ precipitated in other glass powder compacts discussed in this paper during sintering. Grossman has reported that $MgSiO_3$ formed at $\approx 980^\circ C$ in the low- K_2O -high- MgO system.[1]. In our previous experiments, we also found $MgSiO_3$ precipitating on the surface of all the heat-treated bulk glass ceramics, made by the melt-casting method. Combining Grossman's result with our previous experiments, a possible explanation on the occurrence of $MgSiO_3$ in B₀P₀ compacts was given here, i.e. because the original glass particles in B₀P₀ compact did not coalesce when held at 1020°C, many particles were in direct contact with air, KF volatilized and the surface of glass particles were in K_2O -

deficient state. As a result, MgSiO₃ reprecipitated.

4. Conclusions

1. B₂O₃ can be used as a sintering aid in the fluoromica glass system, while P₂O₅ has a contrary effect.

2. An additional crystalline phase, MgSiO₃ precipitated in the sintered powder compact of the base composition, while only K₂Mg_{2.5}Si₄O₁₀F₂ precipitated in the compacts of other compositions.

Acknowledgements

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Садржај: Ради проучавања ефекта B₂O₃ и P₂O₅ на процес синтеровања флуоросиликатне мика стакло-керамике б група K₂O-MgO-SiO₂-F стакла је припремљено коришћењем B₂O₃ и P₂O₅ као додатка. Испресци стакленог праха ду формирану гел ливењем и синтеровани на 800, 850, 900, 950 и 1000°C б сати. Понашање током синтеровања и кристализације проучено је посматрањем топлотног скупљања, рентгенске дифракције и СЕМ. Резултати су показали да је брзина скупљања стакла са 2% B₂O₃ и P₂O₅ највећа, док је најмања брзина скупљања стакла са 5 тежински процената P₂O₅. У стакло-керамици која је добијена синтеровањем стакленог праха примећен је додатни кристал осим флуоросиликатне мике. Добијени резултати су потврдили да чисти прах система K₂O-MgO-SiO₂-F има

лошу синтерабилност, док стаклени прах са малим додацима P_2O_5 и/или B_2O_3 има добру синтерабилност. Ови резултати су такође потврђени СЕМ анализом.

Кључне речи: Флуоросиликатна мика, синтерабилност, P_2O_5 , B_2O_3
