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The Sintering Characteristics of Bi_2O_3 Added MgO–CaO–Al_2O_3–SiO_2 Glass Powder

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Abstract: The coalescence, crystallization processes, and sintering characteristics of the MgO–CaO–Al_2O_3–SiO_2 (MCAS) composite glass, which contains different amounts of Bi_2O_3 addition as a sintering aid, are investigated in this study. X-ray diffraction studies find that cordierite ($Mg_2Al_4Si_5O_{18}$) and anorthite ($CaAl_2Si_2O_8$) are the two mainly crystalline phases. The recrystallization rates of cordierite and anorthite are both sintering temperature and Bi_2O_3 concentration dependent. The dielectric constants of MCAS glass ceramics are also a function of sintering temperature and amount of Bi_2O_3 addition. To densify MCAS glass ceramics, the needed sintering temperature will decrease with the increase of Bi_2O_3 addition, but both the dielectric constants and the thermal expansion coefficients of densified MCAS glass ceramics increase with the amount of Bi_2O_3 addition. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Cordierite ($2MgO–2Al_2O_3–5SiO_2$) and cordierite-based glass ceramics are promising materials for electronic packaging and offer lower dielectric constant (5.0 at 1 MHz) and thermal expansion in comparison to Al_2O_3 or mullite ($3Al_2O_3–2SiO_2$).[1,2] Miller studied the sintering of cordierite glass ceramics and concluded that the stoichiometry of cordierite was difficult to sinter without the addition of sintering aid because of the very narrow sintering temperature range unless it was in the composition range that contains more MgO and less Al_2O_3 than stoichiometric cordierite.[3,4] Another method in improving the sinterability of stoichiometric cordierite glass powders is the addition of sintering aids or nucleating agent.[5] In the past, Cr_2O_3, P_2O_5, ZrO_2, and B_2O_3 were used as the sintering aid or as a nucleating agent to sinter the stoichiometry of cordierite.[5–8] A flux could be used to mix simple starting materials such as magnesia, alumina, and silica to a level that would allow the formation of phase similar to cordierite at modest temperature.[9] That would be a reactive liquid-phase-sintering process involving the dissolution of all the oxide starting materials in the flux, where reaction would occur followed by precipitation of a crystalline product from the flux.

Several criteria govern the choice of a flux. Because a low-temperature process is desirable, the melting temperature of flux must be lower than the precursors.[9] A cationic radius will be much larger than these metals used to avoid substitution on the magnesium, calcium, aluminum, and silicon sites. Bismuth oxide has a large ionic radius, melts at 825°C, and forms eutectics with magnesium, calcium, alumina, and silica.[9] Because Bi_2O_3 fits these criteria, it can be used as a flux to densify cordierite-based glass. A great number of papers concerned with synthesis of cordierite glasses ceramics in the MgO–Al_2O_3–SiO_2 ternary system and the MgO–CaO–Al_2O_3–SiO_2 quaternary system by sol-gel techniques have been extensively used during recent years.[10,11] In this study, Bi_2O_3 was chosen as a sintering aid for its low melting point. Glass with composition in the quaternary primary phase field of MgO–CaO–Al_2O_3–SiO_2 (abbreviated as MCAS) system was prepared by sol–gel method. The first

purpose of the present investigation was to study the possibility of obtaining homogeneous glass powders in the $MgO–CaO–Al_2O_3–SiO_2$ quaternary system, with composition in the cordierite crystallization primary field. In addition, the aim was to know the influence of Bi_2O_3 addition on the mechanism of crystallization. Lastly, the effects of sintering temperature and Bi_2O_3 concentration on the microstructure, TCE, and dielectric characteristics of sintered MCAS glass ceramics were also developed.

2 EXPERIMENTAL PROCEDURES

In the present investigation, a homogeneous glass of composition containing (in wt%) MgO5%, CaO19%, $Al_2O_3$26%, and $SiO_2$50% (with an approximate stoichiometry of MgO : CaO : Al_2O_3 : SiO_2 = 6.5 : 14.5 : 27.5 : 51.5) was prepared by the sol–gel method. In a typical laboratory scale synthesis using the nitrates, colloidal silica was dispersed in 600 ml of deionised water and concentrated nitric acid was also added into the solution. To this acidic suspension we added magnesium nitrate hexahydrate, aluminum nitrate hexahydrate, and calcium nitrate hexahydrate. The subsequent addition of ammonium hydroxide resulted in the quantitative precipitation of magnesium, calcium, and aluminum hydroxides. The solids were collected by filtration and calcined at 300°C for 1 h. The calcination step was desirable to convert any ammonium nitrate present to oxides of nitrogen and water. The resulting material was a white, free-flowing powder, and the material was the MCAS glass precursor. MCAS composite glass containing 0, 1, 3 and 6% by weight of Bi_2O_3 were prepared by slurry method. The powder was dried, ground, and pressed to pellets uniaxially in a steel die. Typical dimension of the pellets were 15 mm in diameter and 1.5 mm in thickness. Sintering of these pellets was carried out at temperature between 870°C and 1000°C under ambient condition for a duration of 40 min.

The microstructure of the sintered specimens was observed under scanning electron micrograph (SEM). The crystalline structures of sintered MCAS glass ceramics were investigated using X-ray diffraction patterns. X-ray diffraction patterns were taken at $2\theta = 4°$ per minute using CuK_α radiation. The shrinkage of the sintered specimens were measured by a digital meter. The densities of sintered specimens as a function of sintering temperature with a sintering time of 40 min was measured by the liquid displacement method using deionised water as a liquid (Archimedes method). Thermal expansion coefficient (TEC) was measured by an automatic recording dilatometer. The range of testing temperature was from 250 to 700°C with a heating rate 300°C h^{-1}, using alumina as a standard. After painting silver paste on both sides of the specimens and firing at 700°C for about 20 min, dielectric properties were measured with a HP4192a impedance analyser. Dielectric constant was measured at 1 MHz.

3 RESULTS AND DISCUSSION

Using MCAS as the starting materials, the series of bismuth levels from 0 to 6 wt% was investigated to explore densification. The relationships between density and sintering temperature for various MCAS–Bi_2O_3 compositions are shown in Fig. 1. For MCAS with different amount of Bi_2O_3 addition, the sintered densification increased with the increase of sintering temperature. The density peaks (highest density) moved to lower sintering temperatures and the value of highest density increased as the contents of Bi_2O_3 addition increased. At 930°C, however, the densification of MCAS with 3 wt% and 6 wt% Bi_2O_3 added had gone to completion (Fig. 2). The prepared sample, but with no bismuth, showed full densification after 40 min at 1000°C. It was observed that all samples from 0 to 6 wt% went to essentially full density with cordierite and anorthite being the crystalline phases (Fig. 3).

The SEM photographs of MCAS glass ceramics sintered at 900°C and 930°C with different amounts of Bi_2O_3 addition were shown in Fig. 2.

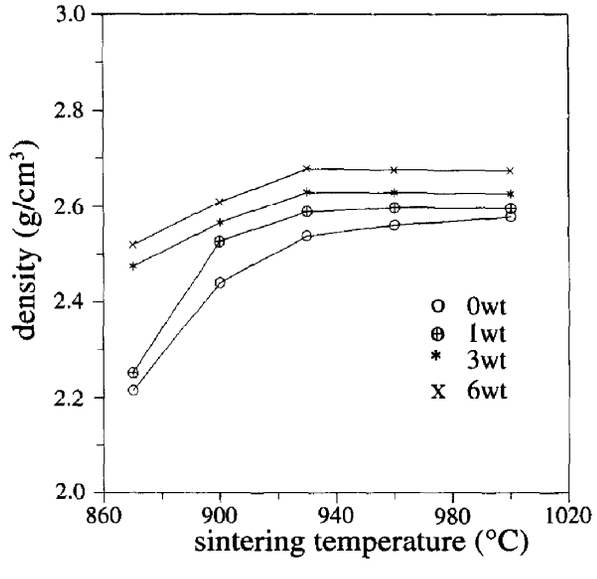

Fig. 1. Densities of sintered MCAS composite glass as a function of sintering temperature and amount of Bi_2O_3 addition.

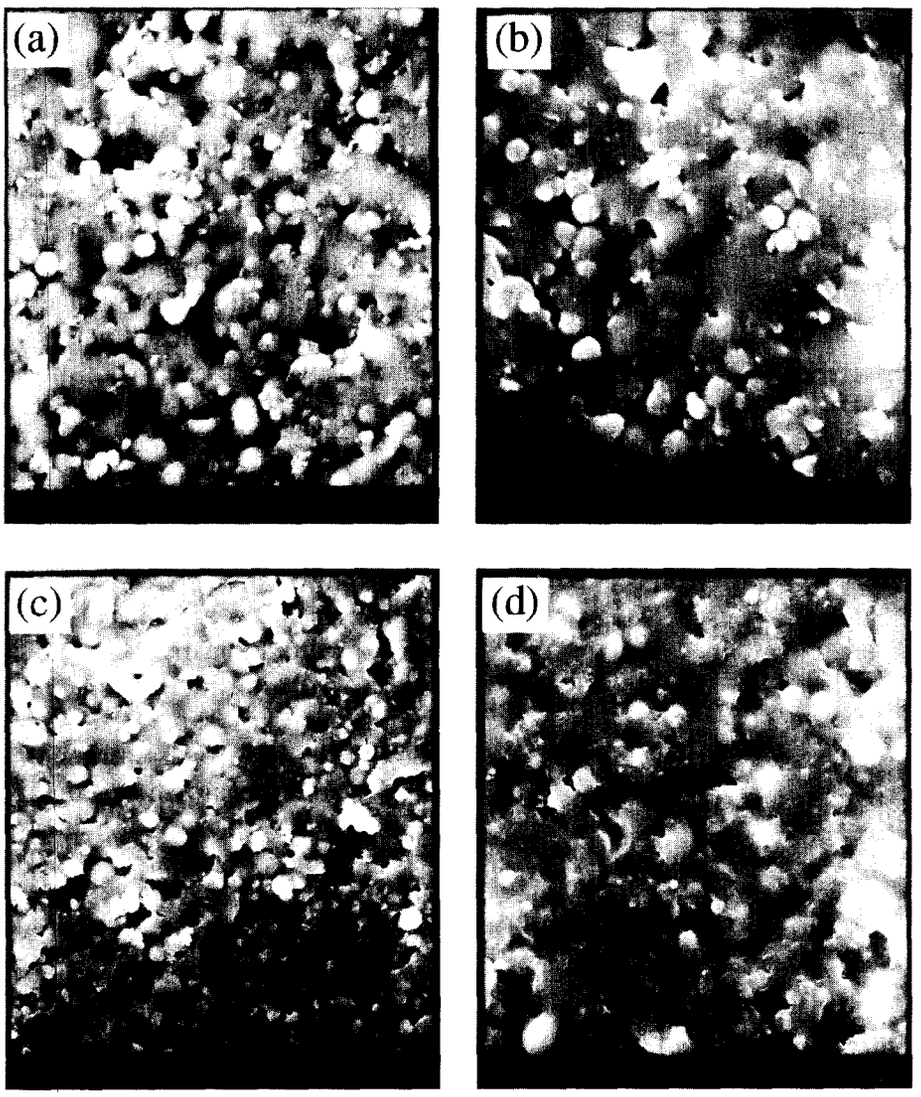

Fig. 2. Microstructures of MCAS specimens sintered at 900°C for (a) 0 wt% and (b) 6 wt% Bi_2O_3 addition, and sintered at 930°C for (c) 0 wt% and (d) 3 wt% Bi_2O_3 addition.

After firing at 900°C, the coalescence of glass particles resulting from viscous flow were easily observed and some isolated glass particles were still residual, as shown in Fig. 2(a) for MCAS with no Bi_2O_3 addition. Pore elimination and the enhancement of densification were promoted by the viscous flow of Bi_2O_3 as the amount of Bi_2O_3 addition was increased to 6 wt%, as shown in Fig. 2(b). For MCAS added with 0 wt% Bi_2O_3 and increased sintering temperature up to 930°C, however, the densification was not obviously increased, as Fig. 2(c) and (a) were compared. As 3 wt% Bi_2O_3 was added into MCAS and the compacts were sintered at 930°C, more complete densification promoted by the viscous flow of Bi_2O_3 was apparent and fewer unsightly pores were left on the surface of the sintered specimens as shown in Fig. 2(d). The MCAS composition with 3 wt% Bi_2O_3 added can be completely densified at about 930°C.

Investigation was begun to see how little bismuth oxide could be used as flux in MCAS composition and still form dense cordierite-based glass ceramics. To do this, X-ray diffraction analyses were used to determine the crystallization and reaction sequences for Bi_2O_3-added MCAS system. An experimental matrix was performed via XRD following crystallisation by varying the temperature between 870°C and 930°C, and these data are shown in Fig. 3. At a sintering temperature of 870°C, as shown in Fig. 3(a), no crystalline phases are revealed in 0 wt%-Bi_2O_3-added MCAS composite, although the samples have partially densified. As the amount of Bi_2O_3 addition increased, the reaction to form $MgAl_2O_4$ proceeded readily, and significant crystallisation of cordierite and anorthite was observed. When the sintering temperature is higher than 900°C, $MgAl_2O_4$ and the amount of glassy phase is reduced, the cordierite

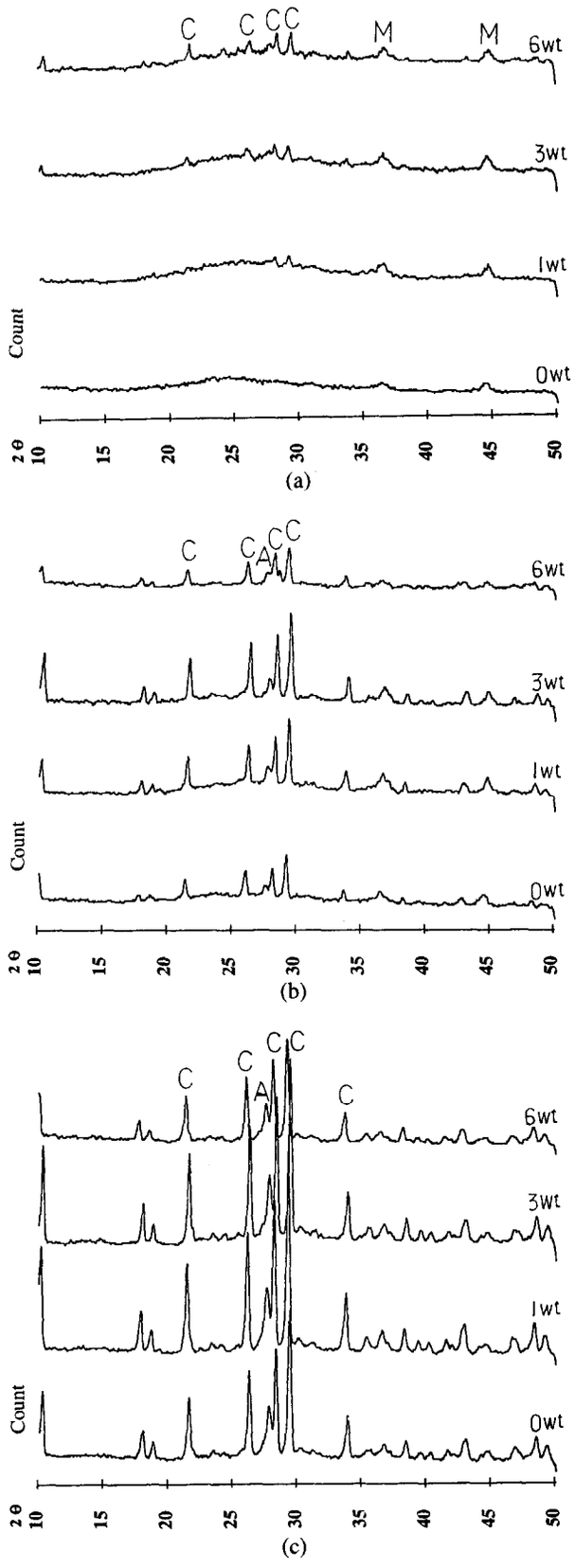

Fig. 3. X-ray diffraction patterns of MCAS-Bi_2O_3 composite glass sintered at (a) 870°C (b) 900°C, and (c) 930°C (A:anorthite, C:cordierite, M: $MgAl_2O_4$).

and anorthite are increased, as shown in Fig. 3(b) and Fig. 3(c). The recrystallization rates of cordierite and anorthite increased (0~3 wt% for 900°C and 0~1 wt% for 930°C) and then decreased (3~6 wt% for 900°C, 1~6 wt% for 930°C) with Bi_2O_3 concentration. Recalling that dilatometry shows rapid densification between 800°C and 930°C, it is clear that MCAS-Bi_2O_3 system fully densifies before crystallisation of cordierite and anorthite occur. At lower sintering temperature (900°C), the liquid-phase-sintering process is more pronounced, because the recrystallisation rates of cordierite and anorthite increase with the amount of Bi_2O_3 addition. For higher sintering temperature (930°C), because the flux of MCAS glass powder will increase with higher sintering temperature, the strongest recrystallisation rates of cordierite and anorthite are shifted to MCAS glass with a smaller amount of Bi_2O_3 addition. The experiments graphically demonstrate that Bi_2O_3 is indeed a useful flux for MCAS to prepare cordierite-based glass ceramics at lower temperature, but too much Bi_2O_3 is not necessary, because too much Bi_2O_3 will inhibit the recrystallisation rates of cordierite and anorthite.

The thermal expansion coefficients (TEC) of densified MCAS glass ceramics vs the amount of Bi_2O_3 addition are shown in Fig. 4. The thermal expansion coefficient of material depends on its densification, crystalline phases, and additives. The TEC value of MCAS glass ceramics without Bi_2O_3 addition and sintered at 1000°C was within 3.2–$4.5\times10^{-6}\,°C^{-1}$ range. The TEC values of MCAS glass ceramics with 1 wt% (sintered at 960°C), 3 wt% (930°C), and 6 wt% (930°C) Bi_2O_3 addition were within $3.3–4.8\times10^{-6}\,°C^{-1}$, $3.6–5.2\times10^{-6}\,°C^{-1}$, and $4.4–6.2\times10^{-6}\,°C^{-1}$ ranges, respectively. The varying ranges of densified Bi_2O_3–MCAS glass

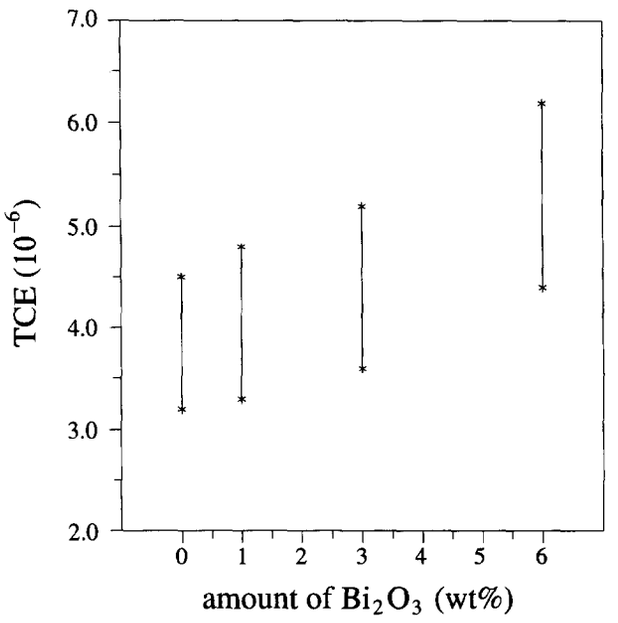

Fig. 4. Thermal expansion coefficient of densified MCAS-Bi_2O_3 composite.

ceramics increase with the amount of Bi_2O_3 addition. For specimens with higher amount of Bi_2O_3 addition, because the sintered ceramics are the near zero bulk modulus, the higher TEC value may be caused by the addition of bismuth oxide. One concern with using a flux is the possibility of substitution of the flux in the crystal lattice of the product. Evidence of substitution is not sought obviously by the thermal expansion coefficient. No matter the metals in the cordierite and anorthite structures are substituted by bismuth or not, the addition of Bi_2O_3 should cause the thermal expansion coefficient to increase because the thermal expansion coefficient of Bi-O bond is much larger than that of Si–O bond.[9]

The dielectric constant response of MCAS glass ceramics is measured as a function of sintering temperature and amount of Bi_2O_3 addition, and the measured data are shown in Fig. 5. For a glass ceramic material, many factors will affect permittivity most significantly, including the contents of the individual crystalline and glass phases, and the level of porosity or the degree of densification. The dielectric constant of undoped MCAS glass ceramics was slightly larger than the value of pure cordierite of 5.0. Larger change in the dielectric constant was observed for specimens fired below 930°C. These results are attributed to the liquid phase effect of Bi_2O_3 addition to promote densification, for that is evidenced from the relationships of density and sintering temperature (Fig. 1). In comparison of Fig. 5 with Fig. 1, the effect of sintering temperature on dielectric constant is similar to that on density. As the sintering temperature increased, the dielectric constant increased. The increase in dielectric constant is attributed to the increase of densification or the elimination of porosity. However, as firing temperature was higher than 960°C and Bi_2O_3 addition was less than 1 wt%, despite of the reduction of porosity that should result in an increase in dielectric constant, the dielectric constant decreased. The reduction of dielectric constant is attributed to the crystallisation of α-cordierite. As the Bi_2O_3 addition was more than 3 wt%, the dielectric constant was increased with the sintering temperature and then saturated at about 930°C. As Fig. 5 shows, the dielectric constants of Bi_2O_3-added MCAS glass ceramics sintered to >98% theoretical density (1000°C, 960°C, 930°C, and 930°C for MCAS with 0 wt%, 1 wt%, 3 wt%, and 6 wt% of Bi_2O_3 addition, respectively) are increased with the increase of Bi_2O_3 content. Besides heat treatment, another factor affecting the dielectric constants of the sintered MCAS specimens is the content of Bi_2O_3 addition. Although the phase of bismuth oxide in the sample is not known, it most likely has a dielectric constant between 12~14, which is the range for the crystalline phases.[9] No matter that Bi_2O_3 was continuously or discontinuously dispersed in the MCAS glass ceramics, by using the logarithmic mixture rule,[12] Bi_2O_3 addition is thought to be the reason that causes the increase in dielectric constant.

The variation of average flexural strengths of densified Bi_2O_3–MCAS glass ceramics is shown in Fig. 6. The average flexural strength showed a slight decrease with the increase of Bi_2O_3 addition from 0 wt% (sintered at 1000°C and 205 MPa) to 3 wt% (930°C, 192 MPa), but showed a larger decrease with the increase of Bi_2O_3 from 3 wt% to 6 wt% (930°C, 170 MPa). There are many factors

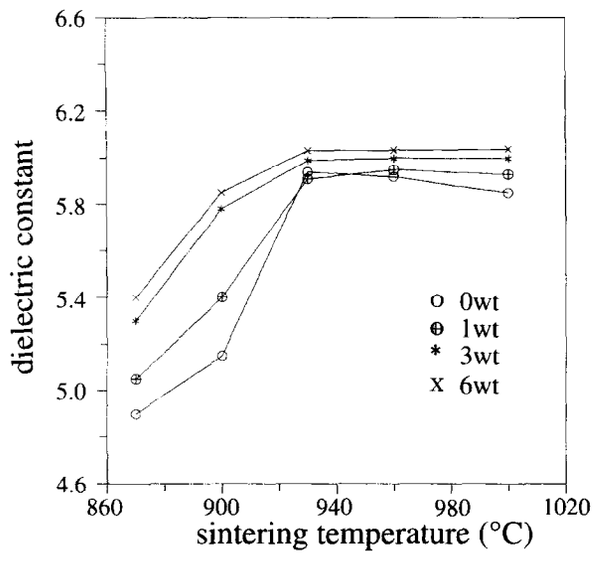

Fig. 5. Dielectric constants versus sintering temperatures and amount of Bi_2O_3 addition.

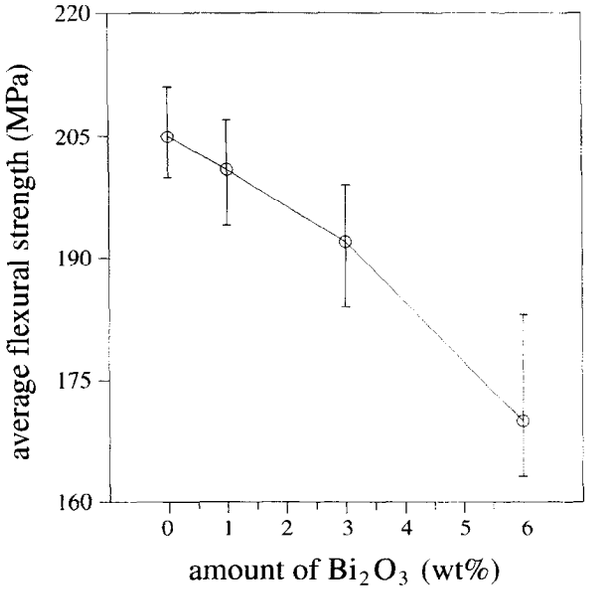

Fig. 6. The flexural strengths of densified MCAS glass ceramics as a function of Bi_2O_3 amount.

that influence the flexural strengths of porous and densified ceramics. For example, the flexural strengths of polycrystalline ceramics increase with decreasing grain size and pore fraction. The major effect of the structure in most ceramics is the result of porosity. Pores obviously decrease the cross-sectional area on which the load is applied but also act as stress concentrators. For densified Bi_2O_3–MCAS glass ceramics, the specimens showed a nearly complete densification and the sintered surfaces did not show any significant difference. There must be a different reason than pore fraction and grain size that will influence the flexural strength. In polycrystalline ceramics, the particles may affect strength because of a difference in moduli or thermal expansion coefficients between glass and added particle present in the body, giving rise to boundary stress.[13] Because Bi_2O_3 had a larger thermal expansion coefficient, the decrease of average flexural strength may be caused by the addition of Bi_2O_3. Although flexural strength of this Bi_2O_3-added MCAS glass system decreases with the increase of Bi_2O_3 amount, yet the sinterability of MCAS glass composite can be effectively improved by Bi_2O_3.

4 CONCLUSIONS

1. With the addition of Bi_2O_3, the sinterability of MCAS glass powders was greatly improved. For specimens to which 3 wt% Bi_2O_3 has been added, densification can be completed at about 930°C.
2. Too much Bi_2O_3 addition (more than 3 wt%) will inhibit the recrystallisation rates of cordierite and anorthite.
3. The amount of Bi_2O_3 addition will dominate both the densification and dielectric constant of MCAS glass ceramics.
4. The shortcoming of the addition of Bi_2O_3 in MCAS composite glass is the decrease in flexural strength and the increase in the thermal expansion coefficients and dielectric constants, and the varying range of TEC values also increases with the amount of Bi_2O_3 addition.

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