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Seeding effects on crystallization temperatures of cordierite glass powder

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The role of solid state epitaxy in the crystallization of nanocomposite cordierite glass to glass ceramic was investigated. The use of isostructural (α-cordierite) seeds in cordierite glass led to a lowering in the crystallization temperature to form glass ceramic by about 50 °C compared to the unseeded glass. The use of non-isostructural seeds such as ZrO_2 and TiO_2 did not lower the crystallization temperature of cordierite glass to glass ceramic, and in the case of the TiO_2-seeded glass the crystallization temperature increased by about 50 °C compared to the unseeded α-cordierite glass. The lowering in crystallization temperature by α-cordierite seeding can be attributed to the nucleation and epitaxial growth mechanism.

1. Introduction

The well known technology of the production of bulk glass-ceramic articles of varying sizes is based on the controlled crystallization of glasses between their glass transition temperatures and melting points [1–3]. Often a few per cent of oxides such as TiO_2, ZrO_2 and P_2O_5 are added to these glass-forming systems [2]. This results in glass ceramics with a large number of fine crystals, attributed to the heterogeneous nucleating characteristics of these oxides, although they do not appear in the nucleating step. Roy [4] proposed a radically different explanation: that metastable liquid immiscibility may be the cause of very fine segregation and fine-structured crystallization in all such systems. This was experimentally confirmed by Porai-Koshits and coworkers [5]. In recent years, Roy *et al.* [6–8] have studied the effects of seeds in monophasic and multiphasic gel powders, which provided unambiguous evidence for the use of isostructural foreign crystalline nuclei as the basis for fine-microstructure crystallization of amorphous solids. It was shown that multiphasic xerogels, enhanced densification of ceramics, and introduction of epitaxial substrate or seed accelerated the kinetics of formation of a thermodynamically stable solid phase, because epitaxial seeds catalyse the growth of a phase by providing a large number of nuclei with the structure of the desired phase. The epitaxial crystallization has been clearly demonstrated in $ThSiO_4$ gels [9] seeded with either huttonite or thorite.

The effect of isostructural and non-isostructural seeds on glass crystallization, however, has not so far been investigated. The manufacture of glass ceramics, by sintering of glass powder, is suitable for the production of small quantities of articles of complicated shapes such as heat exchangers [10]. For instance, if these glasses crystallize from their surface, as in cordierite glass powder, the significant surface area of glass powder ensures very fine-structured crystallization. Seeding by the crystals of the final equilibrium phase or others may help to enhance or regulate the process.

In order to determine the role of nucleation and epitaxial growth in nanocomposite glasses, a study of seeding effects on cordierite glass powder was undertaken. Seeds such as α-cordierite, ZrO_2 and TiO_2 were added to the glass powder, and the phase-transformation mechanism was monitored by differential thermal analysis (DTA) and X-ray diffraction (XRD).

2. Experimental procedure

2.1. Preparation of bulk cordierite glass and fine powder

Bulk cordierite glass was prepared from monophasic cordierite gel; the gel preparation has been discussed in detail elsewhere [11, 12]. Cordierite gel was placed in a 50-ml platinum crucible and heated at 350 and 700 °C to decompose organics and nitrates, respectively. The decomposed material was transferred to a molybdenum disilicide furnace which was kept at 1200 °C. The temperature was then increased to 1600 °C and maintained at this temperature for 12 h. The glass melt in the platinum crucible was removed from the furnace and was shaken occasionally to remove the bubbles and to obtain better homogeneity. Homogeneous cordierite glass rods were formed by pouring the melt into brass moulds, kept at room temperature. The cordierite glass was powdered and sieved through a -325 mesh. Fine powders were produced by further grinding in a Spex mixer/mill (Spex Industries, Metuchen, New Jersey) using methacrylate balls. These powders were then suspended in alcohol and the suspension was collected and dried to obtain fine glass particles.

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2.2. Preparation of seeds

α-Cordierite was prepared by heating cordierite gel to 1300 °C for 12 h. The crystalline material was powdered using an agate pestle and mortar. The powder was suspended in water for several hours to yield an agglomerate-free suspension of fine seed particles (0.05–0.5 μm). Hydrothermally prepared tetragonal ZrO_2 seeds (50–80 nm) were obtained from Chichibu Cement Co, Japan. Anatase seeds (60–100 nm) were prepared by heating TiO_2 gel suspended in water (5 g of gel in 100 ml of water) in a Parr bomb at 150 °C for 3 days. The particle sizes of different seeds were determined using a Phillips 420 transmission electron microscope.

Seeded glass powders were made by thoroughly mixing the powders and appropriate quantities of seeds in alcohol using an agate pestle and mortar. The thermal reactions of the seeded and unseeded glasses were studied by a Perkin Elmer (Model DTA 1700) differential thermal analyser. X-ray diffraction of powder samples heated at various temperatures was carried out using a Scintag USA (Santa Clara, CA) Pad-V diffractometer with Ni filtered CuK_α radiation. The relative intensity of α-cordierite (1 0 0) peak, expressed in arbitrary units, was obtained by comparing the area of the α-cordierite (1 0 0) peak and that of a standard (quartz (1 0 0) peak). The areas of these peaks were calculated by collecting the XRD data at 0.1° 2θ min^{-1} and integrating these data points using the area program of the Scintag (XDS) Fortran IV software package.

3. Results and discussion

3.1. Differential thermal analyses

Fig. 1 shows the DTA curves generated when bulk cordierite glass and cordierite glass powder, without seed and with seeds such as α-cordierite, TiO_2 and ZrO_2, are heated at 10 °C min^{-1}. The less predominant endothermic shifts observed between 820 and 840 °C in all cases are associated with the glass transition temperature of cordierite glass. On further heating, in contrast, prominent features such as two characteristic exothermic peaks were observed (Fig. 1) which are attributed to the formation of μ-cordierite at about 940 °C and α-cordierite at about 1000 °C, based on the following XRD experimental data. These results are consistent with those reported elsewhere [13–15]. In particular, the XRD data of Mussler and Shafer [13] indicated that cordierite glass powder started crystallizing at about 880 °C while α-cordierite began forming around 1000 °C which attained a maximum value at 1046 °C. For the bulk glass (Fig. 1a), the two overlapped crystallization exotherms are seen at 1075 and 1095 °C which are shifted towards lower temperatures for finely ground glass powder (Fig. 2b). This may be explained by the known surface crystallization mechanism of cordierite glass. Furthermore, in the latter case, the peaks are well separated: that is, the temperature difference between the crystallization exotherms of μ-cordierite and α-cordierite is large because in the lower temperature regime a longer temperature interval is necessary for attainment of the maximum heat of crystallization of α-cordierite. Figs 1c, d, and 3e show the DTA curves for cordierite glass powder seeded with 5 wt % α-cordierite, ZrO_2 and TiO_2, respectively. Addition of seed did not seem to affect the maximum in the crystallization temperature of μ-cordierite, while the μ-cordierite to α-cordierite transformation temperature decreased for cordierite glass powder seeded with α-cordierite. On the contrary, the transformation temperature increased slightly for cordierite glass powder seeded with ZrO_2

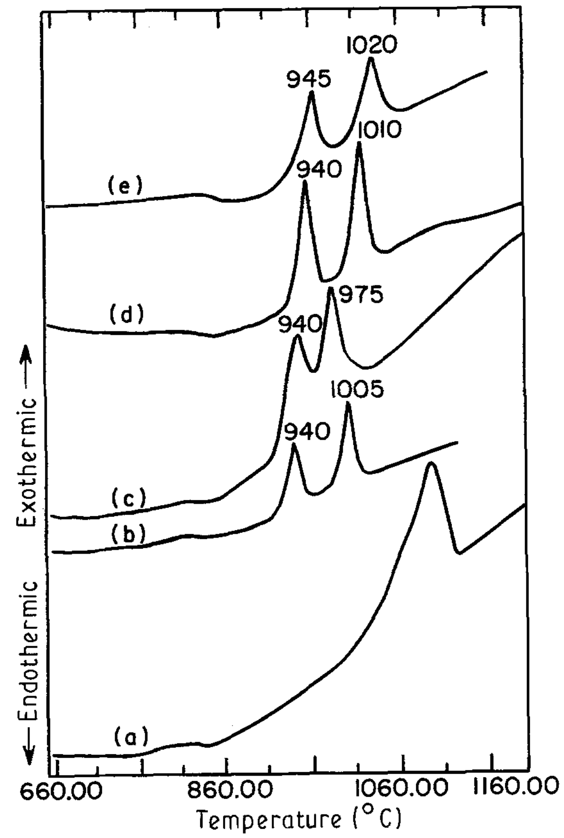

Figure 1 DTA curves at 10 °C min^{-1} for cordierite glasses: (a) bulk sample; (b) powder sample; (c) powder seeded with 5 wt % α-cordierite; (d) powder seeded with 5 wt % ZrO_2; and (e) powder seeded with 5 wt % TiO_2.

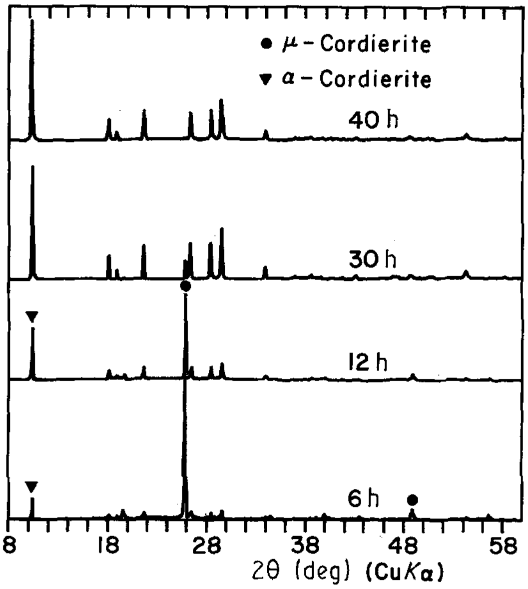

Figure 2 Powder XRD patterns as a function of heat treatment time (h) for cordierite glass powder seeded with 5 wt % α-cordierite, calcined at 875 °C.

and TiO_2 (Fig. 1). Similar effects have been observed in a number of gels seeded with isostructural and non-isostructural seeds [6–8]. The magnitude of lowering in crystallization temperature by isostructural seeding in glasses found here is markedly lower than that in gels [6]. The isostructural and non-isostructural seeding effects became quite clear when these seeded glass pellets were sintered at various temperatures for longer times and the crystallization mechanism was followed by XRD.

3.2. X-ray diffraction analyses

Fig. 2 shows the XRD patterns for glass seeded with 5 wt % α-cordierite, calcined at 875 °C for different lengths of time. It can be seen from Fig. 2 that μ-cordierite transformed completely to α-cordierite within ~ 40 h at 875 °C. However, under similar conditions glass seeded with 5 wt % TiO_2 and ZrO_2 exhibited no evidence for the formation of α-cordierite, although seeded and unseeded glass powders showed the formation of μ-cordierite when heated at 850 °C for 6 h while ~ 5 wt % of α-cordierite was formed in the unseeded glass powder. The transformation of μ-cordierite to α-cordierite is further confirmed by plotting the relative intensity of α-cordierite (1 0 0) peak of seeded and unseeded glasses calcined at 875 °C for different durations (Fig. 3). The trend in Fig. 3 clearly indicates that isostructural α-cordierite seeds catalyse the transformation of μ-cordierite to α-cordierite by providing nuclei of α-cordierite. As a result, the crystallization temperature of α-cordierite is lowered, which is presumably due to solid-state epitaxial growth. The lowering of the crystallization temperature by seeding is also associated with enhanced densification at lower temperatures for a number of monophasic and multiphasic gels, which resulted in lower ceramic processing temperatures. We therefore plan to investigate the densification details of these nanocomposite glass materials at a later date.

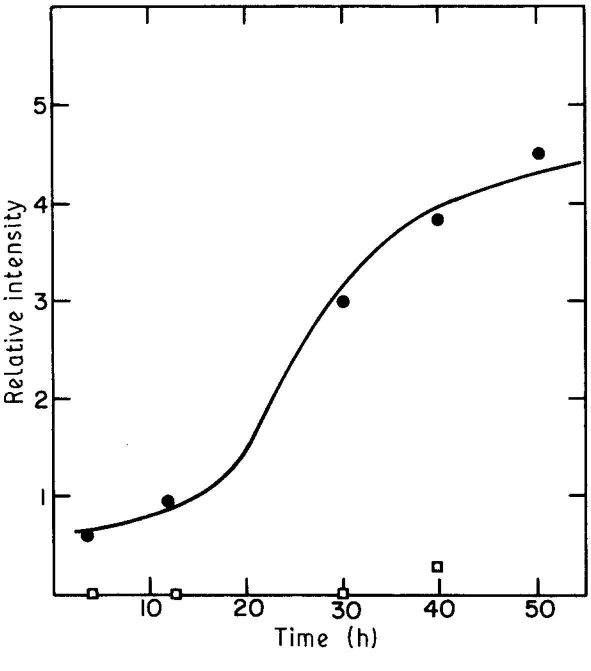

Figure 3 Relative intensity of α-cordierite (1 0 0) peak in comparison with a standard, quartz (1 0 0) peak, heated at 875 °C for different times for cordierite glass powder (☐) without seed and (●) with 5 wt % α-cordierite seed.

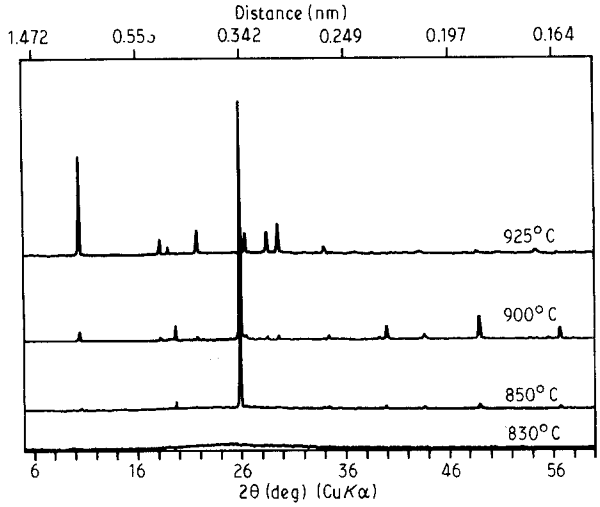

Figure 4 Powder XRD patterns for unseeded cordierite glass powder as a function of temperature at a constant heating time (6 h).

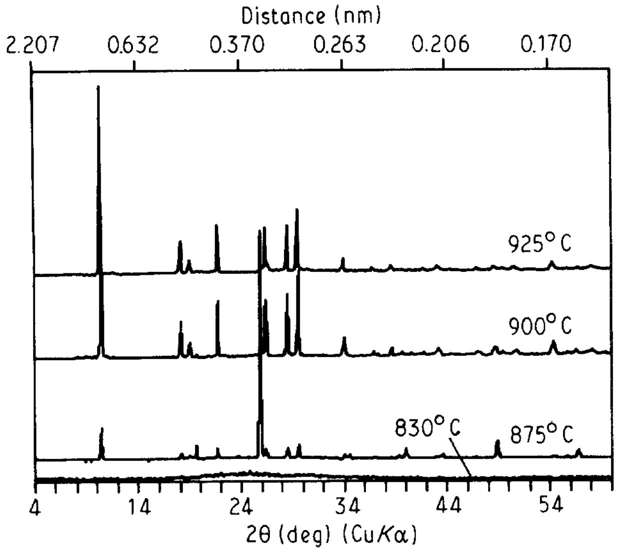

Figure 5 Powder XRD patterns for 5 wt % α-cordierite seeded cordierite glass powder as a function of temperature at a constant heating time (6 h).

The phase evolution for seeded and unseeded cordierite glass powders at various temperatures, but at a constant heating time of 6 h, is depicted in Figs 4–7. These powders remain amorphous up to 830 °C. All these glass powders crystallized to μ-cordierite at 850 °C, while the unseeded (Fig. 4) and α-cordierite (Fig. 5) and ZrO_2 (Fig. 6) seeded glasses transformed completely to α-cordierite at 925 °C. On the contrary, TiO_2-seeded glass powder (Fig. 7) exhibited a definite 'negative catalyst effect': it crystallized to α-cordierite only at 1000 °C. The difference in the crystallization temperature of α-cordierite for glasses seeded with TiO_2 and α-cordierite is approximately 100 °C. The reason for the negative catalyst effect of TiO_2 is not understood. A similar interesting effect has been observed in the crystallization of zircon seeded with α-$ThSiO_4$ [9].

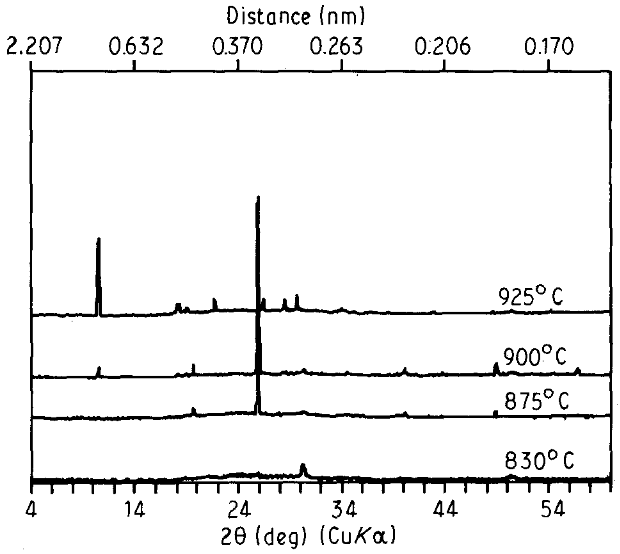

Figure 6 Powder XRD patterns for 5 wt % ZrO_2 seeded cordierite glass powder as a function of temperature at a constant heating time (6 h).

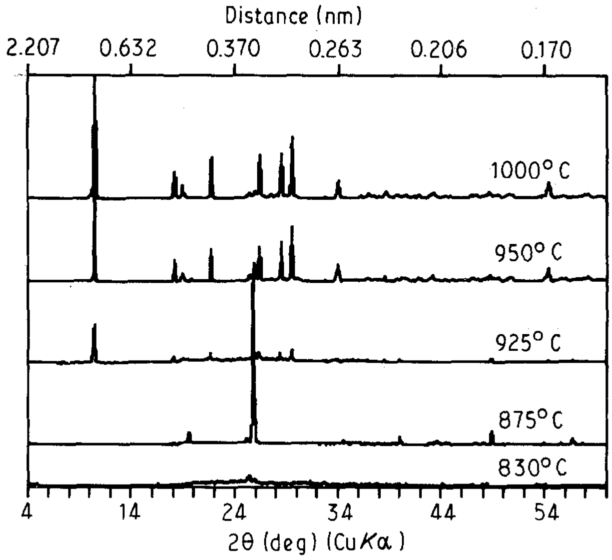

Figure 7 Powder XRD patterns for 5 wt % TiO_2 seeded cordierite glass powder as a function of temperature at a constant heating time (6 h).

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