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Sintering and crystallization behaviour of a glass powder and block with a composition of anorthite and the microstructure dependence of its thermal expansion

BONGI RYU
Department of Inorganic Materials Engineering, Pusan National University, 30 Jangjeon-Dong, Kumjung-Ku, Pusan 609-735 Korea

ITARU YASUI
Institute of Industrial Science, University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo 106, Japan

Two kinds of glass specimens were prepared in the form of powders and blocks with anorthite compositions, and an examination was made of the sintering and crystallization behaviour of the specimens and the microstructure dependence of their thermal expansion. It was found that the addition of a few wt% of TiO_2 was necessary to obtain a good sintered body by heat treatment at 1050°C. Specimens with low expansion coefficients were obtained when no TiO_2 was added and when the grain size of the starting glass powder was large (ca. less than 180 μm). It was estimated that this was mainly due to the presence of orthorhombic and hexagonal anorthite in the central part of each grain. In order to explain the abnormally low expansion coefficient of the sintered specimens, the crystallization behaviour of glass blocks with the same composition was examined. The crystallization proceeded by two mechanisms: the triclinic phase precipitated from the surface, and the orthorhombic and the hexagonal phase precipitated from the central part of the specimens. The orthorhombic phase showed a strong tendency for a preferred orientation, and the thermal-expansion measurements showed strong anisotropy. The addition of TiO_2 to the mother glass suppressed the precipitation of the orthorhombic and hexagonal phases, and the resultant pieces were composed mainly of the triclinic phase; the thermal-expansion coefficient became isotropic.

1. Introduction

Systems of glass powder + ceramic powder such as borate or lead-borate glass powder + alumina [1, 2] were investigated as substrate materials for applications in which lower sintering temperatures are required. Recently, a glass powder with the composition of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) was fully investigated [3, 4, 5, 6] as the starting material for substrates without the addition of any ceramic powders. This kind of system seems to have several advantages, such as the lack of a reaction between the ceramic and glass powders, and the sintering process for the glass and the crystallization process can be operated at different temperatures. In this study, the possibility of using glass powder with the composition of anorthite [7, 8, 9, 10] as the starting material for low-sintering-temperature substrates is examined from the viewpoints of sintering behaviour, crystallization behaviour, the effects of the addition of TiO_2 as a nucleation reagent, etc.; and in order to explain anomalous behaviour in the thermal-expansion coefficient of sintered bodies obtained from the glass powder, the crystallization of glasses with the same composition as anorthite was studied.

2. Experimental procedure

The glass composition was fixed at that of anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$. In order to examine the effect of nucleation, 3–10 wt% of TiO_2 was added with the other compositions unchanged. A mixture of $CaCO_3$, Al_2O_3, SiO_2, (TiO_2) was melted in a Pt–Rh crucible at 1650 °C for 24 h. The melts were quenched by using a twin-roller-type apparatus and the resultant flakes were crushed, ball milled and sieved to obtain two kinds of glass powders, whose maximum grain sizes were 10 μm (10P) and 180 μm (180P). The glass-transition temperatures and crystallization temperatures were examined by means of differential thermal analysis (DTA) (DTA-50 Shimadzu Company). The glass powders were pressed into the shape of pellets of 20 mm diameter and about 2 mm thick with a pressure of 450 $kg\,cm^{-2}$. In order to find out whether a two-step-type heating schedule was effective in obtaining good sintered bodies, the heating schedule was determined in two steps: for the first step, the specimens were heat treated for 2 h at temperatures ranging from 850 to 975 °C, and for the second step the temperature was fixed at 1050 °C for 2 h. The sintered bodies were evaluated by the measurement of the densities and expansion coefficients, and the crystalline phases were identified with an X-ray powder diffraction method. The density was calculated from the dimensions of the outer shape and the weight of the pellets.

The melt, on the other hand, was poured into a steel mould to make block specimens. The block samples thus obtained were 25 mm in diameter and about 6 mm thick.

The glass sample was then heat treated with the following two-step heating schedule: at 950 °C for 2 h and then at 1050 °C for 2 h. The complicated microstructure was observed with an optical microscope. Two procedures were adopted to clarify the microstructure and the preferred orientation of the crystals: (i) sequential polishing from the surface of the block sample to examine the crystal phases, and (ii) examination of the texture and properties of a small sample cut from the central part of the glass-ceramics. The polished surface and the surfaces of the small sample cut from the central part of the glass sample was examined by means of X-ray diffraction (XRD) (Rigaku Denki). The preferred orientation of the crystalline phase was deduced from the intensities of the peak in X-ray powder diffraction patterns in a comparison with the standard specimen without orientation. The expansion coefficients for both samples were measured with a dilatometer (TMA-50 Shimadzu Company) for the temperature range 100–200 °C.

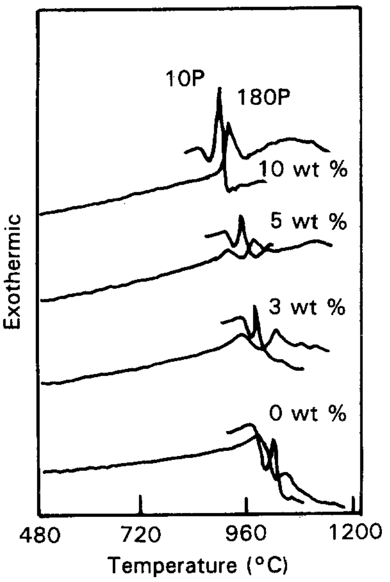

Figure 1 The change in the DTA-measurement curves for glass powders with different TiO_2 concentrations (0, 3, 5, and 10 wt %) and grain sizes (10P, 180P).

3. Results and discussion

3.1. Sintered bodies

3.1.1. T_g and T_x of glasses

Fig. 1 shows the change in the DTA-measurement curves for the glass powders with different TiO_2 concentrations and grain sizes. The crystallization temperatures and glass-transition temperatures, T_g, went down markedly with the addition of TiO_2. The grain size affected the crystallization temperatures: the glass powders with the smaller grain size (10P) exhibited a lower crystallization temperature, which may be attributed to the difference in the area of the surface which is the initiation site for surface crystallization.

3.1.2. Heat-up schedule and sintering behaviour

Fig. 2 summarizes the results of volume changes due to the heat treatment of pellets synthesized from the glass powder with grain sizes under 10 µm (10P). The dimensions of the pellets started to decrease in size with the heat treatment at 850 °C, and at 900 °C the sintering process seemed to be complete. For the specimens without TiO_2, the sintered bodies were translucent and seemed to consist of large crystallines even after the second sintering procedure at 1050 °C; they seem not to be suitable for use as substrates. The addition of 10 wt % of TiO_2 resulted in undesirable phenomena: after the second heat treatment at 1050 °C, the densities decreased due to some microscopic pores created by the crystallization of anorthite. The densities of the pellets obtained after the first stage of heat treatment for the specimen with 10 wt % TiO_2

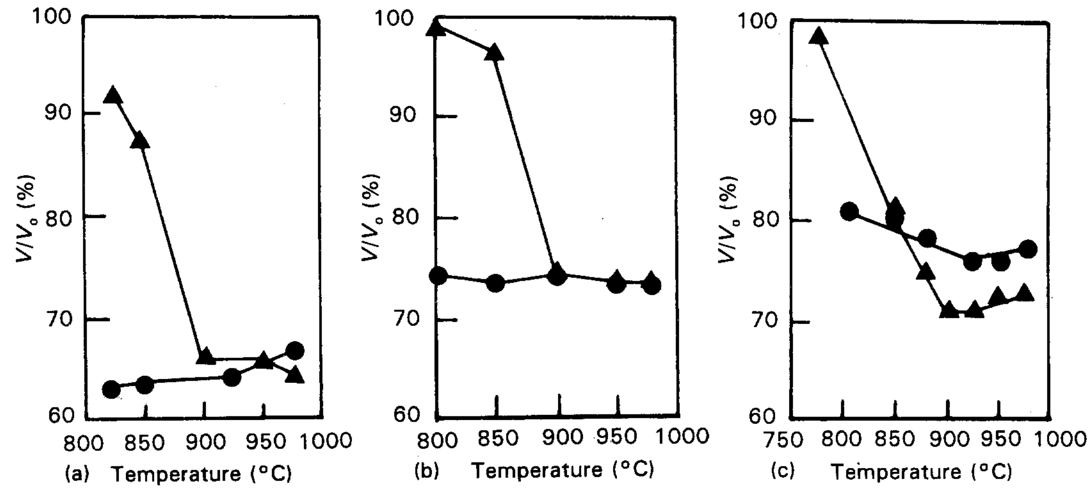

Figure 2 Volume changes of the pellets resulting from heat treatment with different amounts of TiO_2: (a) 0 wt %, (b) 3 wt %, and (c) 10 wt %; (▲) first step, and (●) first and second steps. (1050 °C.)

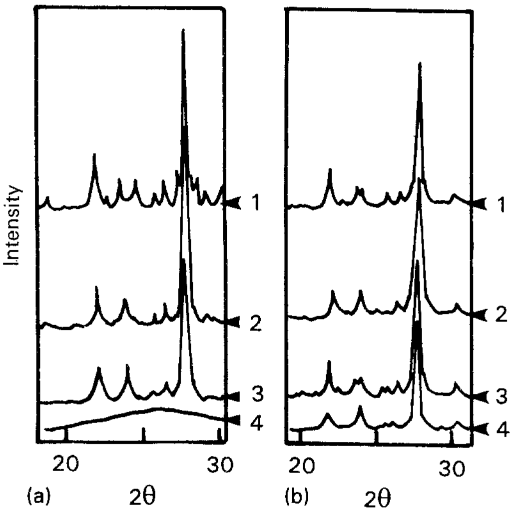

Figure 3 XRD patterns of each specimen with different TiO_2 concentrations: (a) 0 wt %, and (b) 10 wt %. For heat treatments (1) 950 + 1050 °C, (2) 850 + 1050 °C, (3) 950 °C, and (4) 850 °C.

were not low enough when compared with the specimens without TiO_2. This can be explained by Fig. 3, which shows XRD results for the specimens. The addition of TiO_2 lowered the crystallization temperature, and even for the heat treatment at 850 °C large amounts of anorthite were found in the specimen. The presence of crystalline-phase anorthite usually makes viscous flow of the specimen difficult and hindered the specimen to be dense enough. The optimum concentration of TiO_2 judged from the viewpoints of texture and strength of the sintered specimen was less than 3 wt %, and the corresponding volume decrease is shown in Fig. 2b.

3.1.3. *Abnormal behaviour in the thermal-expansion coefficient*

The thermal-expansion coefficients of sintered specimens without TiO_2 had remarkably low values when compared with specimens containing TiO_2. In order to explain this, additional experiments with higher temperatures at the second heat treatment were made. Fig. 4 summarizes the results showing the dependence of the thermal-expansion coefficients on the temperatures. It was found that the specimens heat-treated at about 1000–1050 °C clearly had low values of the thermal-expansion coefficient. XRD revealed that these specimens consisted mainly of hexagonal and orthorhombic phases of anorthite. The thermal-expansion coefficient of specimens made from glass powders with larger particle sizes (180P) had lower values than the smaller particles (10P). Abnormal decreases in the thermal-expansion coefficient gradually disappeared with the addition of TiO_2. It is therefore estimated that the low values in thermal expansion are due to the hexagonal and the orthorhombic phases of anorthite which were precipitated in the central part of each particle. We assumed that the disappearance of abnormal decreases in the thermal-expansion coefficient would be related to the decrease in the ratio of the hexagonal and orthorhombic phases to the triclinic phases when TiO_2 was added.

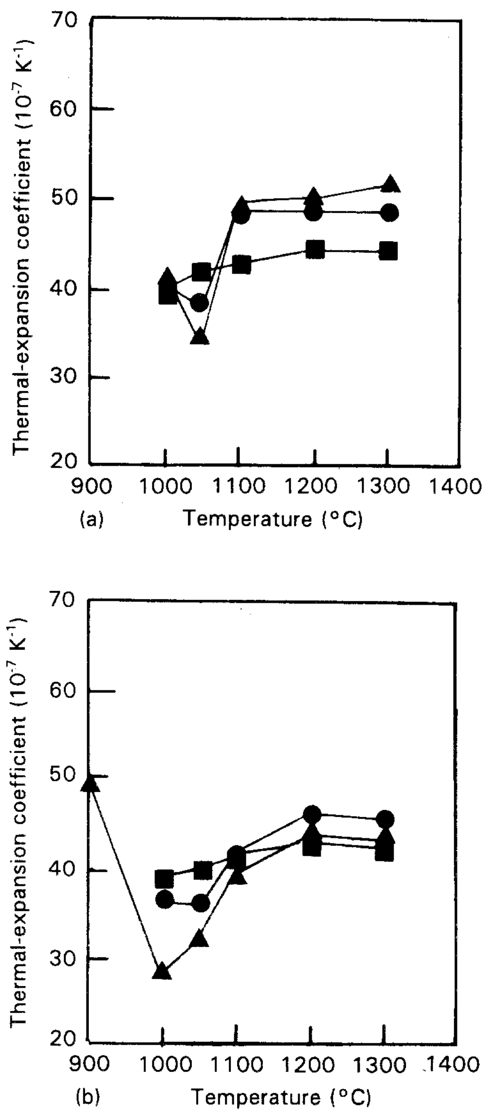

Figure 4 The dependence of the thermal-expansion coefficient for each temperature in resultant samples: (a) 10P, and (b) 180P. (▲) 0 wt %, (●) 3 wt %, and (■) 10 wt %.

3.2. Bulk samples

3.2.1. *Description of the specimens*

Fig. 5 a, b, and c show optical micrographs of the specimens without the addition of TiO_2, which were heat-treated at 1050 °C for 0.6 h, 2 h, and 12 h, respectively. A close examination revealed that the specimen consisted of three parts with different textures. Fig. 5b shows the microstructure in more detail by means of XRD. The layer at the surface, whose thickness was about 1.0 mm, was found to consist mainly of the triclinic phase of anorthite without a preferred orientation. After polishing off this surface layer, the sample was again examined by XRD. The main crystalline phase at the second and third layers was a mixture of hexagonal and orthorhombic phases of anorthite, as shown in Fig. 6. Although the second and third layers were opaque and transparent in optical observation, both of these layers, however, were found, by XRD, to consist of the same crystalline phases. The specimens

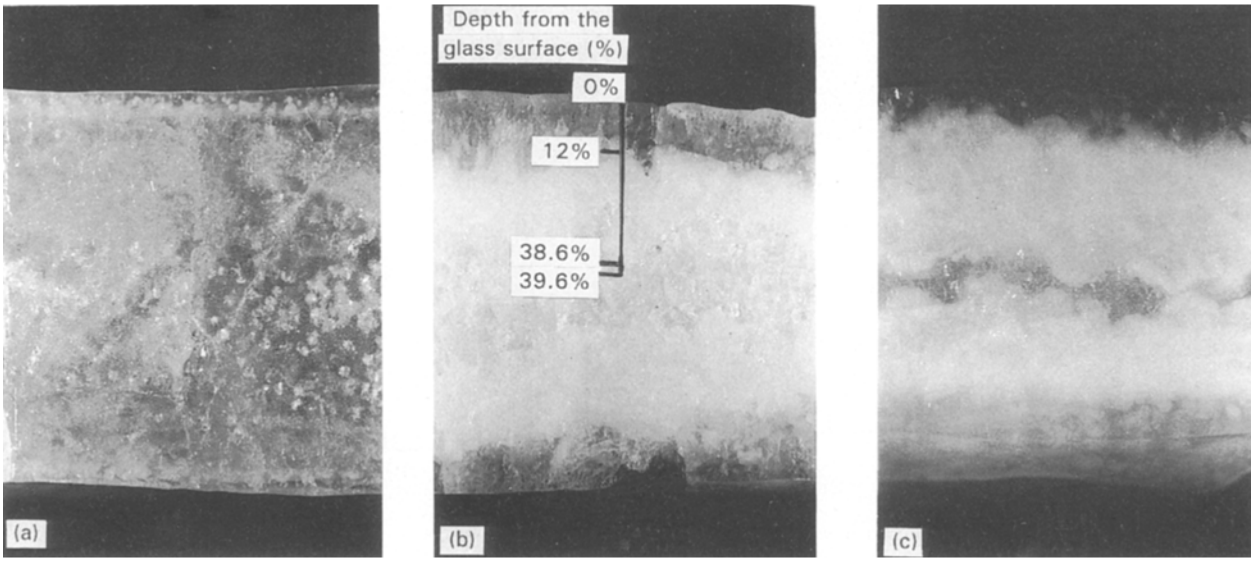

Figure 5 Optical micrographs of specimens without the addition of TiO_2, which were heat-treated at 1050 °C for: (a) 0.6 h, (b) 2 h, and (c) 12 h.

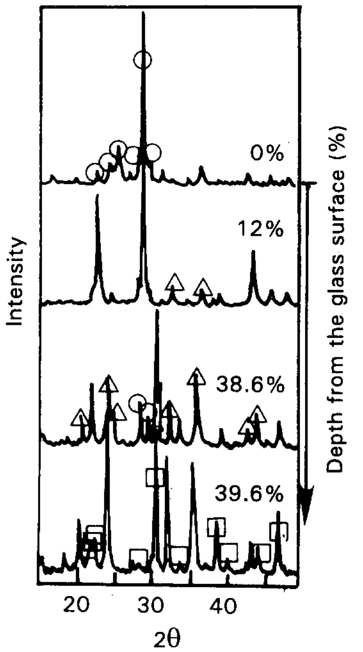

Figure 6 XRD patterns of the crystalline phase at each layer: (○) triclinic, (△) hexagonal, and (□) orthorhombic.

with the addition of TiO_2, on the contrary, consisted mainly of triclinic anorthite throughout every part of the specimens, which was also revealed by XRD. Fig. 7 shows optical micrographs of the specimens with specified amounts of TiO_2; the addition of 3 wt % was even sufficient to initiate uniform crystallization.

3.2.2. Anisotropy in the thermal-expansion coefficient

A small cut-out specimen from the central part of the glass-ceramics prepared from a glass without the addition of TiO_2, which was found to consist of hexagonal and orthorhombic phases, was examined in more detail to study the relation between the thermal-expansion coefficient and the preferred orientation of crystals. Fig. 8 illustrates the geometrical relationship between the small cut-out specimen and the whole pellet.

Fig. 9 shows the thermal-expansion coefficient of the small specimen along with the other similar specimens with the addition of 3–10 wt % of TiO_2. The specimen with no TiO_2 showed a large anisotropy in its thermal-expansion coefficient; measurement along the A–A′ and C–C′ directions showed larger thermal-expansion coefficients than for measurements in the B–B′ direction. When 3–10 wt % of TiO_2 was added to the mother glass, the thermal-expansion coefficient of the small cut-out piece was almost isotropic and the value was itself smaller. The decrease in the thermal-expansion coefficients with the addition of TiO_2 was also observed in the case of glasses shown in Fig. 9 by (▲). The main crystalline phase in the glass–ceramics prepared from the glasses with 3–10 wt % TiO_2 was triclinic, and in the case of the glasses with no TiO_2 the main phase was orthorhombic with some amounts of the hexagonal phase. This difference in the crystalline phases will explain the sudden decrease in the thermal-expansion coefficient and its isotropic nature with the addition of TiO_2.

Each surface of the small cut-out piece was examined by XRD. Fig. 10 summarizes the results; the most prominent difference in the X-ray powder diffraction patterns was the presence of a (1 3 0) peak of orthorhombic phase in the measurement of surface (A) which is perpendicular to the direction of A–A′ and the presence of a (0 4 1) orthorhombic phase in the diffraction of surface (C). (Surface (B) and (C) are perpendicular to directions B–B′ and C–C′, respectively.) This result strongly suggests that the orthorhombic phase had a strongly preferred orientation.

It is quite difficult to explain why the orthorhombic phase precipitates with a strongly preferred orientation. Several mechanisms can be postulated: (i) the triclinic phase crystallized from the surface and the orthorhombic phase started to crystallize from the interface between the triclinic and the mother glass;

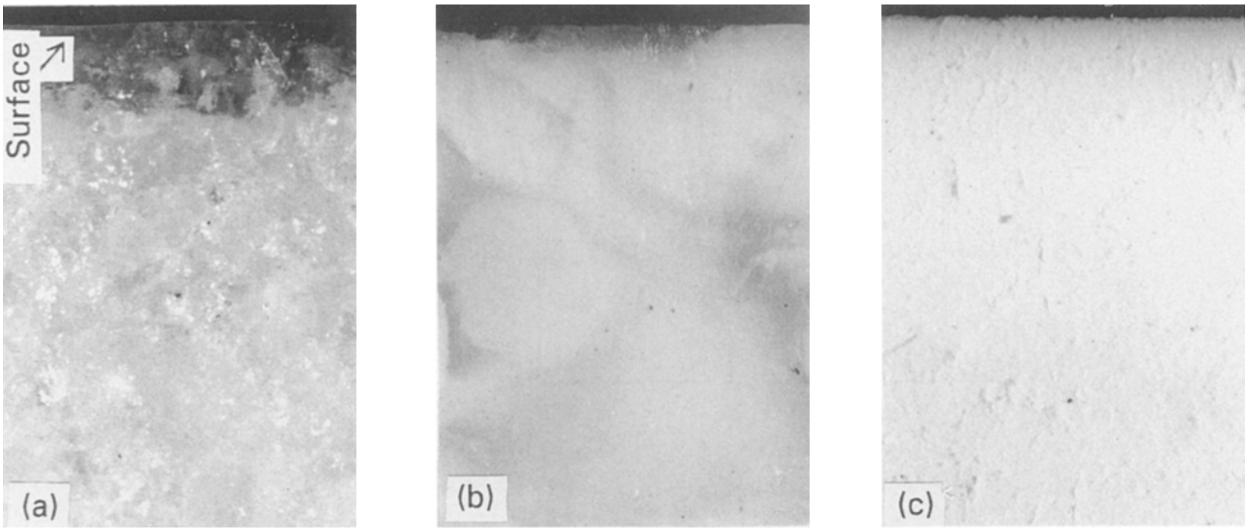

Figure 7 Optical micrographs of the specimens with the following amounts of TiO_2: (a) 0 wt %, (b) 3 wt %, and (c) 10 wt %.

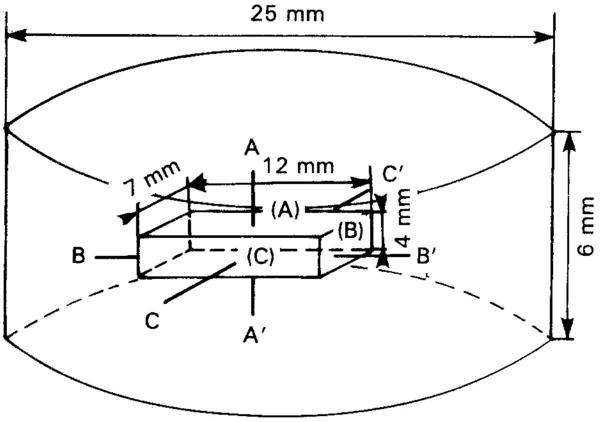

Figure 8 The geometrical relationship between the small cut-out specimen and the whole pellet.

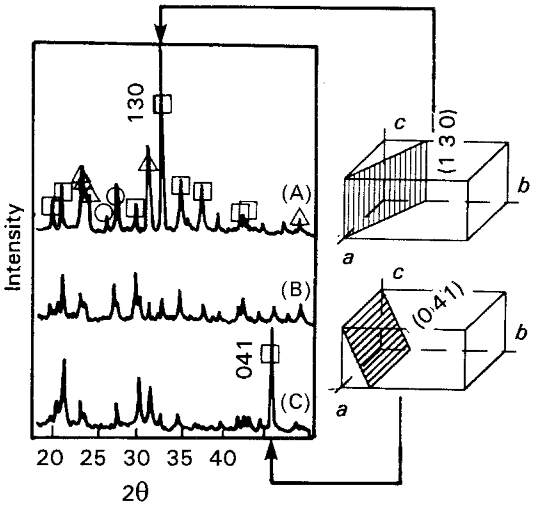

Figure 10 XRD patterns of each surface of the small cut-out specimen without the addition of TiO_2: (○) triclinic, (△) hexagonal, and (□) orthorhombic. ((A), (B), (C) are defined in text.)

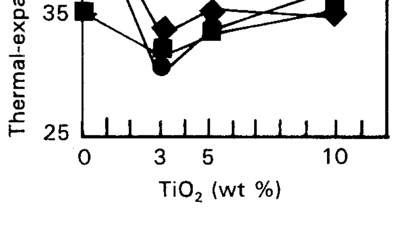

Figure 9 Thermal-expansion coefficient of specified axes of the small specimen (the glass) with the addition of 3–10 wt % TiO_2: (▲) glass, (■) B–B′, (●) A–A′, and (◆) C–C′.

(ii) some residual stress remains, and this is the cause of the preferred orientation; and (iii) a slight temperature gradient in the samples while they are being heat treated may have caused the preferred orientation. We are still not confident in proposing one theory to explain whole phenomena. Fig. 11 shows similar XRD results for the cut-out piece from the glass–ceramics with 3–10 wt % TiO_2. In Fig. 11a, several peaks were identified which belong to either hexagonal or orthorhombic phases, but most of the other peaks were indexed with the triclinic lattice. These results were in agreement with the isotropic nature of the thermal coefficient of the samples with 3–10 wt % TiO_2 shown in Fig. 9.

4. Conclusion

The possibility of using glass powder with the composition of anorthite has been examined with the aim of preparing glass–ceramic substrates with low sintering temperatures. It was found that the glass powder could be sintered above 900 °C, but the addition of small amounts of TiO_2 was required to obtain uniform textures composed of the triclinic anorthite.

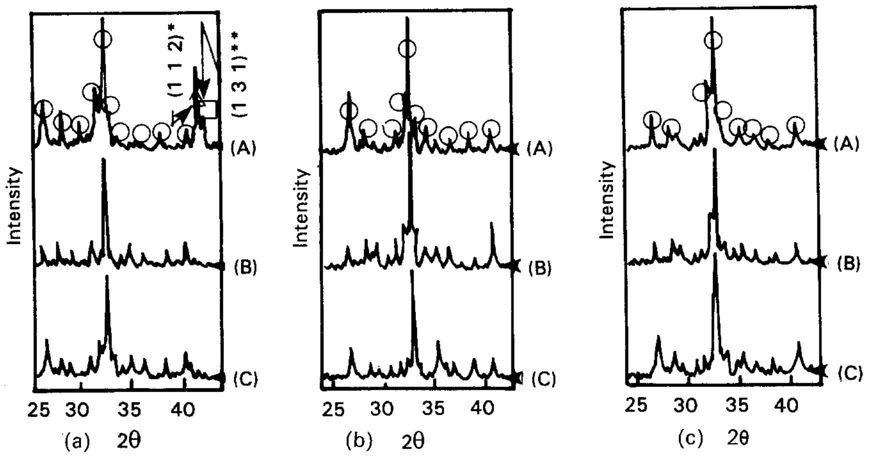

Figure 11 XRD patterns of each surface of the small cut-out specimen with the addition of 3–10 wt % TiO_2 (*, hexagonal; **, orthorhombic).

Glass–ceramics made from glass powder without TiO_2 showed anomalous behaviour in their thermal-expansion coefficients, which was attributed to the precipitation of orthorhombic and hexagonal anorthite in the central part of the glass grains. The orthorhombic phase of anorthite precipitated with a preferred orientation and its thermal expansion also showed a strongly anisotropic nature. The addition of TiO_2 to the mother glass decreased the anisotropy, because the main crystal phase was triclinic when more than 3 or 5 wt % TiO_2 was added.

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