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The stability of mother glass for porous glass–ceramics of the TiO_2–SiO_2 system

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The stability of the glasses of TiO_2–SiO_2–Al_2O_3–B_2O_3–CaO–MgO and TiO_2–SiO_2–Al_2O_3–P_2O_5–CaO–MgO systems during formation has been investigated as a basic study on the preparation of porous glass–ceramics. The main factor affecting the stability of these glasses which are used as mother glasses of porous glass–ceramics was CaO content. The stability was remarkably improved by increasing the CaO content.

The preparation of porous glass–ceramics with an appropriate amount of pore volume was possible from a glass containing CaO up to 30 mol %. The DTA trace of the glasses showed two distinct exothermic peaks in the ranges 30–130° C and 140–300° C above glass transition temperatures. The porous glass–ceramics of TiO_2–SiO_2 system containing more than 60 mol % TiO_2 and having a surface area larger than 400 $m^2 g^{-1}$, a pore volume of 0.3–0.5 $ml g^{-1}$, and average pore radius between 1 and 20 nm were fabricated.

1. Introduction

Porous glass–ceramics of the TiO_2–SiO_2 system containing about 50 mol % of TiO_2 as rutile and/or anatase, are prepared from glasses of the TiO_2–SiO_2–Al_2O_3–B_2O_3–CaO–MgO system [1] by a similar process to the fabrication of a high silica porous glass from a soda–borosilicate glass, i.e., of Vycor process [2–7].

TABLE I Glass compositions employed (mol %)

Sample	TiO_2	SiO_2	Al_2O_3	B_2O_3	P_2O_5	CaO	MgO
B-1	25.0	31.0	12.5	7.5	–	22.5	1.5
B-2	22.5	31.5	13.0	7.5	–	24.0	1.5
B-3	22.5	30.5	13.0	7.5	–	25.0	1.5
B-4	22.5	29.5	13.0	7.5	–	26.0	1.5
B-5	22.5	27.5	13.0	7.5	–	28.0	1.5
B-6	22.5	26.5	13.0	7.5	–	29.0	1.5
B-7	22.5	25.5	13.0	7.5	–	30.0	1.5
B-8	22.5	27.5	13.0	5.0	–	30.0	1.5
B-9	22.5	23.0	13.0	10.0	–	30.0	1.5
P-1	22.0	35.0	14.0	–	3.5	24.0	1.5
P-2	22.0	35.0	14.0	–	4.0	23.5	1.5
P-3	22.0	35.0	14.0	–	6.5	21.0	1.5*
P-4	22.0	35.0	12.0	–	3.5	26.0	1.5
P-5	22.0	35.0	13.5	–	4.0	24.0	1.5
P-6	22.0	35.0	15.5	–	2.0	24.0	1.5
P-7	22.0	35.0	14.0	–	3.5	22.5	3.0
P-8	24.8	29.0	13.0	–	3.5	27.5	2.0
P-9	23.6	27.9	13.0	–	3.5	30.0	2.0
P-10	22.6	26.7	13.0	–	3.5	32.2	2.0
P-11	21.3	25.2	13.0	–	3.5	35.0	2.0
P-12	20.0	23.7	13.0	–	3.5	37.8	2.0

*This composition yielded a precipitate during melting.

This porous glass–ceramics of TiO_2–SiO_2 system is superior to the high silica porous glass of Vycor type in both thermal stability at high temperature and chemical durability in alkali solution [8]. The mother glasses for the porous glass–ceramics of this system, however, are thermally unstable and easily turn opaque during formation of the melt into a plate, due to precipitation of crystals. For the preparation of porous glass–ceramics having controlled pore-size distribution, improvement of the stability of glass to minimize the precipitation of crystals during the forming process is necessary. In the present study, the relation between chemical composition and the stability of the glass during formation has been investigated on the glasses of TiO_2–SiO_2–Al_2O_3–B_2O_3–CaO–MgO and TiO_2–SiO_2–Al_2O_3–P_2O_5–CaO–MgO systems, using the difference between the temperatures of exothermic peak and glass transition point on DTA trace as the parameter of the stability. A porous glass–ceramic was prepared from the glass that showed the largest value of the temperature difference, and the characterization of the material was made.

2. Experiments

2.1. Survey of the stability of mother glasses

The stability of a glass during formation was evaluated from a DTA trace obtained for pulverized glass of 74–149 μm. The value of $\Delta T = (T_{c1}$ or $T_{c2}) - T_g$, which is the difference between the temperature T_{c1} or T_{c2}, the beginning of exothermic reactions due to crystallization, and the glass transition temperature T_g, was used as the parameter of the stability. The

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maximum thickness of the glass plate obtained without precipitation of any crystal was also examined for double checking purposes. The investigation was carried out on both TiO_2-SiO_2-Al_2O_3-B_2O_3-CaO-MgO and TiO_2-SiO_2-Al_2O_3-P_2O_5-CaO-MgO systems. The glass compositions studied are shown in Table I.

In the system containing B_2O_3, the investigation was made on two series of glasses by systematically changing the chemical composition starting from B-1 which was employed in our previous report [1]. In one series, the molar ratio $TiO_2:Al_2O_3:B_2O_3:MgO$ was fixed at 22.5 : 13.0 : 7.5 : 1.5 and the ratio $SiO_2:CaO$ was varied from 31.5 : 24.0 to 25.5 : 30.0 (B-2–B-7). In the other series, B-7–B-9, the ratio $SiO_2:B_2O_3$ was varied with the molar ratio $TiO_2:Al_2O_3:CaO:MgO$ being fixed at 22.5 : 13.0 : 30.0 : 1.5.

In the system containing P_2O_5, the investigation was made first on the series in which the ratio between $TiO_2:SiO_2$ was fixed at 22.0 : 35.0, and the amount of other constituents was varied (P-1–P-7). Then the influence of CaO was investigated by substituting CaO for TiO_2 and SiO_2 holding the molar ratio $Al_2O_3:P_2O_5:MgO$ at 13.0 : 3.5 : 2.0 and the ratio $TiO_2:SiO_2$ at 0.85 : 1 (P-8–P-12).

The raw materials employed were analar grade reagent of titanium dioxide, silicic acid anhydrous, aluminium oxide, boron trioxide, calcium hydrogenphosphate dihydrate, calcium carbonate and magnesium oxide. A batch mixture obtained by briefly mixing the chemicals in a porcelain mill was melted at 1400° C for 1 h in a Pt–2% Rh crucible using an electrical furnace. The melt was quenched to a glass by pouring into water, and then pulverized to 74–149 μm to be used for DTA measurement. The fabrication of

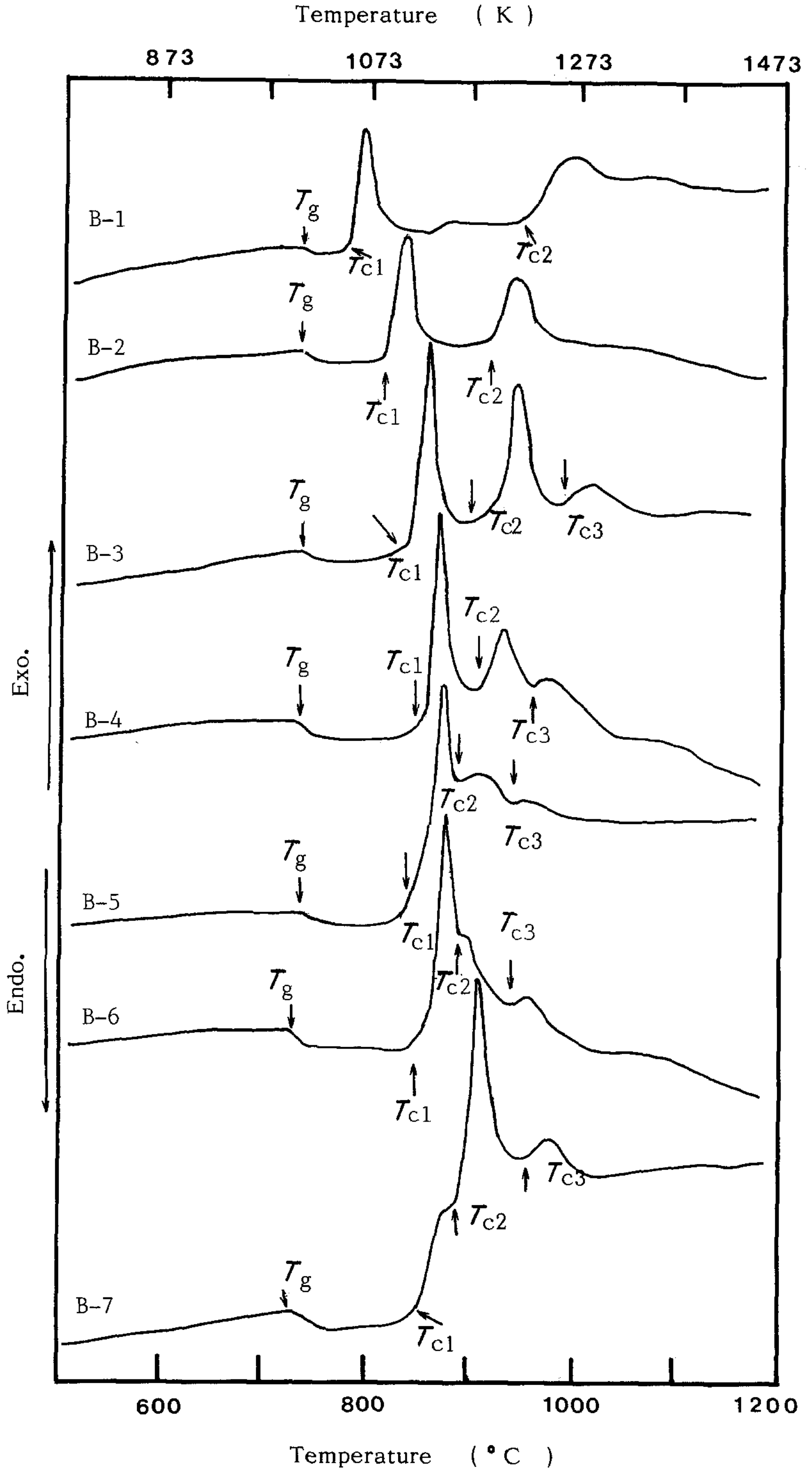

Figure 1 DTA traces of B_2O_3-containing glasses.

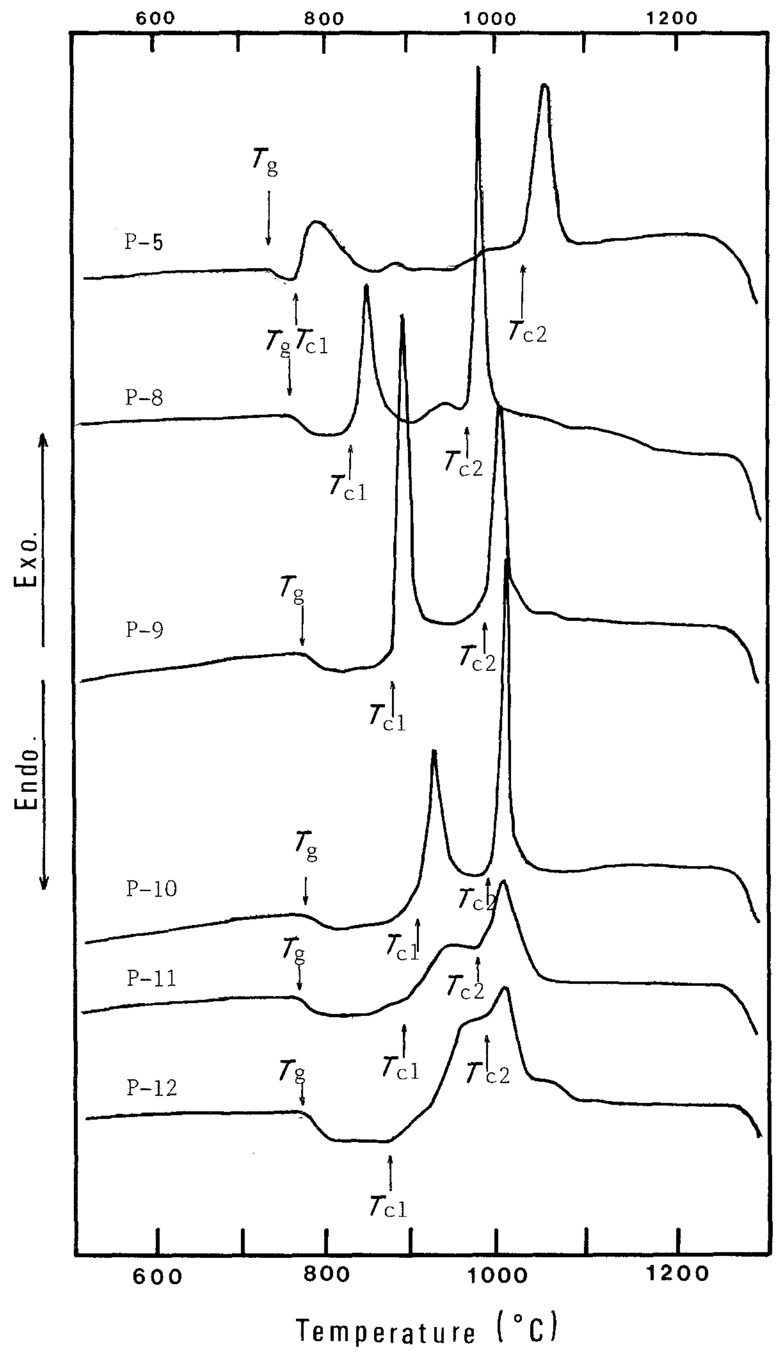

Figure 2 DTA traces of P_2O_5-containing glasses. (R rutile, C $CaAl_2Si_2O_8$, A analase).

a glass plate to examine the maximum thickness attained without crystal precipitation was made by pressing the melt with two carbon plates using carbon spacers of various thickness. DTA was carried out with a Rigaku Denki 8076 D-1 thermal analyser on 80 mg powder samples at a rate of 10 K min^{-1} using alumina as reference.

2.2. Assignment of DTA exothermic peaks and characterization of porous glass-ceramics

Crystalline phases depositing at a temperature in the vicinity of exothermic peaks of DTA trace were determined by powder X-ray diffraction technique on both samples B-3 and P-5. B-3 was relatively stable among the glasses whose DTA trace had two distinct exothermic peaks. P-5 showed the largest value of $T_{c2} - T_g$ among the glasses studied. An X-ray diffraction study was made with a Shimadzu XD 5-A diffractometer using nickel-filtered Cu$K\alpha$ radiation at 30 kV, 20 mA. The 80 mg of pulverized glass to be used for X-ray study was heated at a constant rate of 10 K min^{-1} in a furnace for DTA apparatus, to a temperature below or above the respective peaks of the DTA trace, and cooled from there as soon as the temperature was attained.

The glass particles of P-5 which was subjected to a heat treatment at a temperature below or above the respective peaks of the DTA trace for 15 h were subjected to leaching with 0.5 N HCl at 100° C for 4 h, to be used for chemical analysis and the measurements of pore characteristics, as well as X-ray diffraction study.

Chemical analysis was carried out by the same method as that in the previous report [1], except P_2O_5 which was analysed by spectroscopic Vanado-Molybdophosphoric method [9].

Pore volume, pore-size distribution, pore radius, and specific surface area of the glass ceramics were measured by nitrogen adsorption technique with a Sorptomatic Series 1800 of Carlo Erba Co. The

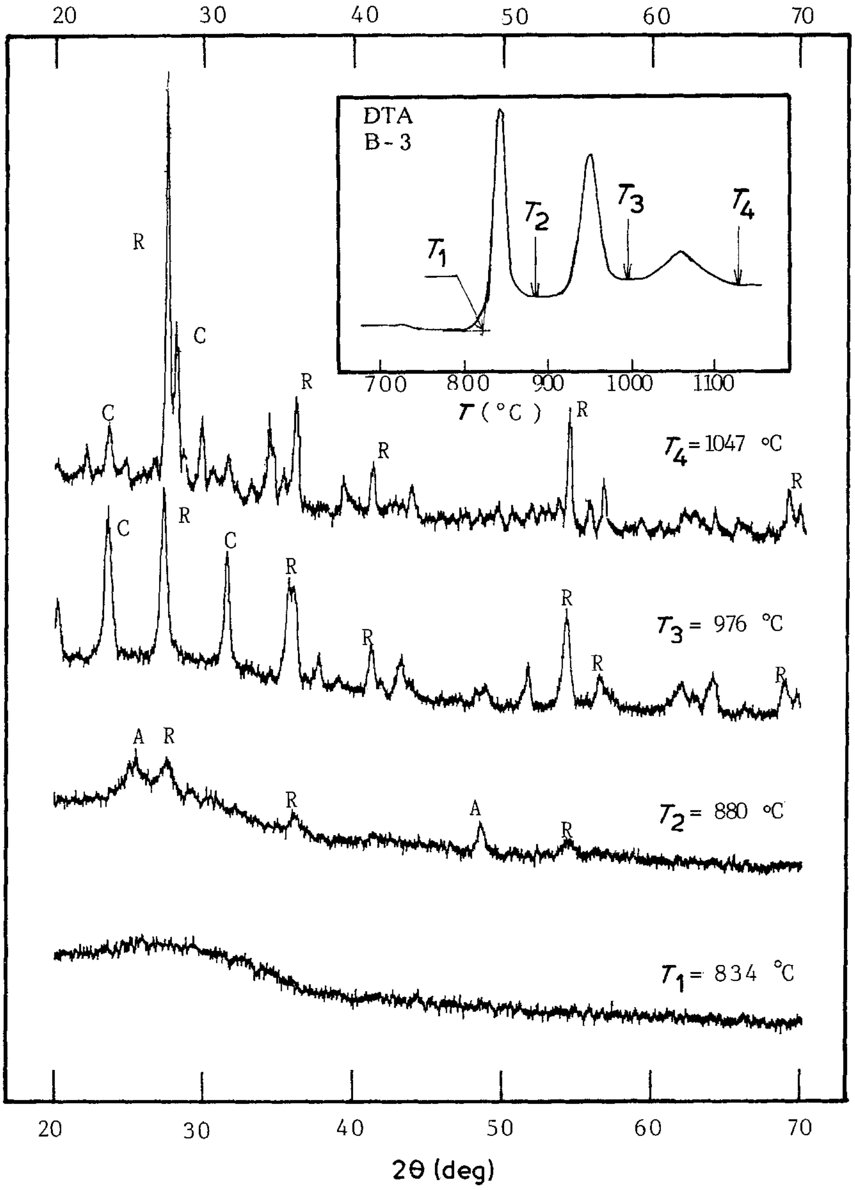

Figure 3 Powder X-ray diffraction patterns of Glass B-3 heated at 10 K min^{-1} to respective temperatures on the DTA trace (insert). (A) anatase, (R) rutile, (C) $CaAl_2SiO_8$.

surface area was also measured by BET method with a Surface Area Apparatus P-700 type of Sibata Scientific Technology LTD. In each measurement, the powdery sample was degassed at 200° C.

3. Results and discussion

3.1. Stability and crystallization tendency of glass

DTA traces of samples B-1–B-7 are shown in Fig. 1, and these of P-5 and P-8–P-12 are shown in Fig. 2. As shown in these figures, there are two distinct exothermic peaks in the ranges 30–130° C and 140–300° C above the glass transition temperature.

The values of T_g, T_{c1}, T_{c2}, $T_{c1} - T_g$ and $T_{c2} - T_g$ are shown in Table II along with the maximum thickness of glass obtained without precipitation of crystals. It is known from the table that a sample having a large value of $T_{c1} - T_g$ gave a thick plate. The value of $T_{c1} - T_g$ for sample B-1 which was used in the previous study [1], was 40° C and very small compared with $T_{c1} - T_g$ of other samples in the table, whereas the value of $T_{c2} - T_g$ was comparable to the others. The melt of B-1 always turned opaque when simply pressed with carbon plates due to rapid deposition of crystals. However, the melt could be fabricated to a glass plate of 2 mm thickness when marble plates were employed instead of carbon plates.

It is also known from Tables I and II that the value of $T_{c1} - T_g$ and the thickness of the plate increased with the amount of CaO content. It is, therefore, considered that the main factor affecting the ease of forming which depends on the stability of glass, was CaO content. The other constituents of the glass did not exhibit distinctive positive effect as it is understood from the data of B-8–B-9 and P-1–P-7. Although the stability of glass increased with the increasing amount of CaO content, the introduction of CaO above 27 mol % was not preferable. As shown in DTA traces of B-5 and P-11, the two exothermic peaks came close to each other when the content of CaO exceeded 27 mol %, and it became difficult to control the crystal phases by the heat treatment for phase separation. Furthermore, the introduction of CaO content more than 30 mol % resulted in the decrease of pore volume of eventual porous glass-ceramics as it will be mentioned below.

There was no distinctive difference of stability between systems containing B_2O_3 and P_2O_5 when the CaO content was not very large. When the CaO content exceeded 30 mol %, however, the stability of

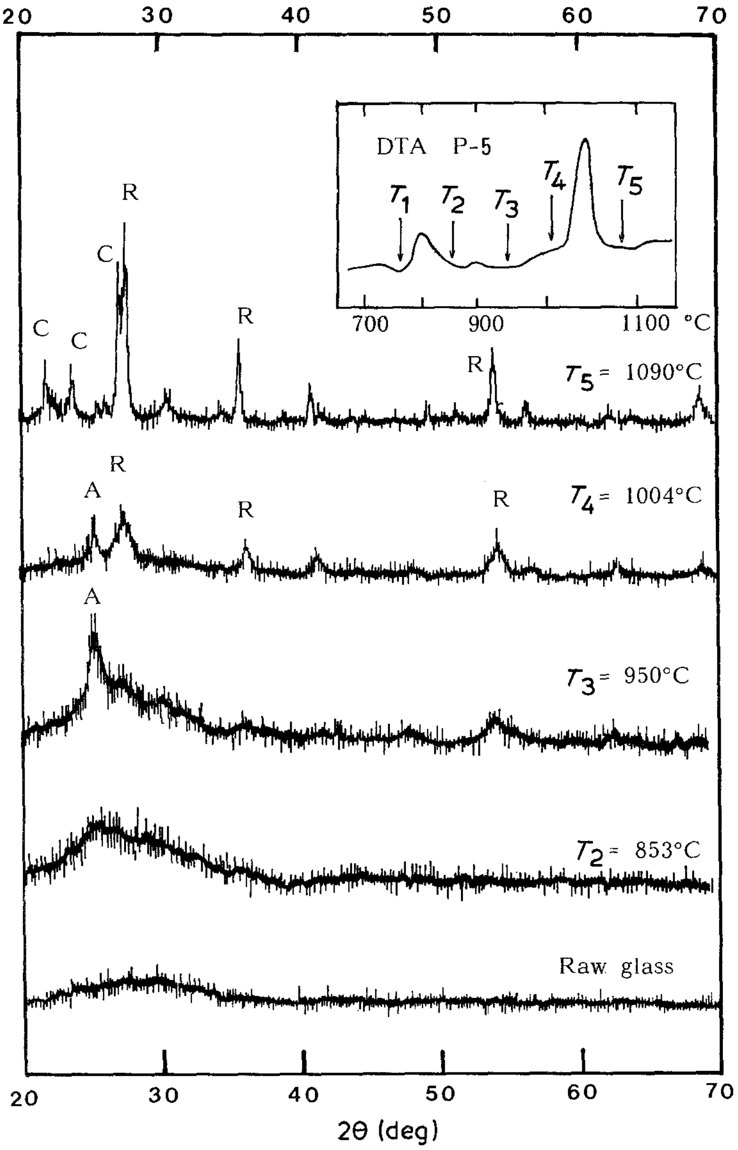

Figure 4 Powder X-ray diffraction patterns of glass P-5 heated at $10\,\mathrm{K\,min^{-1}}$ to respective temperatures on the DTA trace (insert). (A) anatase, (R) rutile, (C) $CaAl_2Si_2O_8$.

TABLE II Data from DTA (°C), and the thickness of glass plate or block fabricated

Sample	T_g (°C)	T_{c1} (°C)	T_{c2} (°C)	$T_{c1} - T_g$ (°C)	$T_{c2} - T_g$ (°C)	Thickness (mm)
B-1	732	774	941	42	209	2*
B-2	732	806	905	74	173	3
B-3	740	831	911	91	171	3
B-4	727	839	902	112	175	10
B-5	724	836	949	112	225	10
B-6	725	846	890	121	165	20
B-7	724	827	871	103	147	30
B-8	749	842	892	93	143	–
B-9	724	823	879	99	155	–
P-1	732	782	995	50	263	–
P-2	742	806	979	64	237	–
P-3	707	742		35		–
P-4	743	793	1011	72	238	–
P-5	735	767	1034	32	299	3
P-6	707	768	923	61	216	–
P-7	714	763	951	49	237	5
P-8	744	816	952	72	208	20
P-9	773	874	967	101	194	30
P-10	768	902	992	134	224	30
P-11	766	867	980	101	214	30
P-12	768	871	980	103	212	30

*Marble stone plates were employed instead of carbon plates in the fabrication into a plate.

– Glass plate was not fabricated.

P_2O_5-containing glasses become higher than that of B_2O_3-containing glasses. Although the value of $T_{c1} - T_g$ for P-5 was smaller than that for B-1, the fabrication of P-5 glass into platelet of 3 mm in thickness was possible. The value of $T_{c2} - T_g$ was rather related to the ease of controlling the depositing crystal phases during thermal treatment for phase separation.

3.2. Assignment of exothermic peaks

The powder X-ray diffraction patterns of pulverized samples of B-3 and P-5 heated to the temperatures indicated on the inserted DTA trace are shown in Figs 3 and 4. Both B-3 which exhibited distinct exothermic peaks and P-5 which had the largest value of $T_{c2} - T_g$ among those studied, were amorphous up to the starting point of the first exothermic peak. The crystalline phases of anatase, rutile, and $CaAl_2Si_2O_8$, which appeared by the heating up to the temperatures of the second exothermic peak were found in both samples. This was the same as the result for sample B-1 shown in a previous report [1].

It is noteworthy that there is no distinct peak of anatase or rutile in the diffraction pattern for P-5 heated to temperature T_2 which was well above the first exothermic peak. Although there is no distinct peak, the diffraction pattern for the sample heated to

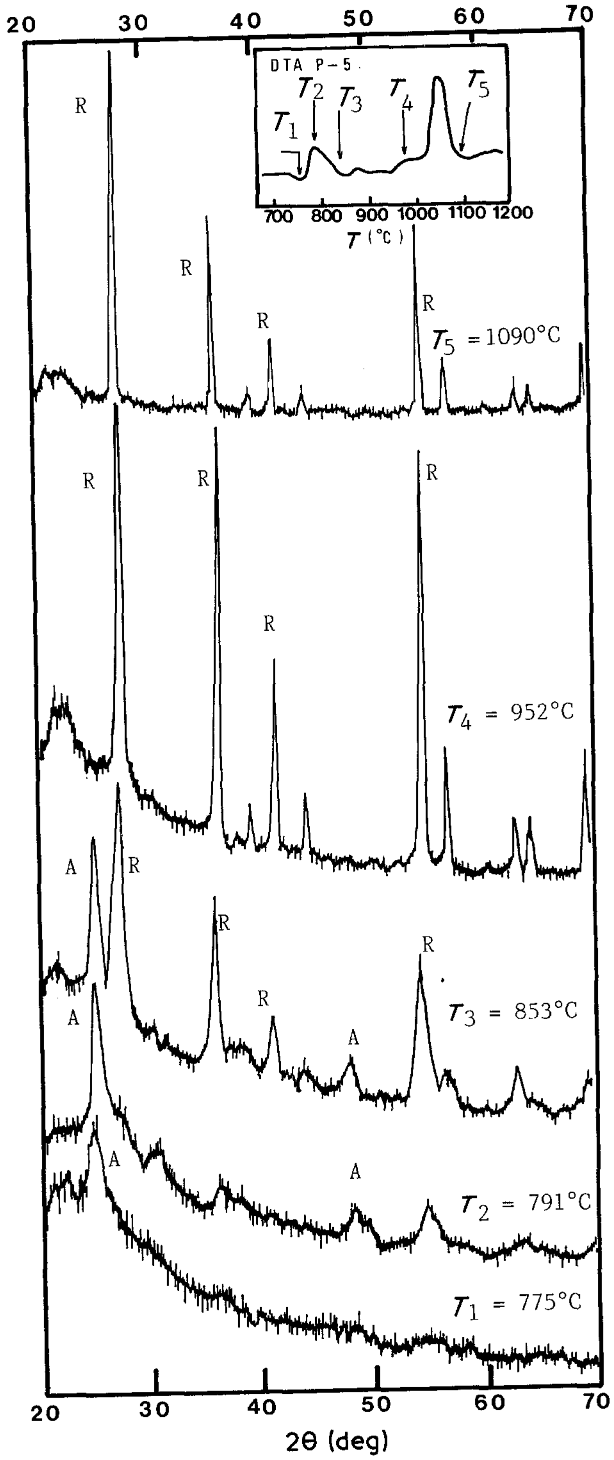

Figure 5 Powder X-ray diffraction patterns of porous glass–ceramics prepared from isothermal treatment of P-5 at various temperatures for 15 h.

T_2 is clearly different from the diffraction pattern for raw glass, suggesting that there was some structural change in the sample during heating. It is known from Fig. 4 that the diffraction peak of anatase becomes distinctive for P-5 glass by the heating to a temperature between T_2 and T_3. The anatase then turns to rutile in the temperature range between T_3 and T_4. It is, therefore, considered that a structural rearrangement to separate glassy TiO_2–SiO_2 phase from mother glass takes place in this glass during heating up to the temperature of the first exothermic peak, and then the crystallization of TiO_2 occurs successively.

Fig. 5 shows the powder X-ray diffraction pattern of pulverized samples of porous glass–ceramics prepared from P-5 by the isothermal treatment at various temperatures and times. As it was reported in the previous paper on B_2O_3-containing system [1], crystal phase of $CaAl_2Si_2O_8$ which was observed in the phase separated glass (T_5 in Fig. 4) were completely disappeared by the leaching with an acid. It is clear from the figure that the preparation of porous glass–ceramics containing anatase alone, anatase plus rutile, or rutile alone is possible by properly selecting the conditions for heat treatment.

3.3. Chemical composition and pore characteristics

Chemical compositions of two kinds of porous glass ceramics prepared from P-5 are shown in Table III along with the conditions for heat treatment to cause phase separation and crystallization. It is known that Al_2O_3, P_2O_5, CaO and MgO in the mother glass subjected to the heat treatment at 853° C for 24 h dissolved out except for a trace of Al_2O_3 and P_2O_5 by acid leaching, whereas a trace of CaO was remaining in the sample heated for 60 h. About 50 wt % of original weight was recovered in the former sample as TiO_2–SiO_2 porous glass–ceramics containing about 60 mol % of TiO_2, which is 1.5 times the TiO_2 content in the latter sample. These results suggest that the composition of a glass–ceramics obtained from P-5 is different depending on the conditions for heat treatment. The increase in the temperature and time of the treatment generally resulted in the formation of the ceramics containing a smaller amount of TiO_2 but larger amounts of SiO_2, Al_2O_3, P_2O_5, and CaO, as it is known from the data in Table III.

Fig. 6 shows the dependence of the surface area of glass–ceramics from P-5 and P-9 on the heating period for phase separation and crystallization. In silicate porous glass, the relation among surface area A ($m^2 g^{-1}$), heating period for phase separation t (h) and phase separation temperature T(K) are given by the following formula [10, 11]

$$A^{-2} t^{-1} = K \exp(-E/RT) \qquad (1)$$

where, E is the activation energy for diffusion and R the gas constant.

When the temperature is kept constant, the formula

TABLE III Chemical compositions of porous glass–ceramics prepared from P_2O_5-containing system P-5

Sample	Thermal temperature (°C)	Treatment period (h)	TiO_2	SiO_2	Al_2O_3	P_2O_5	CaO	MgO
P-5	853	24	60.98	36.97	1.18	0.87	0.00	0.00
	853	60	38.9	56.4	2.24	0.89	1.49	0.00
			(22.0)	(35.0)	(13.5)	(4.0)	(24.0)	(1.5)

Numbers in the parentheses represent nominal composition of mother glass.

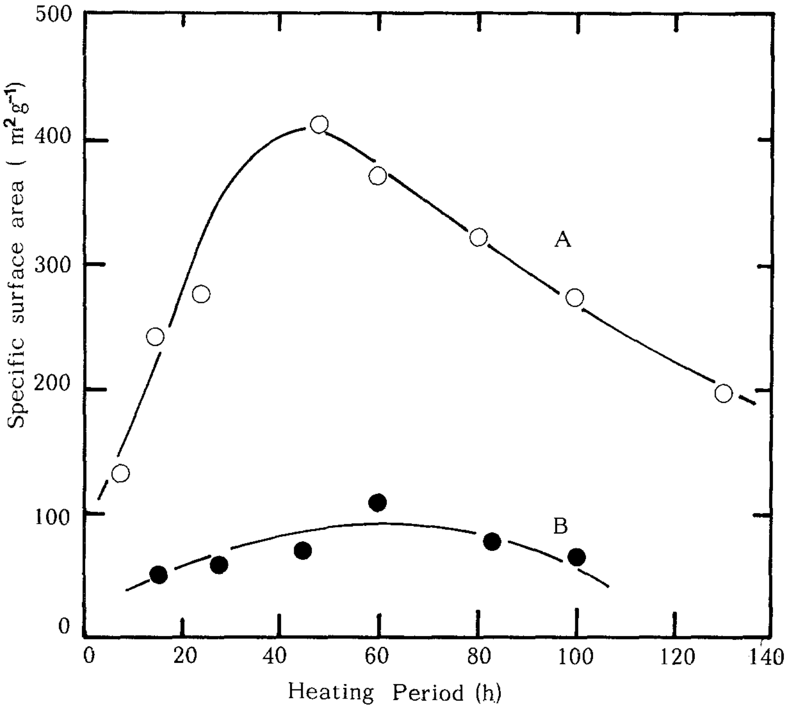

Figure 6 Change in specific surface area with heat treatment, A: at 853° C for P-5, and B: at 825° C for P-9.

is simplified to

$$A = K't^{-1/2} \qquad (2)$$

where K' is $[K \exp(-E/RT)]^{-1/2}$

The results shown in Fig. 6, however, did not obey the relation in Equation 2. This difference may be attributable to the very complicated mechanism of phase separation and crystallization which accompanies the structural rearrangement and subsequent deposition of crystallites giving the two distinct exothermic peaks in DTA curve. Further investigation of the phenomena taking place during heating is necessary in order to elucidate the unusual behaviour observed in Fig. 6.

The change of pore volume of the glass–ceramics with heating period for phase separation and crystallization is shown in Fig. 7 for the samples containing various amounts of CaO content. The pore volume decreased with the increase in the heating period in all samples. The pore coarsening after phase separation might be depressed by the deposition of crystallites out of the glassy TiO_2–SiO_2 phase. The maximum value of pore volume decreased with increasing CaO content. Although the stability of the mother glass was increased, the introduction of more than 30 mol % CaO was not preferable, because the pore volume decreased to less than 0.2 ml g^{-1}, which is inadequate for practical use.

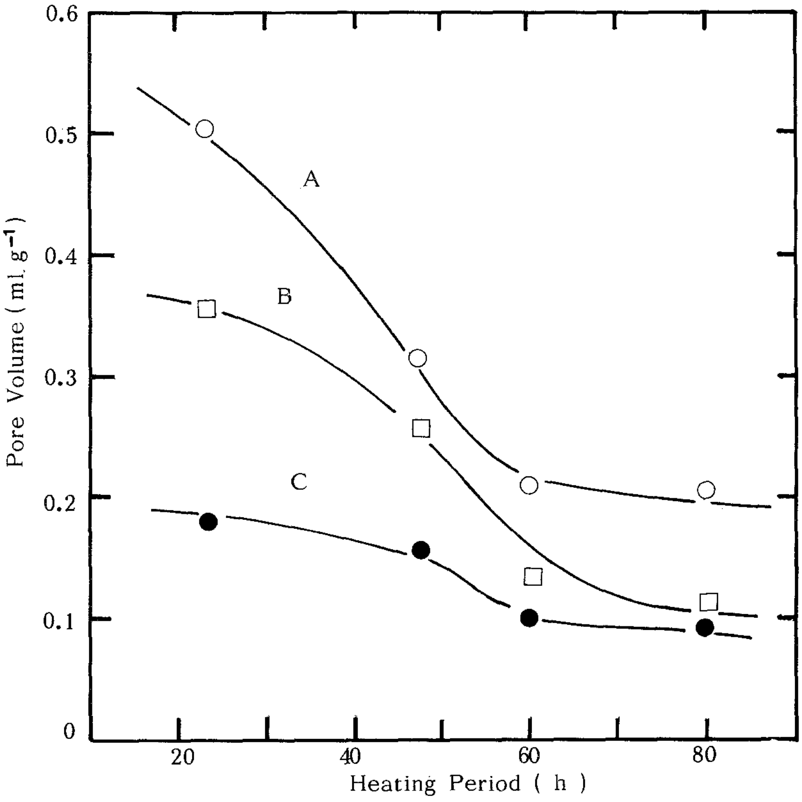

Figure 7 Change in pore volume with heat treatment, A: at 853° C for P-5, B: at 825° C for P-8 and C: at 825° C for P-9.

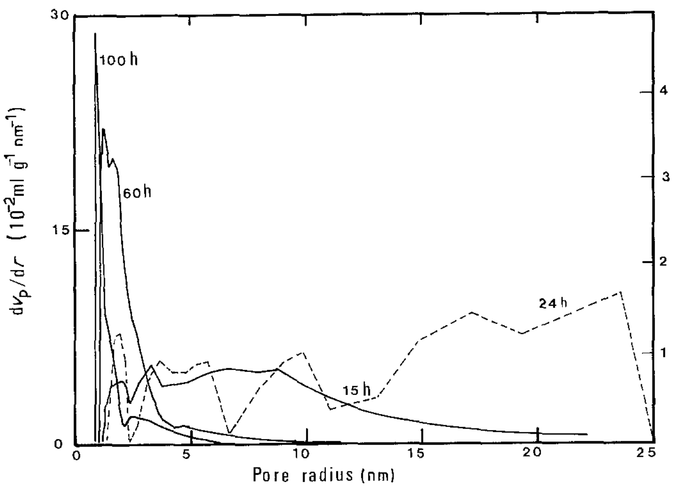

Figure 8 Change in pore-size distribution of porous glass–ceramics from P-5 by respective heating 15, 60, and 100 h at 853° C (full lines) P-8 by the heating 825° C for 24 h, (dotted lines).

Fig. 8 shows the pore size distribution of porous glass–ceramics prepared from P-5 by the heat treatment at 853° C for respective heating periods of 15, 60, 100 h and the one from P-8 heated at 825° C for 24 h. It is clear from the figure that the average pore radius became smaller as the heating period was increased, which is again unusual. This unusual phenomenon may also be attributed to the deposition of TiO_2 out of glassy TiO_2–SiO_2 phase which depressed the pore coarsening. This may be the reason for the unusual decrease of pore volume and pore size, and therefore, a decrease of surface area with heating time.

Owing to these unusual phenomenon, preparation of glass–ceramics of various pore size can be made without difficulty, as is demonstrated in Fig. 8 in which the porous glass–ceramics having large pore radius of about 20 nm and small pore radius of 2 nm are shown.

The TiO_2–SiO_2 porous glass-ceramics developed by the authors had excellent thermal stability at high temperatures and chemical durability in alkali solution [8]. In the present study, the chemical composition of mother glass suitable to the formation of a glass plate which can be fabricated into a porous glass–ceramics having large surface areas of 50–400 $m^2 g^{-1}$ and pore volume of 0.2–0.5 ml g^{-1} was known to be 22.0–25.0 TiO_2–28–35.0 SiO_2–12.5–13.5 Al_2O_3–3.5–4.0 P_2O_5–24.0–30.0 CaO–1.5–2.0 MgO (mol %). Commercial production and utilization of the porous glass–ceramics will be realized in near future to be employed advantageously as functional materials in various applications such as supports for catalysts, photocatalyst [12–17], gas sensors [18–21], and so on [22–27].

References

1. T. KOKUBU and M. YAMANE, *J. Mater. Sci.* **20** (1985) 4309.
2. C. J. PLANK and N. J. WOODBURY, US patent 2472490 (1949).
3. E. M. RABINOVICH, *J. Mater. Sci.* **15** (1980) 2027.
4. M. A. RES, J. T. FOURTE, R. W. WHITE and J. BENDNARIK, *J. Amer. Ceram. Soc.* **65** (1982) 184.
5. J. J. HAMMEL and TIES ALLERSMA, US Patent 3843341 (1974).
6. R. MADDISON and T. W. McMILLAN, *Glass Technol.* **21** (1980) 297.
7. T. NAKASHIMA and Y. KUROKI, *Nippon Kagaku-kai Shi.* **8** (1981) 1231.
8. T. KOKUBU and M. YAMANE, *J. Mater. Sci.* **22** (1987) 2583.
9. Z. KASHIMA, "Zikken kagaku kouza 15, Analytical Chemistry", Compilation of Nippon Kagaku-kai (Maruzen Co., Tokyo, 1971) p. 373.
10. W. HALLER, *J. Chem. Phys.* **42** (1965) 686.
11. P. F. JAMES, *J. Mater. Sci.* **10** (1975) 1802.
12. A. FUJISHIMA and K. HONDA, *Nature* **238** (1972) 37.
13. L. KURUZYNSKI, H. D. GESSER, C. W. TURNER and E. A. SPEERS, *ibid.* **291** (1981) 399.
14. D. DUONGHONG, E. BORGARELLO and M. GRATZEL, *J. Amer. Chem. Soc.* **103** (1981) 4685.
15. M. GRATZEL, *Acc. Chem. Res.* **14** (1981) 376.
16. S. SATO and J. M. WHITE, *J. Catal.* **69** (1981) 128.
17. H. YONEYAMA, Y. TOMOGUCHI and H. TAMURA, *J. Phys. Chem.* **76** (1972) 3460.
18. T. Y. TIEN, H. L. STADLER, E. F. GIBBONS and P. J. ZACMANIDS, *Amer. Ceram. Soc. Bull.* **54** (1975) 280.
19. F. BONON-VERDURAZ, A. OMAR, J. ESCARD and B. PONTVIANNE, *J. Catal.* **53** (1978) 126.
20. L. A. HARRIS, *J. Electrochem. Soc.* **127** (1980) 2657.
21. N. YAMAMOTO, S. TONOMURA, T. MATSUOKA and H. TONOMURA, *Surf. Sci.* **92** (1980) 402.
22. I. ASO, M. NAKAO, N. YAMAZOE and T. SEIYAMA, *J. Catal.* **56** (1979) 287.
23. M. A. VANNICE and R. L. GARTEN, *ibid.* **56** (1979) 236. *Idem., ibid.*, 63 (1980) 255.
24. M. A. VANNICE and C. J. SUDHAKER, *J. Phys. Chem.* **88** (1984) 2429.
25. G. B. RAUPP and J. D. DUMESIC, *ibid.* **89** (1985) 5240.
26. P. W. McMILLAN and C. E. MATTHEWS, *J. Mater. Sci.* **11** (1976) 1187.
27. N. OGATA, *Nippon-Kaisui-Gakkai-Shi* **31** (1977) 97.

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