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Incorporation of transition metal in porous glass–ceramics of TiO_2–SiO_2 system

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Incorporation of transition metals in porous glass–ceramics of TiO_2–SiO_2 system was made by the phase separation and crystallization of the glasses of TiO_2–SiO_2–Al_2O_3–P_2O_5–CaO–MgO system containing various kinds of transition metals. The amount of transition metals incorporated in the skeleton of the porous glass–ceramics was dependent on both chemical composition of mother glass and conditions of heat treatment. In general the amount decreased with the increasing amount of rutile in the skeleton. In the glass of high TiO_2/SiO_2 ratio, the incorporation of relatively large amounts of transition metals was possible even if the precipitation of a fairly large amount of rutile occurred. The crystallization of rutile and in porous glass–ceramics was essential to fabricate rigid platelet porous glass–ceramics.

1. Introduction

Porous glasses have been applied to a variety of fields of engineering, such as supports of catalysts [1–3], column packing of liquid chromatograph [4–6], reverse osmosis [7–8], reactive filters for separation [9–11] and so on [12, 13]. In general, a porous glass which is fabricated by the leaching of phase separated soda borosilicate glass, i.e. by the Vycor process, is a colourless high silica glass [14–17], because a transition metal, if added in a mother glass, is not incorporated into high silica phase but goes into the boron rich phase upon phase separation and the boron rich phase completely dissolves out from the system in the subsequent acid leaching process. The introduction of transition metals in the skeleton of a porous glass or porous glass–ceramics is an interesting subject because a transition metal may not only give colour but also give catalytic property to activating the adsorbed materials on the porous surface [18–19]. In high silica porous glass, generally, the introduction of transition metals such as nickel, cobalt and copper affording or modifying the catalytic property, has been carried out by ion exchange or impregnation [20–22].

On the other hand, TiO_2–SiO_2 porous glass–ceramics which were prepared by the authors from glasses of TiO_2–SiO_2–Al_2O_3–P_2O_5 (or B_2O_3)–CaO–MgO systems [23–25] by a similar process to the Vycor process contains large amounts of TiO_2 and is expected to show different behaviour from silica glass on the incorporation of transition metals in their skeleton. The property of porous glass–ceramics which is expected to be applied in the fields of functional materials like photocatalyst [26–34], gas sensors [35–36] and adsorbents [37] will be improved if the incorporation of transition metals is made.

This paper reports the investigation on the incorporation of transition metals in porous glass–ceramics and discusses conditions on the incorporation into the skeleton of the porous glass–ceramics from the point of chemical composition of mother glass and conditions of heat treatment for phase separation and crystallization of the glass.

2. Experimental procedure

2.1. Fabrication of mother glasses for coloured platelet porous glass–ceramics

Coloured platelet porous glass–ceramics were made from the glasses of the compositions shown in Table I containing 0.5 to 0.75 mol % of various transition metal oxides, CoO, Ni_2O_3, Fe_2O_3. The introduction of ZrO_2 and MoO_3 was also tried to see its effect on the improvement of chemical durability and of oxidation–reduction sensitivity to the exposure to visible light.

In the series for samples 1, 2 and 3 the molar ratio between $TiO_2 : Al_2O_3 : P_2O_5$: MgO : CoO was fixed at 22.0 : 13.0 : 3.5 : 1.5 : 0.5 and the ratio between SiO_2 : CaO was varied from 34.5 : 25.0 to 30.0 : 29.5. In samples 1, 4 and 5, the molar ratio between $SiO_2 : Al_2O_3 : P_2O_5$: MgO : CoO was fixed at 34.5 : 13.0 : 3.5 : 1.5 : 0.5 and the ratio between TiO_2 : CaO was varied from 20.0 : 27.0 to 24.0 : 23.0. In samples 2, 4 and 6 the molar ratio between $Al_2O_3 : P_2O_5$: CaO : MgO : CoO was fixed at 13.0 : 3.5 : 27.0 : 1.5 : 0.5 and the ratio between $TiO_2 : SiO_2$ was varied from 20.0 : 34.5 to 24.0 : 30.5. In samples 2, 7 and 9 the molar ratio between $TiO_2 : SiO_2 : P_2O_5$: MgO : CoO was fixed at 22.0 : 32.5 : 3.5 : 1.5 : 0.5 and the ratio

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between Al_2O_3 : CaO was varied from 10.0 : 30.0 to 14.0 : 26.0. In samples 10 to 12, other transition metal oxides such as Fe_2O_3(No. 10), Ni_2O_3 (No. 11) or MoO_3(No. 12) were introduced instead of cobalt oxide.

Raw materials employed were analytical grade reagents of titanium dioxide, anhydrous silicic acid, aluminium oxide, calcium carbonate, magnesium oxide, cobalt (II) oxide, ferric oxide, molybdenum trioxide, nickel (II) oxide and zirconium oxide.

A batch mixture obtained by briefly mixing the chemicals within a glass mill was melted at 1400° C for 1 h in a Pt-2% Rh crucible using an electrical furnace. A platelet disc of mother glass was made by pressing the melt with two carbon plates using a 2 mm thick spacer.

2.2. Heat treatment and acid leaching

The glass cut into a platelet about 50 mm wide and 50 mm long and 1 to 2 mm in thickness was subjected to heat treatment for phase separation and crystallization, and then to acid leaching to fabricate into porous glass–ceramics.

As shown in differential thermal analysis (DTA) traces in our previous reports [23–25], glasses in this work have the glass transition temperature in the range around 760 to 780° C and two distinctive exothermic peaks in the range above 840° C. The heat treatment was carried out in steps at temperatures between 780 and 820° C in order to attain precise control of the crystal phase depositing during the treatment. For example, the samples with and without ZrO_2 were firstly heated at 780° C for 24 h and then held at 800° C for 24 h. The samples containing CoO, Ni_2O_3, Fe_2O_3 and MoO_3 were subjected to isothermal treatment at 800° C for 24 h, followed by holding at 820° C for 24 h. After these heat treatments, the thickness of the glass plate was reduced to 0.5–1.0 mm by grinding.

The plates of phase separated glasses were then subjected to acid leaching with 100 ml of mixed acid of 0.5 N HCl and 0.1 N HNO_3 containing both 5% ammonium chloride and 5% sodium acetate anhydrous under refluxing at 100° C. Acid leaching was continued for about 24 h.

For the purpose of investigating the amount of transition metals incorporated in the skeleton, glasses of samples 1 to 9 shown in Table I were heat-treated for 12 h at the temperature of the first exothermic peak in their DTA curves. 1 g of the heat-treated glasses was leached in 800 ml of 0.5 N HCl solution at 100° C for 1 h under refluxing and stirring. Leached solutions and porous products were then subjected to chemical analysis to determine the content of transition metals in the various phases.

In order to see the colour change at various stages of the treatments, platelets of samples of 2, 3 and 6 were subjected to heat-treatment at 790° C for 24 h and at 820° C for 24 h, followed by acid leaching at the same conditions as those for platelets of porous glass–ceramics mentioned above.

Since there were differences in the amount of incorporated transition metals with heat treatment, particulate samples of No. 2 were subjected to heat treatment at various characteristic temperatures with respect to the DTA trace of the mother glass in order to investigate the mechanism of incorporation. The first sample of 5 g was treated for 12 h at 790° C, the temperature between glass transition temperatures (Tg) and the temperature of the onset of the first exothermic peak (Tc1). The second sample of 5 g was heat-treated in steps at 790° C for 12 h and at 840° C for 6 h. The third sample of 5 g was treated for 12 h at 870° C, the temperature of the first exothermic peak of mother glass. Glass of sample 7 was also subjected to the treatment for 12 h at 800° C, the temperature between Tg and Tc1 of this mother glass for comparison. The heat-treated glasses were subjected to acid leaching in 0.5 N HCl solution by the same conditions mentioned above, and the leached solution and porous product were subjected to chemical analysis.

2.3. Chemical analysis and property measurements

Chemical analysis of porous glass–ceramics was carried out by the same method as those in previous

TABLE I Glass compositions employed in the present study

Sample No.	TiO_2	SiO_2	Al_2O_3	P_2O_5	CaO	MgO	CoO
1	22.0	34.5	13.0	3.5	25.0	1.5	0.5
2	22.0	32.5	13.0	3.5	27.0	1.5	0.5
3	22.0	30.0	13.0	3.5	29.5	1.5	0.5
4	20.0	34.5	13.0	3.5	27.0	1.5	0.5
5	24.0	34.5	13.0	3.5	23.0	1.5	0.5
6	24.0	30.5	13.0	3.5	27.0	1.5	0.5
7	22.0	32.5	10.0	3.5	30.0	1.5	0.5
8	22.0	32.5	12.0	3.5	28.0	1.5	0.5
9	22.0	32.5	14.0	3.5	26.0	1.5	0.5
10	22.0	30.0	13.0	3.5	29.5	1.5	0.5 (Fe_2O_3)
11	22.0	30.0	13.0	3.5	29.25	1.5	0.75 (Ni_2O_3)
12	22.0	30.0	13.0	3.5	29.25	1.5	0.75 (MoO_3)

Figure 1 Colours of porous glass–ceramics incorporating Co, Ni, Fe, Mo and Zr.

Figure 2 Colour changes of samples 2, 3 and 6, A : Mother glass B : phase separated glasses, C : porous glass–ceramics.

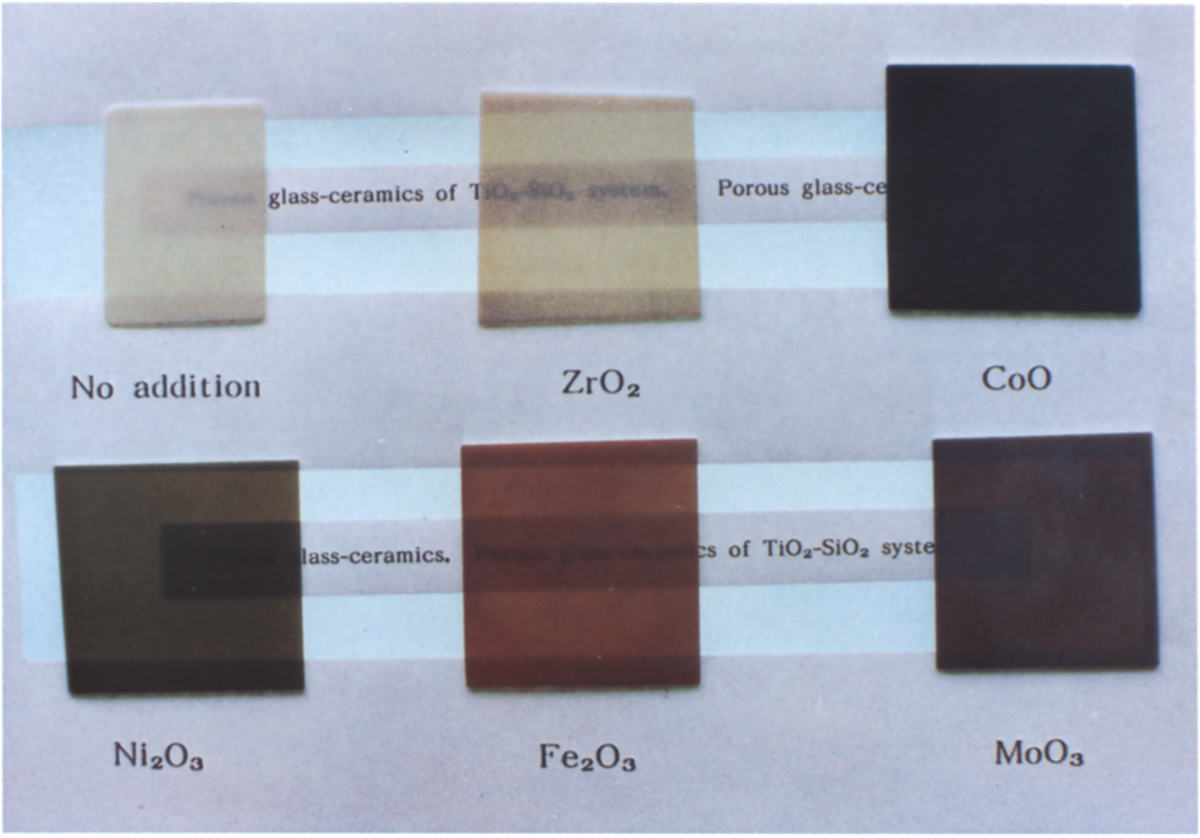

Figure 1

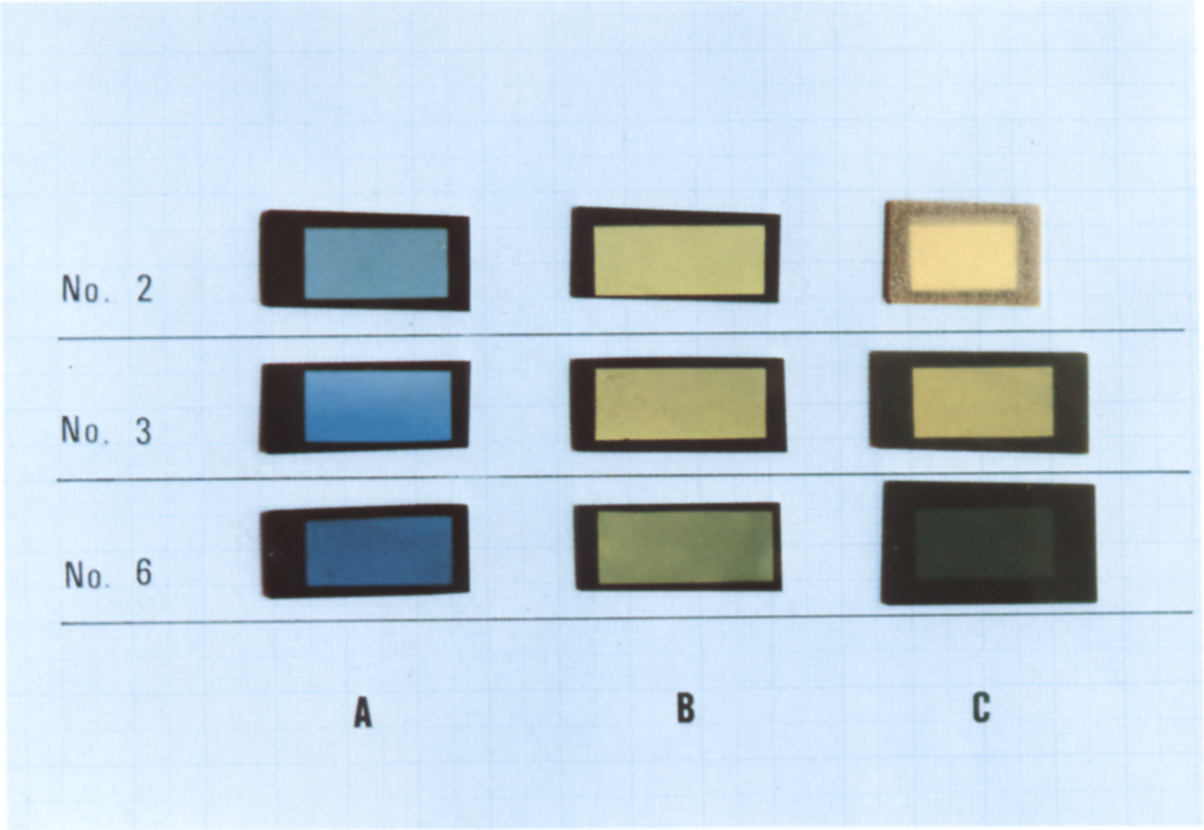

Figure 2

TABLE II Chemical compositions of coloured glass–ceramics (mol %)

Incorporated element	TiO_2	SiO_2	Al_2O_3	P_2O_5	CaO	MgO	MO*
Co	55.8	35.6	5.1	1.9	0.2	0.3	1.1
Ni	51.3	36.7	7.3	2.3	0.4	0.2	1.9
Fe	54.2	36.1	6.8	1.7	0.3	0.2	0.7
Mo	52.6	38.4	6.2	1.7	0.3	0.2	1.4
Zr	56.1	34.2	6.6	1.5	0.1	0.3	1.2

*MO is oxide of incorporated metal.

reports [23–25]. The amount of transition metals incorporated in the skeleton of the ceramics was estimated from the analysis on the solution used for leaching which was filtered and subjected to atomic absorption spectrometry. The amount of the incorporated transition metals was calculated by the following equation:

$$\text{Incorp.}(\%) = \frac{[\text{M}]\text{m} - [\text{M}]\text{L}}{[\text{M}]\text{m}} \times 100 \qquad (1)$$

where, [M]m and [M]L are the contents (μg) of transition metal introduced in 1 g of mother glass and the amount detected in the solution used for leaching of 1 g of glass–ceramics, respectively.

Differential thermal analysis (DTA) was carried out with a RIGAKU DENKI 8076 D-1 thermal analyser on 100 mg samples at a rate of $10\,\text{K}\,\text{min}^{-1}$ using alumina as reference. The glass transition temperature (Tg), the temperature of the onset of the first exothermic reaction (Tc1), and the peak temperatures of distinct exothermic reaction (Tcp1, Tcp3) of all the glasses shown in Table I were determined by the same method as those in previous reports [23–25]. DTA was also made on the heat-treated samples of glass No. 2 at various conditions in order to investigate the effects of heat treatment on the incorporation of cobalt.

X-ray diffraction study was made on the same samples of glass No. 2 as those used for the DTA study with RIGAKU DENKI RAD-IIB diffractometer using nickel-filtered CuKα radiation at 30 KV and 20 mA.

TABLE III Data from DTA (° C), percentage of incorporated transition metal and colour of porous glass–ceramics

No.	Tg	Tc1	Tcp1	Tcp3	THt	Incorp. (%)	Colour
1	758	800	850	1036	850	14.0	Y
2	770	847	870	1000	847	13.5	Y
3	786	890	914	1001	914	49.8	G
4	766	840	871	990	871	20.9	Y
5	749	770	800	1040	800	25.8	Y
6	767	850	880	1010	880	51.2	G
7	768	904	925	1000	925	31.2	Y
8	765	850	870	972	870	22.3	Y
9	772	806	840	1010	840	23.7	Y
10	790	902	920	1010	840	50.0 (Fe)	LB
11	790	850	875	1033	840	74.4 (Ni)	LG
12	780	910	926	1010	840	54.2 (Mo)	Wh

THt is the heat treatment temperature for phase separation and crystallization. Y : Yellow, G : Green, LB : Light brown, LG : Light green, Wh : White.

3. Results

3.1. Colours of porous glass–ceramics

The coloured TiO_2–SiO_2 porous glass–ceramics were obtained from mother glasses containing various transition metals, that is dark green from CoO, light green from Ni_2O_3, brown from Fe_2O_3, and yellow from MoO_3 which turned to bluish grey upon exposure to visible light in ambient atmosphere, as shown in Fig. 1. The recovery of these porous glass–ceramics was about 40 wt % of original mother glass. These platelet porous glass–ceramics of about 1 mm thickness were translucent except for the one containing CoO and had specific surface areas in the range of 120 to $200\,\text{m}^2\,\text{g}^{-1}$, pore volumes of 0.3 to $0.45\,\text{ml}\,\text{g}^{-1}$ and average pore radii of 5 to 15 nm, respectively. Their chemical compositions are shown in Table II.

3.2. Relations between mother glass composition and incorporation of transition metals

Fig. 2 shows the colour of mother glasses, phase separated glasses and porous glass–ceramics of samples 2, 3 and 6 containing CoO but having different compositions from mother glasses. As shown in the figure, the colour of the mother glass was blue and turned to green upon heat treatment for phase separation in all samples. The colour of the eventual porous glass–ceramics obtained by leaching, however, was different to each other depending on the composition of the mother glasses. That is, sample 2 whose TiO_2:SiO_2 in mother glass is 22.0 : 32.5 (= 0.676) gave yellow porous glass–ceramics. Sample 3 whose TiO_2:SiO_2 in mother glass is 22.0 : 30.0 (= 0.733) gave yellowish green. And sample 6 whose TiO_2 : SiO_2 in mother glass is 24.0 : 30.5 (= 0.787) gave dark green.

Table III shows the characteristic temperatures obtained by DTA, temperature of heat treatment, amount of incorporated transition metal in the skeleton, and the colour of porous glass–ceramics. It is known from the table that the green colour for the samples from high TiO_2:SiO_2 ratio (samples 3 and 6) is attributed to the large amount of incorporated cobalt oxide i.e. about 50 wt % of original amount in the mother glasses.

The change in the alumina content in mother glass (samples 7 to 9) had almost no influence on the incorporation of cobalt. The other transition metal oxides such as ferric oxide, nickel oxide and molybdenum oxide were all incorporated into the porous skeleton at amounts more than 50 wt % of that in the mother glasses.

3.3. Effect of the conditions of heat treatment on the incorporation of cobalt

The effect of the condition of heat treatment on the cobalt incorporation is shown in Table IV for samples No. 2. It is known that porous glass–ceramics of high cobalt content could be prepared from sample No. 2 when they had been heat-treated at 790° C, the temperature between Tg and Tc1 in DTA, although the incorporation ratio decreased when heat treatment was carried out at higher temperatures of 840 or 870° C (Tcp1).

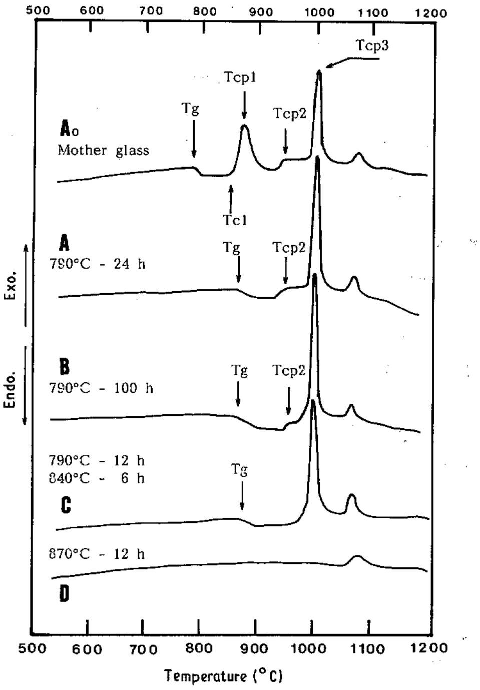

Figure 3 DTA traces of sample 2 after the respective heat treatments, A_0 : mother glass, **A** : at 790° C – 24 h, **B** : 790° C – 100 h, **C** : 790° C – 12 h + 840° C – 6 h, **D** : 870° C – 12 h.

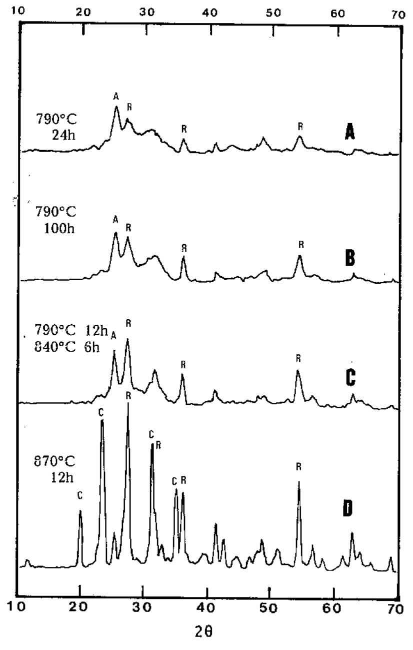

Figure 4 X-ray diffractions of sample 2 after the respective heat treatments; **A** : at 790° C – 24 h, **B** : 790° C – 100 h, **C** : 790° C – 12 h + 840° C - 6 h, **D** : 870° C – 12 h. A-anatase, R-rutile, C–$CaAl_2Si_2O_8$.

The curves in Fig. 3 are the DTA traces of sample 2, after heat treatment at various conditions shown in Table IV. The mother glass had the transition temperature (Tg) at 770° C distinct exothermic peaks of Tcp1 and Tcp3 at 870 and 1003° C, respectively, and a small exothermic peak (Tcp2) between Tcp1 and Tcp3 at 940° C. When the glass was subjected to heat treatment at 790° C for 24 h or 100 h, the first distinct exothermic peak at 870° C disappeared and the Tg shifted up to 870° C. When the sample was heat-treated in steps at 790° C and at 840° C, both of the peaks Tcp1 at 870° C and Tcp2 at 940° C disappeared and the Tg shifted up to 881° C. And when the sample was heat-treated at 870° C, all the peaks disappeared and Tg became obscure.

X-ray diffraction patterns of respective samples employed in DTA were shown in Figure 4. In the samples heat-treated at 790° C, anatase and rutile were observed with the former as the main crystal. When the glass was subjected to stepped heat-treatment, crystals of both anatase and rutile were observed, however, rutile was dominant. When the glass was heat-treated at 870° C, i.e. Tcp1, the development of rutile and $CaAl_2Si_2O_8$ was remarkable.

4. Discussion

4.1. Relations between compositions of mother glass and incorporation of transition metals

It is known from the results shown in Tables I, III and IV that there are two factors governing the amount of cobalt incorporation in the porous glass–ceramics. One is the TiO_2:SiO_2 ratio in mother glass and the other is the condition of heat treatment for phase separation.

The blue colour of all the mother glasses indicates the presence of cobalt (II) in tetrahedral coordination as it is in alkali borate glass [38, 39]. However, when those glasses were heat-treated at a temperature just above the glass transition temperature (Tg) their colour turned to dark green like the colour of Li_2O-(1-x)MgO-xCoO-TiO_2 glass [40]. This colour change may be attributable to the separation of glass into acid-soluble and -insoluble phases. The acid-insoluble phase mainly contains TiO_2 and SiO_2 and the acid-soluble phase consists of CaO, MgO, Al_2O_3, P_2O_5 and SiO_2. Since the colour of all the mother glass turned from blue to green by the treatment at a temperature slightly above Tg, and since cobalt was incorporated in TiO_2–SiO_2 porous glass–ceramics, it is considered that cobalt was incorporated in TiO_2–SiO_2 rich phase, at least in the initial stage of phase separation in all glasses.

There were, however, large differences in cobalt incorporation with the difference of mother glass compositions as shown in Table III when the heat treatment was carried out at the temperature of the first exothermic peak, Tcp1. The heat treatment at Tcp1 enhanced the precipitation of rutile and $CaAl_2Si_2O_8$ in the phase separated glass. These crystallizations, therefore, may be the reason of low cobalt incorporation in those glasses but samples 3 and 6 whose TiO_2:SiO_2 ratios were higher than the others have a

TABLE IV The effect of the condition of heat treatment on the cobalt incorporation for sample No. 2

Sample	Heat treatment conditions	Incorp. (%)	Colour	Crystal
A	790° C 24 h	47.7	G	A, R
B	790° C 100 h	45.1	G	A, R
C	790° C 12 h 840° C 6 h	13.3	Y	A, R
D	870° C 12 h	13.5	Y	C, R

G : green, Y : yellow, R : rutile, A : anatase, C : $CaAl_2Si_2O_8$.

much higher cobalt incorporation. One of the reasons for the high cobalt incorporation for sample 3 and 6 may be that the glassy TiO_2–SiO_2 phase remained in these samples even though they were subjected to heat treatment at the temperature of Tcp1 and crystallizations of rutile and $CaAl_2Si_2O_8$ had taken place.

In order to obtain a rigid porous glass–ceramics of TiO_2–SiO_2 systems, the crystallization of rutile was essential. If the precipitation of rutile was not enough, cracking in the drying process of the porous was almost inevitable. As it was seen in the case of sample 2, the heat treatment at high temperature to allow the deposition of enough rutile led to the reduction in the cobalt incorporation in the eventual porous glass–ceramics. Therefore, a mother glass composition of high TiO_2:SiO_2 ratio, i.e. above 0.73 like samples 3 and 6, is recommended to fabricate a rigid platelet of porous glass–ceramics incorporating transition metals with high content. Although further investigation is necessary in order to decide the optimum value of the TiO_2:SiO_2 ratio to give a high amount of cobalt incorporation, it is considered that the ratio should be higher than 0.75.

4.2. Relations between the conditions of heat treatment and incorporation of transition metals

Relations between heat treatment conditions and cobalt incorporation ratio can be discussed on the basis of the results for DTA shown in Fig. 3 and the X-ray diffraction shown in Fig. 4 on sample 2. As seen from those figures and Table IV, there was a remarkable difference in cobalt incorporation between the samples A and B heat-treated at 790° C, and sample C which was heat-treated by steps at 790 and 840° C. Samples A and B, green in colour, contained anatase and rutile with anatase as the dominant crystal while, yellow in colour, sample C rutile as the dominant crystal. It is therefore considered that the cobalt incorporated in the glassy TiO_2–SiO_2 phase by treatment at 790° C had been excluded to the acid-soluble phase with the development of crystals of rutile during the subsequent treatment at 840° C. In order to offset this effect of exclusion the employment of mother glass of high TiO_2:SiO_2 ratio is essential.

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