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Formation and crystallization of gels in the Na_2O-SiO_2-TiO_2-ZrO_2 system

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$5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels together with Na_2O-MO_2 gels ($MO_2 = SiO_2$, TiO_2, ZrO_2) were synthesized and effect of Na_2O addition to the gel formation and crystallization behavior were studied. From $Si(OC_2H_5)_4$, $Ti(iso\text{-}OC_3H_7)_4$, $Zr(n\text{-}OC_3H_7)_4$ and $NaOCH_3$ solutions in EtOH without H_2O, transparent, opaque and heterogeneous gels were obtained. By SEM observation, it was found that the opague bulk gels, rich in TiO_2 or ZrO_2 component, contain agglomerated spherical particles of less than 10 μm diameter. Crystallization temperature (Tc) measured by DTA decreased sharply from 1258°C (SiO_2) to 613°C ($30Na_2O{\cdot}70SiO_2$) due to the increasing non-bridging oxygens in the Na_2O-SiO_2 system. But in the Na_2O-TiO_2 and Na_2O-ZrO_2 systems, Tc increased as Na_2O content was increased up to 10 mol%. The thermal stability, defined by Tc/TL ratio, decreased from Tc/TL = 0.77 (SiO_2) to 0.57 ($5Na_2O{\cdot}95SiO_2$) or increased from Tc/TL = 0.30 (TiO_2) to 0.67 ($30Na_2O{\cdot}70TiO_2$) with Na_2O addition. In the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ system maximum Tc was 891°C at $5Na_2O{\cdot}76SiO_2{\cdot}19ZrO_2$ composition and decreased as TiO_2 or ZrO_2 contents increased. Compared with the SiO_2-TiO_2-ZrO_2 gels, Tc of the 5 mol%Na_2O containing gels (Na_2O-SiO_2-TiO_2-ZrO_2) was lower in SiO_2 rich composition and higher in TiO_2 or ZrO_2 rich compositions. It is assumed that addition of Na_2O changed the structure of amorphous TiO_2 and ZrO_2 someway to increase their thermal stability or amorphous forming ability. After DTA run up to 1000°C, cystalline phases precipitated in the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels were determined by XRD analysis. © *2000 Kluwer Academic Publishers*

1. Introduction

In previous works [1–3], gel formation, morphology, crystallization and thermal stability of gels in the SiO_2-TiO_2-ZrO_2 system were reported. Transparent bulk gels were formed in the range of 30–100 mol% SiO_2, 0–7 mol% TiO_2 and 0–50 mol% ZrO_2, and opaque bulk gels in the rest compositions. It was observed that the crystallization temperature Tc of gels determined by DTA was low in the TiO_2 or ZrO_2 rich compositions (Tc = 366°C for TiO_2 and 419°C for ZrO_2 gels) and increased with increasing SiO_2 content up to 1258°C (SiO_2). The thermal stability, expressed by Tc/TL (TL = liquidus temperature) ratio, was in the range 0.23 (ZrO_2) to 0.86 ($90SiO_2{\cdot}10TiO_2$). An interesting aspect of the Tc variation and thermal stability of gels in the SiO_2-TiO_2-ZrO_2 system containing given amount of SiO_2 is that (1) Tc attains a maximum at approximately equimolar concentration of TiO_2 and ZrO_2 for 0 mol% SiO_2 and show a convex for other SiO_2 concentrations, and (2) Tc/TL ratio exhibits a convex having a maximum at the compositions where Tc attains maxima. Kamiya *et al.* [4] studied the resistance to alkaline solution of glass fibres from gels in the ZrO_2-SiO_2 and Na_2O-ZrO_2-SiO_2 systems containing up to 33 wt% ZrO_2. Hara *et al.* [5] investigated gel formation and drying characteristics of gels of $xNa_2O\text{-}yZrO_2{\cdot}(100 - x - y)SiO_2$ system ($x = 0, 7, 13, 18$, $y = 3, 6, 10$ mol%). They showed that addition of Na_2O shortens the gelation time, and makes shrinkage of gels smaller and pore size broader. Wakasugi *et al.* [6] showed that addition of Na_2O (<30 mol%) to the SiO_2-ZrO_2 system greatly improved the thermal stability, and the $20Na_2O{\cdot}10ZrO_2{\cdot}70SiO_2$ gel remained amorphous after a 1200°C-1h heat-treatment. Effects of Na_2O in Na_2O-SiO_2 gels were studied by many researchers. Phalippou *et al.* [7] prepared Na_2O-SiO_2 gels and measured Tc = 842°C ($0.4Na_2O{\cdot}99.6SiO_2$) and 746°C ($10Na_2O{\cdot}90SiO_2$). Prassas *et al.* [8, 9] prepared xNa_2O-$(100 - x)SiO_2$ ($x = 0$–40 mol%) gels and showed that Tc decreases as the Na_2O content increases. Ota *et al.* [10] showed Tc/TL for Na_2O-SiO_2 gels in the composition range $Na_2O = 0$–30 mol%. Different starting materials and procedures have been performed.

There are few reports on the crystallization of gels in the Na_2O-TiO_2 and Na_2O-ZrO_2 systems. In the present work, the effect of Na_2O addition on gel formation, gel morphology and crystallization behavior in the Na_2O-SiO_2-TiO_2-ZrO_2 system were studied.

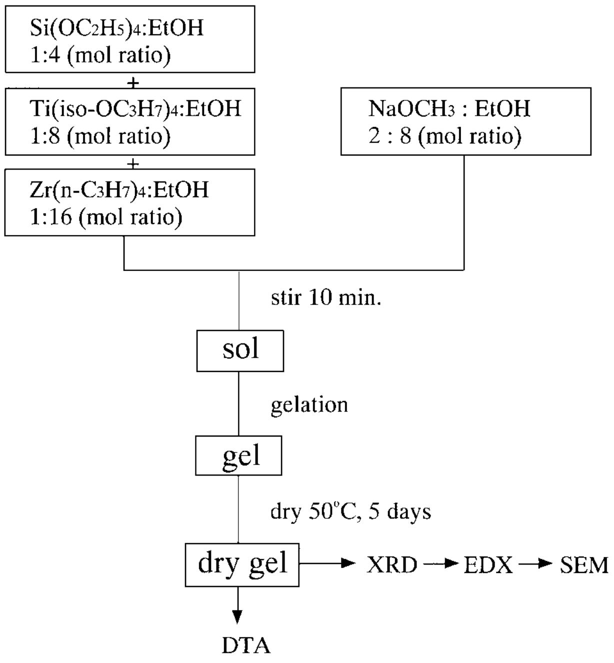


Figure 1 Procedure for sol preparation and gel processing in the Na_2O-SiO_2-TiO_2-ZrO_2 system.

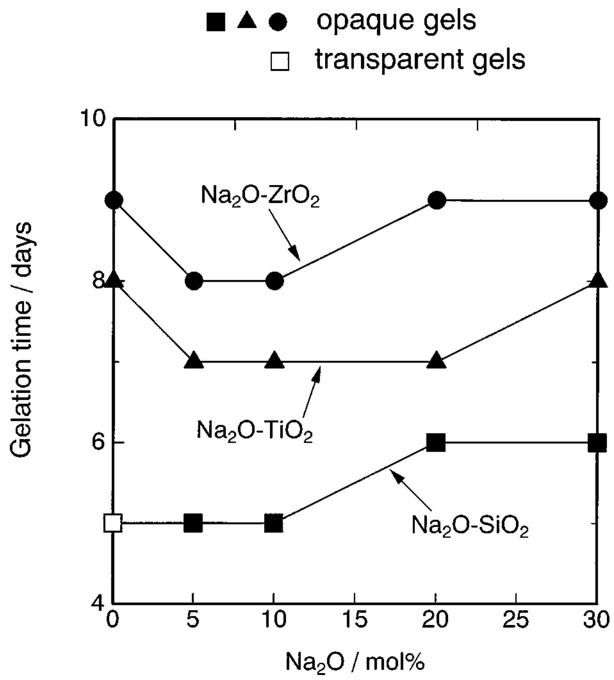


Figure 2 Gelation time in the Na_2O-SiO_2 (□ ■), Na_2O-TiO_2 (▲) and Na_2O-ZrO_2 (●) systems as a function of Na_2O.

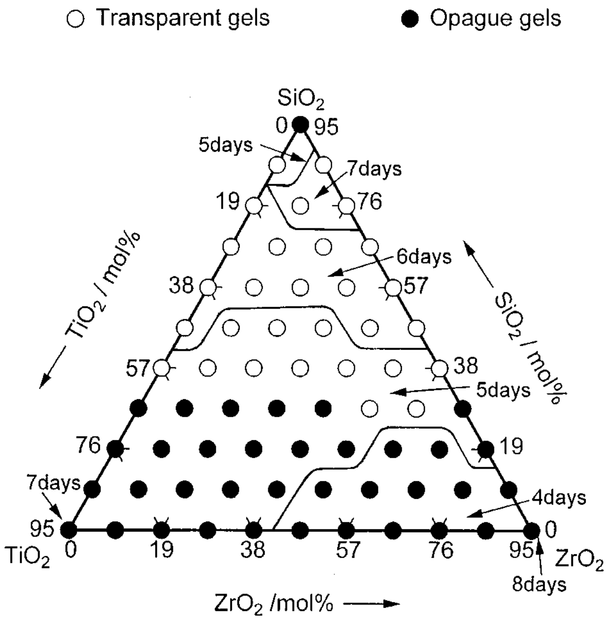


Figure 3 Gelation time in the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ system; (○) transparent gels and (●) opaque gels.

2. Experimental

Gels in Na_2O-SiO_2-TiO_2-ZrO_2 system were prepared from EtOH solution of the alkoxides $Si(OC_2H_5)_4$ (TEOS), $Ti(iso\text{-}OC_3H_7)_4$, $Zr(n\text{-}OC_3H_7)_4$ (70 wt% in propanol) and $NaOCH_3$ (28 wt% in methanol). Na_2O content was fixed at 5 mol% and SiO_2, TiO_2, ZrO_2 contents varied in the range 0–95 mol%. The procedure for the sol preparation, gelation and gel procession is shown in Fig. 1. Water was not added to the solutions. The mixing sequence of the alkoxide solutions was TEOS, $Ti(iso\text{-}OC_3H_7)_4$, $Zr(n\text{-}OC_3H_7)_4$ and $NaOCH_3$ in accordance with the increasing hydrolysis rate of the alkoxides. For additional work, we prepared Na_2O containing binary gels in the Na_2O-MO_2 system ($MO_2 = SiO_2$, TiO_2, $ZrO_2 = 0$–100 mol%) to investigate the role of Na_2O to each component, (SiO_2, TiO_2 or ZrO_2) in Tc and Thermal stability.

After stirring for 10 min, the sol mixtures were put in a glass container with a plastic cover and laid for gelation at room temperature. Several pinholes were opened in the cover so that water vapor comes into the solution from the air. Gel regions and gelation time were determined as the sols became solid either in bulk or in powder state. Wet gels or precipitated powders were dried at 50°C for 3–5 days and amorphous composition (amorphous region) was confirmed by XRD method. The morphology of dried gels were observed by SEM. DTA runs were performed on dried gels with a heating rate of 5°C/min up to 1000°C. Crystallization temperatures Tc were determined from exothermal peak of the DTA curves. After the DTA run cystalline phases precipitated in the specimen were determined by XRD analysis.

3. Results and discussion

3.1. Gelation and appearances of gels

Gelation times of the Na_2O-MO_2 ($MO_2 = SiO_2$, TiO_2, ZrO_2) and the Na_2O-SiO_2-TiO_2-ZrO_2 systems are shown in Figs 2 and 3, respectively.

In the Na_2O-SiO_2 system, transparent gels formed in SiO_2, but opaque gels formed in 5–30 mol% Na_2O compositions. Gels did not form in the rest composition. Gelation time was in the range 5-6 days (Fig. 2). X-ray diffraction measurement (XRD) indicated a trace of unknown crystalline phases in $20Na_2O{\cdot}80SiO_2$ and $30Na_2O{\cdot}70SiO_2$ gels possibly hydrated sodium-silicate or Na_2CO_3. Prassas *et al.* [8] showed that exposure of Na_2O–SiO_2 gels to the air gives rise of precipitation of hydrated compound or carbonate due to the reactions of gels with CO_2 and H_2O. In the Na_2O-TiO_2 system, white powder gels formed in 0–30 mol% Na_2O compositions. Double layered gels formed in 40–80 mol% Na_2O compositions. Gelation time decreased with

Na_2O addition from 8 days in TiO_2 to 7 days in 5–20 mol% Na_2O compositions (Fig. 2). In the Na_2O-ZrO_2 system, white powder gels formed in 0–30 mol% Na_2O compositions and double layered gels in 40–80 mol% Na_2O compositions. Gelation time was 9 days in ZrO_2 and decreased to 8 days with 5–10 mol% Na_2O addition (Fig. 2).

In the $5Na_2O \cdot 95(SiO_2 + TiO_2 + ZrO_2)$ system, transparent bulk gels formed in 28.5–85.5 mol% SiO_2, 0–57 mol% TiO_2 and 0–57 mol% ZrO_2 compositions and opaque gels or white powder gels formed in 95 mol% SiO_2 or SiO_2 poor compositions (0–28.5 mol% SiO_2, 28.5–95 mol% TiO_2 and 28.5–95 mol% ZrO_2). Gelation time was 4-5 days in 0–47.5 mol% SiO_2 and 85.5–95 mol% SiO_2 compositions, and 6-7 days in 47.5–85.5 mol% SiO_2 compositions (Fig. 3). XRD indicated no traces of crystalline product in the dried gels. Transparent gel region extends to ZrO_2-rich compositions (~57 mol% ZrO_2) in Na_2O containing SiO_2-TiO_2-ZrO_2 system compared with that (~50 mol% ZrO_2) obtained in alkali-free SiO_2-TiO_2-ZrO_2 system [1]. Gelation time decreased with Na_2O addition to 4–7 days in $5Na_2O \cdot 95(SiO_2 + TiO_2 + ZrO_2)$ system (Fig. 3) compared with 5–13 days in alkali-free SiO_2-TiO_2-ZrO_2 system [1].

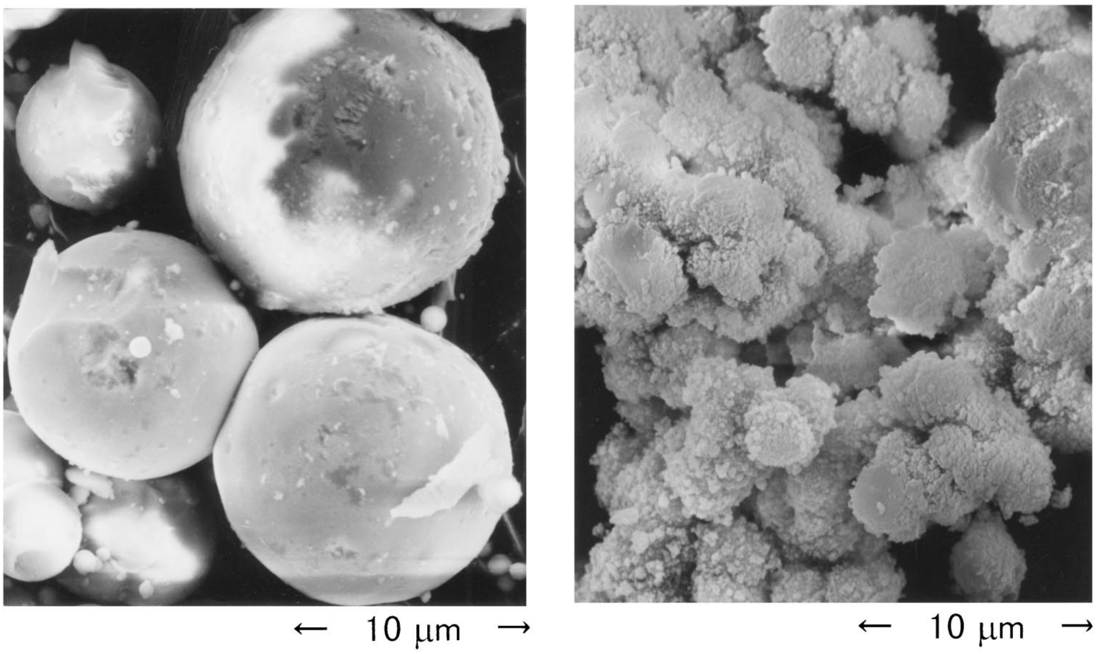
3.2. Morphology of gel

By SEM obeservation, Wannagon *et al.* [2] have reported that the opaque gels in the alkali-free SiO_2-TiO_2-ZrO_2 system contain spherical particles of <30 μm redius. As an example, microfigure change of ZrO_2 gel particles before and after Na_2O addition in Na_2O-ZrO_2 system is shown in Fig. 4. It is seen that the uniform and discrete spherical particles of ZrO_2 gel of 10 μm redius (Fig. 4a) become much coagulated and the redius decreased to <5 μm in $5Na_2O \cdot 95ZrO_2$ composition (Fig. 4b). The general trend that discrete particles in alkali-free gels are coagulated with Na_2O addition applies to Na_2O-TiO_2 system.

3.3. Crystallization temperature Tc and thermal stability Tc/TL

It is clear that the addition of Na_2O to SiO_2 gels gives a strong effect to acceralate the crystallization of gels, resulting in a drastic decrease of Tc. Fig. 5a indicates that Tc of Na_2O-SiO_2 gels decreases with Na_2O addition sharply from 1258°C (SiO_2) [1] to 613°C ($30Na_2O \cdot 70SiO_2$). The Tc value of SiO_2 gel is considerably higher than that reported by Phalippou *et al.* [7] or Ota *et al.* [10]. This may be discussed in term of gel preparation conditions. Ota *et al.* added H_2O but in poor concentration ($H_2O/TEOS = 0.5$). Wannagon *et al.* [1] added enough amount of H_2O ($H_2O/TEOS = 3$) more than stoichiometric ($H_2O/TEOS = 2$). Phalippou *et al.* [7] stated that there is an effect of the texture of the Na_2O-SiO_2 gels on the crystallization behavior and Brinker *et al.* [11] stated that a high density gel obtained when stoichiometrical amount of H_2O is added. A high density gel was assumed to give a high temperature Tc. Fig. 5b indicates that Tc of Na_2O-TiO_2 gels increases with Na_2O from 366°C (TiO_2) to 560°C ($10Na_2O \cdot 90TiO_2$). Two peaks were detected when the Na_2O content was more than 10 mol%. XRD analysis showed that the lower temperature peak is attributed to precipitation of TiO_2 (Rutile) and the higher temperature peak to $Na_2Ti_5O_{11}$. Fig. 5c indicates that Tc of Na_2O-ZrO_2 gels increases with Na_2O from 418°C (ZrO_2) to 527°C ($10Na_2O \cdot 90ZrO_2$) and stays almost constant at >10 mol% Na_2O content.

Liquidus temperture TL of the Na_2O-MO_2 ($MO_2 = SiO_2$, TiO_2, ZrO_2) system was taken from references



(a) $100ZrO_2$ (b) $5Na_2O \cdot 95ZrO_2$

Figure 4 SEM photographs of ZrO_2 gel (a), $5Na_2O \cdot 95ZrO_2$ gel (b), dried at 50°C for 5 days.

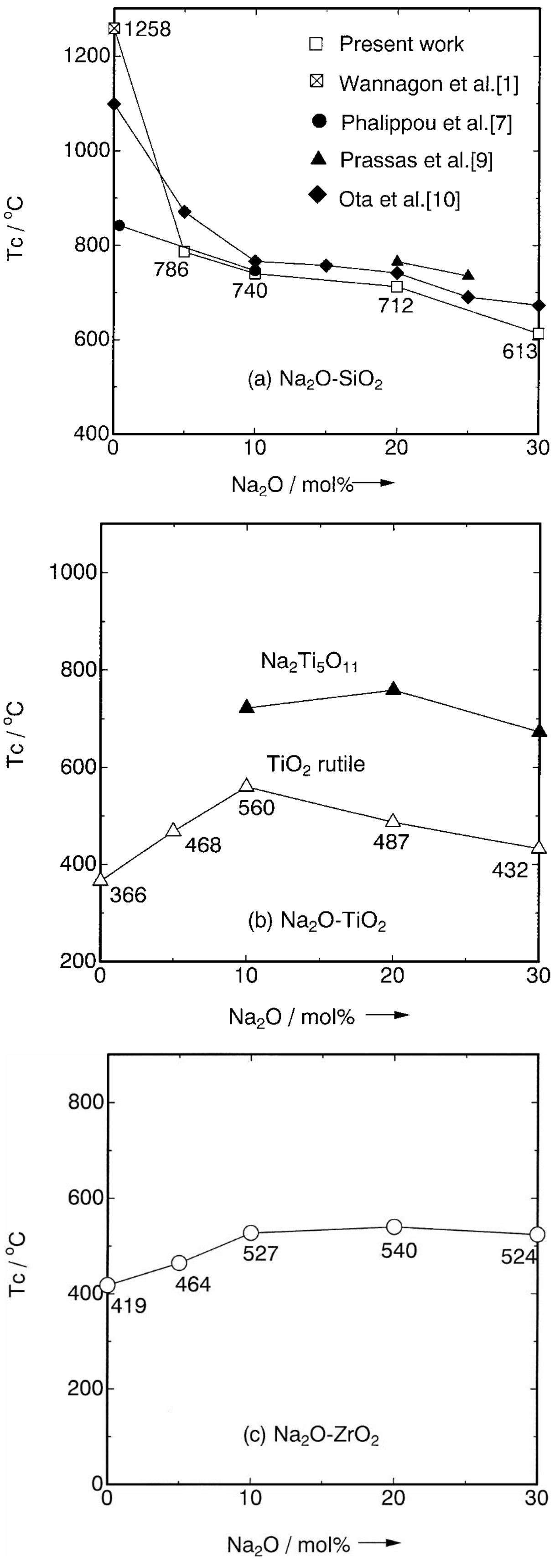


Figure 5 Crystallization temperature Tc of the Na_2O-SiO_2 (a), Na_2O-TiO_2 (b) and Na_2O-ZrO_2 gels (c) as a function of Na_2O content.

[12, 13] and thermal stability, defined by Tc/TL, was calculated in the Na_2O-MO_2 ($MO_2 =$ SiO_2, TiO_2, ZrO_2) system and summarized in Table I. Variation of Tc/TL ratio of the binary systems are illustrated in Fig. 6 as a function of Na_2O content. In the Na_2O-SiO_2 system (□ and ■), Tc/TL decreases with Na_2O from 0.77 (SiO_2) to 0.57 ($5Na_2O{\cdot}95SiO_2$). In the Na_2O-TiO_2 system (△), Tc/TL increases with Na_2O from 0.30 (TiO_2) to 0.4C ($5Na_2O{\cdot}95TiO_2$). TL values are not available but presumed to decrease with Na_2O addition in the Na_2O-ZrO_2 system (○). Tc/TL was estimated to increase from 0.23 (ZrO_2) to more than 0.27 at 10–30 mol% Na_2O compositions.

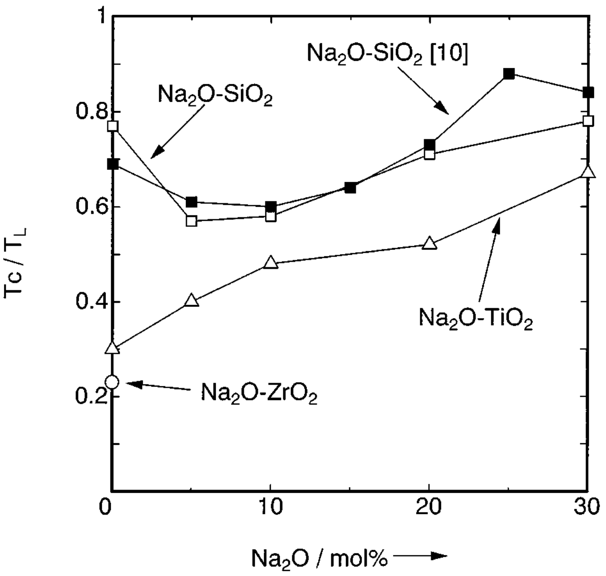


Figure 6 Tc/TL ratio of Na_2O-SiO_2 (□ and ■), Na_2O-TiO_2 (△) and Na_2O-ZrO_2 (○) gels. The Tc/TL values for the Na_2O-ZrO_2 system are not shown because true TL values are not available.

EDX (Energy Dispersive X-ray spectrometry) analysis was done to analyze the chemical composition of double layered gels in the Na_2O-TiO_2 system (>40 mol% Na_2O) and Na_2O-ZrO_2 system (>40 mol% Na_2O). Within the analytical accuracy for Na_2O content, the upper layer tend to show a higher concentration of Na_2O than the lower layer.

Fig. 7 shows some typical DTA curves obtained for $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels. The exothermic peak located at 700–800°C was taken as crystallization temperature Tc. Table II summarizes the Tc values measured for the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels. It is seen that the lowest Tc 464°C is at $5Na_2O{\cdot}95ZrO_2$ composition and highest Tc 891°C is at $5Na_2O{\cdot}76SiO_2{\cdot}19ZrO_2$ composition.

Tc isotherms for the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ system are illustrated in Fig. 8. Tc isotherm increases with the increase of SiO_2 content up to 85.5 mol% but attains a maximum at approximately equimolar contents of SiO_2 and ZrO_2 for fixed TiO_2 concentration.

Variation of Tc for fixed concentration of SiO_2, TiO_2 and ZrO_2 are shown in Fig. 9. Fig. 9a shows that Tc values of $5Na_2O{\cdot}95(TiO_2 + ZrO_2)$ gels exhibit a convex as a function of $ZrO_2/(TiO_2 + ZrO_2)$ ratio and becomes highest at midpoint between $5Na_2O{\cdot}95TiO_2$ and $5Na_2O{\cdot}95ZrO_2$ compositions. Tc curves increase and flatten out with the increase of SiO_2 content ($x = 0.2$–0.6) in the $5Na_2O{\cdot}95\{xSiO_2 + (1 - x)(TiO_2 + ZrO_2)\}$ series. Fig. 9b indicates that Tc curves of $5Na_2O{\cdot}95(SiO_2 + ZrO_2)$ gels attain a maximum at $SiO_2/(SiO_2 + ZrO_2) = 0.8$ composition. With TiO_2

TABLE I Crystallization temperature Tc, Liquidus temperature TL and Tc/TL ratios, determined on gels in the Na_2O-SiO_2, Na_2O-TiO_2 and Na_2O-ZrO_2 systems in the range 0–30 mol% Na_2O. T_L of Na_2O-ZrO_2 system is lacking and presumed to be lower than TL 2700°C (ZrO_2)

Composition/mol%		Tc/°C	Tc/K	TL/K	Tc/TL
Na_2O	SiO_2				
0	100	1258	1531	1983	0.77
5	95	786	1059	1873	0.57
10	90	740	1013	1743	0.58
20	80	712	985	1383	0.71
30	70	613	886	1123	0.78
Na_2O	TiO_2				
0	100	366	639	2103	0.30
5	95	468	741	1873	0.40
10	90	*560, 722	833, 995	1723	0.48, 0.58
20	80	*487, 759	760, 1032	1453	0.52, 0.71
30	70	*432, 673	705, 946	1053	0.67, 0.90
Na_2O	ZrO_2				
0	100	419	691	2973	0.23
5	95	464	737	<2973	>0.25
10	90	527	800	<2973	>0.27
20	80	540	813	<2973	>0.27
30	70	524	797	<2973	>0.27

*Two peaks was detected

TABLE II Crystallization temperature Tc of the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels determined by DTA in the composition range 0–95 mol% SiO_2, 0–95 mol% TiO_2 and 0–95 mol% ZrO_2

Composition/mol%				Tc/°C	Composition/mol%				Tc/°C
Na_2O	SiO_2	TiO_2	ZrO_2		Na_2O	SiO_2	TiO_2	ZrO_2	
5	95	0	0	786	5	57	28.5	9.5	733
5	85.5	9.5	0	805	5	57	19	19	779
5	76	19	0	795	5	57	9.5	28.5	824
5	66.5	28.5	0	636	5	47.5	38	9.5	715
5	57	38	0	633	5	47.5	28.5	19	757
5	47.5	47.5	0	629	5	47.5	19	28.5	794
5	38	57	0	629	5	47.5	9.5	38	825
5	28.5	66.5	0	625	5	38	47.5	9.5	704
5	19	76	0	637	5	38	38	19	747
5	9.5	85.5	0	587	5	38	28.5	28.5	776
5	0	95	0	468	5	38	19	38	802
5	0	85.5	9.5	522	5	38	9.5	47.5	824
5	0	76	19	640	5	28.5	57	9.5	636
5	0	66.5	28.5	684	5	28.5	47.5	19	733
5	0	57	38	697	5	28.5	38	28.5	763
5	0	47.5	47.5	702	5	28.5	28.5	38	779
5	0	38	57	698	5	28.5	19	47.5	796
5	0	28.5	66.5	678	5	28.5	9.5	57	809
5	0	19	76	636	5	19	66.5	9.5	700
5	0	9.5	85.5	560	5	19	57	19	728
5	0	0	95	464	5	19	47.5	28.5	752
5	9.5	0	85.5	668	5	19	38	38	764
5	19	0	76	757	5	19	28.5	47.5	773
5	28.5	0	66.6	803	5	19	19	57	775
5	38	0	57	841	5	19	9.5	66.5	778
5	47.5	0	47.5	861	5	9.5	76	9.5	717
5	57	0	38	872	5	9.5	66.5	19	720
5	66.5	0	28.5	877	5	9.5	57	28.5	721
5	76	0	19	891	5	9.5	47.5	38	743
5	85.5	0	9.5	854	5	9.5	38	47.5	748
5	76	9.5	9.5	777	5	9.5	28.5	57	744
5	66.5	19	9.5	741	5	9.5	19	66.5	740
5	66.6	9.5	19	812	5	9.5	9.5	76	718

addition, Tc increases in the ZrO_2 rich composition but decreases in the rest composition and Tc curve shows a slight convax. Fig. 9c indicates that Tc curve of $5Na_2O{\cdot}95(SiO_2 + TiO_2)$ gels shows a maximum at $SiO_2/(SiO_2 + TiO_2) = 0.9$ composition. However, Tc values increase with the increase of ZrO_2 content in the $5Na_2O{\cdot}95\{xZrO_2 + (1 - x)(SiO_2 + TiO_2)\}$ series.

Comparing the Tc values of Na_2O containing SiO_2-TiO_2-ZrO_2 system with that of alkali-free SiO_2-TiO_2-ZrO_2 system [1, 2], it is obvious that Tc

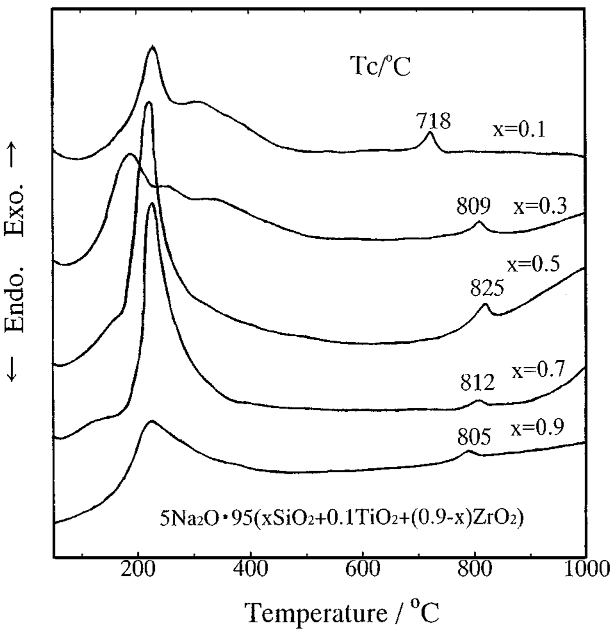


Figure 7 Typical DTA curves of dried gels in the $5Na_2O{\cdot}95(xSiO_2 + 0.1TiO_2 + (0.9 - x)ZrO_2)$ compositions; $x = 0.1-0.9$.

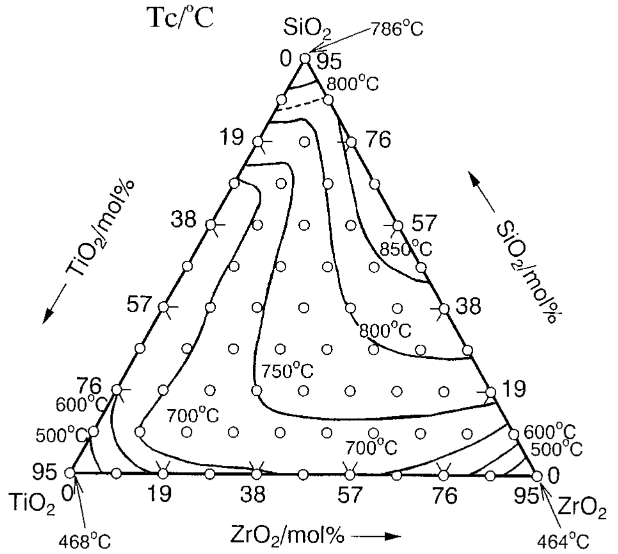


Figure 8 Tc isotherms of the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels.

decreases drastically with Na_2O addition in SiO_2-rich compositions. For example, the highest Tc 1294°C observed in alkali-free gels ($90SiO_2{\cdot}10TiO_2$) decreases to 891°C observed in the the alkali containing gels ($5Na_2O{\cdot}76SiO_2{\cdot}19ZrO_2$). On the other hand, Tc increases with Na_2O containing gels in TiO_2 or ZrO_2 rich compositions (>70 mol% TiO_2 or >70 mol% ZrO_2 content); For example, Tc = 366°C (TiO_2) increases to 468°C ($5Na_2O{\cdot}95TiO_2$) and Tc = 419°C (ZrO_2) increases to 464°C ($5Na_2O{\cdot}95ZrO_2$). From the supplementary experiments on the Na_2O-SiO_2, Na_2O-TiO_2 and Na_2O-ZrO_2 systems (Fig. 5a–c), we can speculate that Na_2O combines with SiO_2 network to weaken the network structure. But Na_2O combines with TiO_2 or ZrO_2 components to strengthen the amorphous structure of TiO_2 or ZrO_2 gels. Because of the lack of TL values and consequently lack of Tc/TL ratios in the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ system, we can only

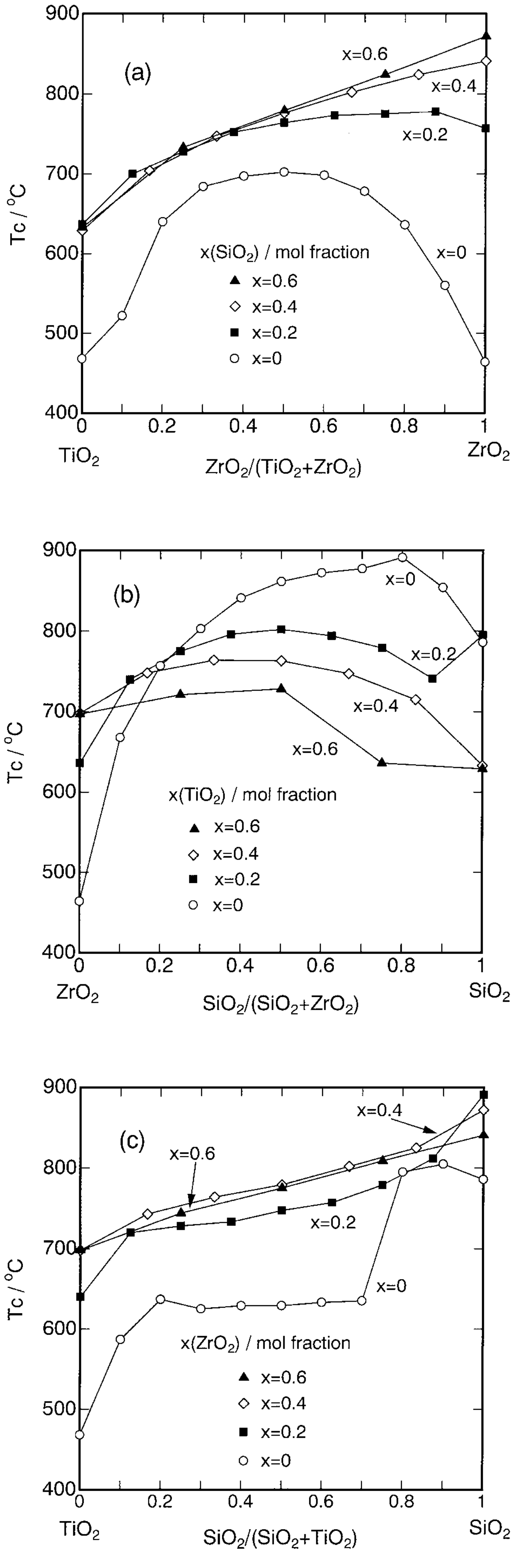


Figure 9 Tc isotherms of $5Na_2O{\cdot}95\{xSiO_2 + (1 - x)(TiO_2 + ZrO_2)\}$ gels for fixed SiO_2 concentration : $x = 0$–0.6 (a), $5Na_2O{\cdot}95\{xTiO_2 + (1 - x)(SiO_2 + ZrO_2)\}$ gels for fixed TiO_2 concentration : $x = 0$–0.6 (b), $5Na_2O{\cdot}95\{xZrO_2 + (1 - x)(SiO_2 + TiO_2)\}$ gels for fixed ZrO_2 concentration : $x = 0$–0.6 (c).

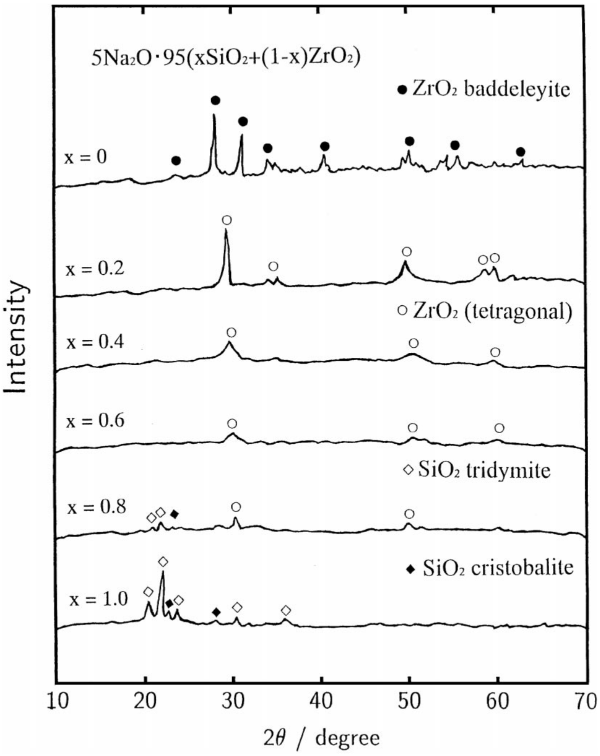


Figure 10 Typical XRD patterns of the $5Na_2O{\cdot}95(xSiO_2 + (1-x)ZrO_2)$ ($x = 0$–1.0) gels after DTA run up to 1000°C, and quenched.

imagine the variation in the thermal stability or amorphous forming ability of the system. However notice some advantageous aspects in Na_2O containing SiO_2-TiO_2-ZrO_2 system; (1) Tc and thermal stability are enhanced in TiO_2/TiO_2 rich compositions and ZrO_2/ZrO_2 rich compositions and (2) processing is easy because TL must be lowered with Na_2O inclusion.

3.4. Precipitated crystalline phases after DTA runs

Some of XRD patterns obtained after the DTA run up to 1000°C are shown in Fig. 10. Crystalline phases precipitated in the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels are summerized in Fig. 11. Cristobalite (SiO_2), denoted as Sc, was precipitated in SiO_2 rich compositions (76–95 mol% SiO_2) in the $5Na_2O{\cdot}95(SiO_2 + ZrO_2)$ system. Tridymite (SiO_2), St, precipitated in SiO_2 rich compositions (66.5–95 mol% SiO_2). Rutile (TiO_2), Tr, precipitated in the ZrO_2 poor compositions (0–76 mol% SiO_2 and 0–28.5 mol% ZrO_2) in the $5Na_2O{\cdot}95(SiO_2 + TiO_2)$ system. Monoclinic ZrO_2, Zm, precipitated in the ZrO_2 rich composition (>57 mol% ZrO_2) and tetragonal ZrO_2, Zt, appeared in wide range of comositions (9.5–76 mol% ZrO_2) in the $5Na_2O{\cdot}95(SiO_2 + ZrO_2)$ system. $Na_2Ti_5O_{11}$, NT, precipitated in the TiO_2 rich compositions (>57 mol% TiO_2). Orthorhombic $ZrTiO_4$, ZT, emerged in the central area down to the midpoint ($SiO_2 = 0$–57 mol%, $TiO_2 = 19$–85.5 mol%) of the TiO_2-ZrO_2 system.

At TiO_2 rich compositions in the Na_2O-TiO_2-SiO_2 system, titanium atoms are considered to be octahedrally coordinated by oxygen [14–16]. On Na_2O addition the coordination number of titanium atom is reduced from 6 to 4 [17, 18]. Compared to the precipitated cystalline phases of tetragonal ZrO_2, Zt and monoclinic ZrO_2, Zm in alkali-free SiO_2-TiO_2-ZrO_2 system [1], tetragonal ZrO_2 was found in a wider range of area instead of monoclinic phase in this present work. It is inferred that from increased thermal stabilitity related with amorphous-forming ability, Na_2O addition may have reduced coordination number of zirconium atom from 8 to 5 or 4.

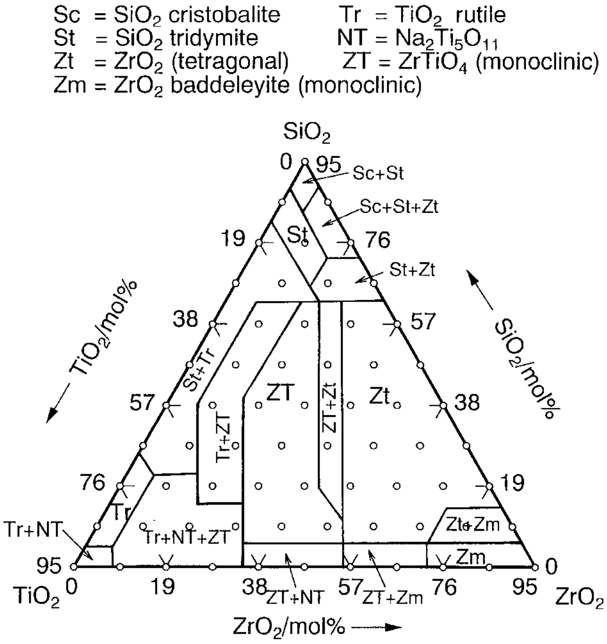


Figure 11 Precipitated crystalline phases in the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels after DTA run up to 1000°C, and quenched.

4. Summary

Gels were prepared in the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ system together with Na_2O-MO_2 ($MO_2 = SiO_2$, TiO_2 and ZrO_2) system using $Si(OC_2H_2)_4$, $Ti(iso\text{-}OC_3H_7)_4$, $Zr(n\text{-}OC_3H_7)_4$ and $NaOCH_3$ solutions in EtOH without H_2O. For the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels, transparent bulk gels formed in the range 28.5–85.5 mol% SiO_2, 0–57 mol% TiO_2 and 0–57 mol% ZrO_2, and opaque gels in the rest compositions. SEM observation showed that the opague gels consist of spherical particles of less than 5 μm in diameter. Crystallization temperature, Tc was measured by DTA. With Na_2O addition, Tc decreased from 1258°C (SiO_2) [1] to 786°C ($5Na_2O{\cdot}95SiO_2$) in the Na_2O-SiO_2 system but increased from 366°C (TiO_2) [1] to 468°C ($5Na_2O{\cdot}95TiO_2$) in the Na_2O-TiO_2 system and from 419°C (ZrO_2) [1] to 464°C ($5Na_2O{\cdot}95ZrO_2$) in the Na_2O-ZrO_2 system. Therefore Tc in the SiO_2 rich compositions in the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ system was lower than in the alkali-free SiO_2-TiO_2-ZrO_2 system. On the other hand Tc in the TiO_2 rich or ZrO_2 rich compositions in the $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ system was higher than in the SiO_2-TiO_2-ZrO_2 system. After DTA run of $5Na_2O{\cdot}95(SiO_2 + TiO_2 + ZrO_2)$ gels up to 1000°C, cristobalite (SiO_2), tridymite (SiO_2), rutile (TiO_2), baddeleyite (ZrO_2) and tetragonal ZrO_2, $Na_2Ti_5O_{11}$ and monoclinic $ZrTiO_4$ precipitated. It is assumed that Na_2O combines with SiO_2 to weaken the SiO_2 network, but combines with TiO_2 or ZrO_2 to trengthen the structure of amorphous TiO_2 and ZrO_2 network.

References

1. A. WANNAGON, N. MISHIMA, T. WAKASUGI, R. OTA and J. FUKUNAGA, *J. Ceram. Soc. Japan* **105** (1997) 940.
2. A. WANNAGON, N. MISHIMA, R. OTA, T. WAKASUGI and J. FUKUNAGA, *Mat. Sci. Res. Inter.* **3** (1997) 210.
3. R. OTA, A. WANNAGON, T. WAKASUGI and J. FUKUNAGA, Proc. 18th ICG, Am. Ceram. Soc. (1998) CD-Rom E1:25.
4. K. KAMIYA, S. SAKKA and Y. TATEMACHI, *J. Mater. Sci.* **15** (1980) 1765.
5. T. HARA, R. OTA, J. FUKUNAGA, T. WAKASUGI and A. MIYAKE, *J. Ceram. Soc. Japan* **100** (1992) 905.
6. T. WAKASUGI, R. OTA, T. TAWA and J. FUKUNAGA, *Mat. Sci. Res. Inter.* **1** (1995) 65.
7. J. PHALIPPOU, M. PRASSAS and J. ZARZYCKI, *J. Non-Cryst. Solids* **48** (1982) 17.
8. M. PRASSAS, J. PHALIPPOU, L. L. HENCH and J. ZARZYCKI, *ibid.* **48** (1982) 79.
9. M. PRASSAS, J. PHALIPPOU and L. L. HENCH, *ibid.* **63** (1984) 375.
10. R. OTA, J. FUKUNAGA and T. WAKASUGI, Proc.Intn'l Conf.Sci&Tech.New Glasses (1991) 59.
11. C. J. BRINKER, K. D. KEEFER, D. W. SCHAEFER and C. S. ASHLEY, *J. Non-Cryst. Solids* **48** (1982) 47.
12. E. M. LEVIN, C. R. ROBBINS and H. F. McMURDIE, “Phase Diagrams for Ceramists,” Vol. 1 (Am. Ceram. Soc., 1987) p. 94.
13. R. S. ROTH, J. R. DENNIS and H. F. McMURDIE, “Phase Diagrams for Ceramists,” Vol. 6 (Am. Ceram. Soc., 1987) p. 254.
14. H. SCHOLZE, “Glass Nature, Structure and Properties,” Translated edn. (Springer-Verlag New York, Inc., 1991) p. 142.
15. N. IWAMOTO, N. UMESAKI, H. HIDAKA, K. HIRAO and N. SOGA, *Yogyo-Kyokai-Shi* **94** (1986) 160.
16. T. HANADA and N. SOGA, *J. Non-Cryst. Solids* **38/39** (1980) 105.
17. K. TAKAHASHI, N. MOCHIDA and Y. YOSHIDA, *Yogyo-Kyokai-Shi* **85** (1977) 26.
18. C. W. PONAFER, H. BACK and J. E. DICKINSON JR., *Non-Cryst. Solids* **201** (1996) 81.
19. M. YAMAMOTO *et al.*, “Handbook of Industrial Crystal,” Jpn. (Kyoritsu Publishing Co. Ltd., 1971) p. 42.

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