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Transparency of $LiTaO_3$-SiO_2-Al_2O_3 glass-ceramics in relation to their microstructure

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The glasses with various compositions in the $LiTaO_3$–SiO_2–Al_2O_3 system were heated from room temperature to temperatures ranging from 750° to 1050° C at a rate of 5° C min^{-1}. From the glasses in the $LiTaO_3$–SiO_2 system no transparent glass-ceramic was obtained even when their $LiTaO_3/SiO_2$ mole ratios were as high as 2.33. The diameter and number of the $LiTaO_3$ crystal grains precipitated in the glasses were 5–15 μm and 10^8–10^{10} grains cm^{-3}, respectively. On the contrary, transparent glass-ceramics were obtained from the glasses containing Al_2O_3; their compositions covered a fairly large area in the $LiTaO_3$–SiO_2–Al_2O_3 system, which encompasses the compositions with the $LiTaO_3/SiO_2$ + $AlO_{1.5}$ mole ratio as low as 0.25. The diameter and number of the $LiTaO_3$ crystal grains precipitated in the transparent glass-ceramics were as small as 10–20 nm and as many as 10^{16}–10^{18} grains cm^{-3}, respectively. High nucleation rates of the $LiTaO_3$ crystals in the Al_2O_3-containing glasses were interpreted in terms of structural inflexibility induced in the glass-network by the addition of Al_2O_3 to the $LiTaO_3$–SiO_2 system.

1. Introduction

In 1965, Borrelli *et al.* [1] succeeded in producing transparent glass-ceramics composed essentially of $NaNbO_3$ crystals which exhibit a fairly large electro-optic effect, and since then searches for new transparent glass-ceramics containing other ferroelectric crystals have been made by many researchers [2–4]. One of the important properties required for this kind of glass-ceramics is high optical transparency.

Generally, glass-ceramics are transparent when their constituent crystalline particles are so small in size that they produce no effective light scattering even at the shorter wavelengths of the visible spectrum, or when the refractive index difference between crystalline and glassy phases is sufficiently small [5]. For obtaining transparent glass-ceramics containing ferroelectric crystals, the former condition must be satisfied, since the refractive index of ferroelectric crystals is generally much higher than that of the glassy matrix.

Layton *et al.* [6] reported that the glass-ceramics containing ferroelectric crystals are transparent, provided that the content of the network-formers such as SiO_2 and Al_2O_3 in their parent glasses is very low. The present authors, however, have found that some systems such as the $LiTaO_3$–SiO_2–Al_2O_3 system do not follow their criterion.

This paper presents results obtained in a study of the transparent glass-ceramics prepared from the glasses of the $LiTaO_3$–SiO_2–Al_2O_3 system, with particular regard to the relationship between their chemical composition and transparency.

Beall [3] has already reported that the transparent $LiTaO_3$ glass-ceramics can be obtained from a system similar to the one noted above.

However, only limited compositions have been investigated by him.

2. Experimental

2.1. Preparation of glass

About 15 g of batch mixtures with the compositions given in Table 1 were prepared from the reagent grade chemicals of Li_2CO_3, Ta_2O_5, SiO_2 and $Al(OH)_3$. They were melted in Pt10Rh crucibles at 1550° C for 3 h in a SiC electric furnace. The melts were poured onto a steel plate and pressed into plates approximately 1 mm thick. A number of melts, which were too viscous to be poured out, were cooled in the crucibles by dipping the bottom of the crucibles in water. Appearance of the cooled substances is shown in Table 1 and Fig. 1. The compositions which gave clear glasses lie in a region bounded by line G in Fig. 1.

TABLE I Glass composition

No.	Composition (mol %)			B/N*	Appearance of the molten specimens†
	$LiTaO_3$	SiO_2	$AlO_{1.5}$		
1	70	30		2.33	C
2	65	35		1.86	C
3	50	50		1.00	C
4	40	60		0.66	C
5	30	70		0.43	C
6	20	80		0.25	C
7	15	85		0.18	C
8	65	32.8	2.2	1.86	C
9	20	77.5	2.5	0.25	C
10	65	30	5	1.86	C
11	40	55	5	0.66	C
12	25	70	5	0.33	C
13	20	75	5	0.25	C
14	65	25	10	1.86	C
15	20	70	10	0.25	C
16	10	78.8	11.2	0.11	C
17	30	50	20	0.43	C
18	20	57.1	22.9	0.25	C
19	65	17.5	17.5	1.86	C
20	55	22.5	22.5	1.22	C
21	40	30	30	0.66	C
22	30	35	35	0.43	C
23	50	10	40	1.00	C
24	40	15	45	0.66	C
25	30	25	45	0.43	C
26	20	40	40	0.25	C
27	10	70	20	0.11	C
28	75	25		3.00	I
29	70	15	15	2.33	I
30	65	10	25	1.86	I
31	50		50	1.00	I
32	30	15	55	0.43	I
33	10	45	45	0.11	I

* B/N = Ta/(Si + Al) (atomic ratio)

† C clear glass, I imperfect melts (a part of the raw materials remained undissolved in the melt).

2.2. Heat treatment of glass

The clear glass plates thus obtained were cut into slabs of 10 x 5 x 1 mm in size, heated on a platinum sheet in an electric furnace up to various temperatures below 1000° C at a rate of 5° C min^{-1}, taken out from the furnace and allowed to cool in air. The specimens which showed no or only a trace of $LiTaO_3$ crystal on heating to 1000° C were further heated up to 1050° C. The transparency of the heat-treated specimens was examined visually. The results are summarised in Table II, in which "transparent" means that letters placed beneath the specimens which were approximately 1 mm thick could be read clearly through the specimen.

2.3. X-ray diffraction analysis

All the heat-treated specimens were subjected to powder X-ray diffraction analysis for identification of the crystalline phases precipitated (Table II). For the specimens in which more than two kinds of crystal phase were precipitated, the names of the crystals were noted in the decreasing order of their amount of precipitation; e.g. for the specimen No. 22 heated up to 1000° C, the amount of β-quartz solid solution was the largest and that of the $LiTaO_3$ crystal was the smallest. Compositions of the glasses in which the ferroelectric $LiTaO_3$ crystals precipitated alone or together with the other crystals lie in a region bounded by lines G and L in Fig. 1. Among these compositions, those bounded by lines G and T are transparent and the others are opaque.

2.4. Electron microscopy

The surface of the heat-treated glasses was ground with Al_2O_3 powders to the depth of 0.2 mm from their original surfaces, polished with CeO_2 powders and etched with 5% hydrofluoric acid for 2–30 min. Figs. 2 and 3 are electronmicrographs of their platinum palladium pre-shadowed carbon replicas.

The micrographs in Fig. 2 represent the compositions containing no Al_2O_3 (Nos. 2, 4 and 6), i.e. those of the system $LiTaO_3$–SiO_2, from which only opaque glass-ceramics were obtained. All the glasses in this system, when heated from room temperature, first showed a metastable liquid phase separation (Fig. 2a, d and g) and then formation of crystalline clusters (Fig. 2b, e and h).

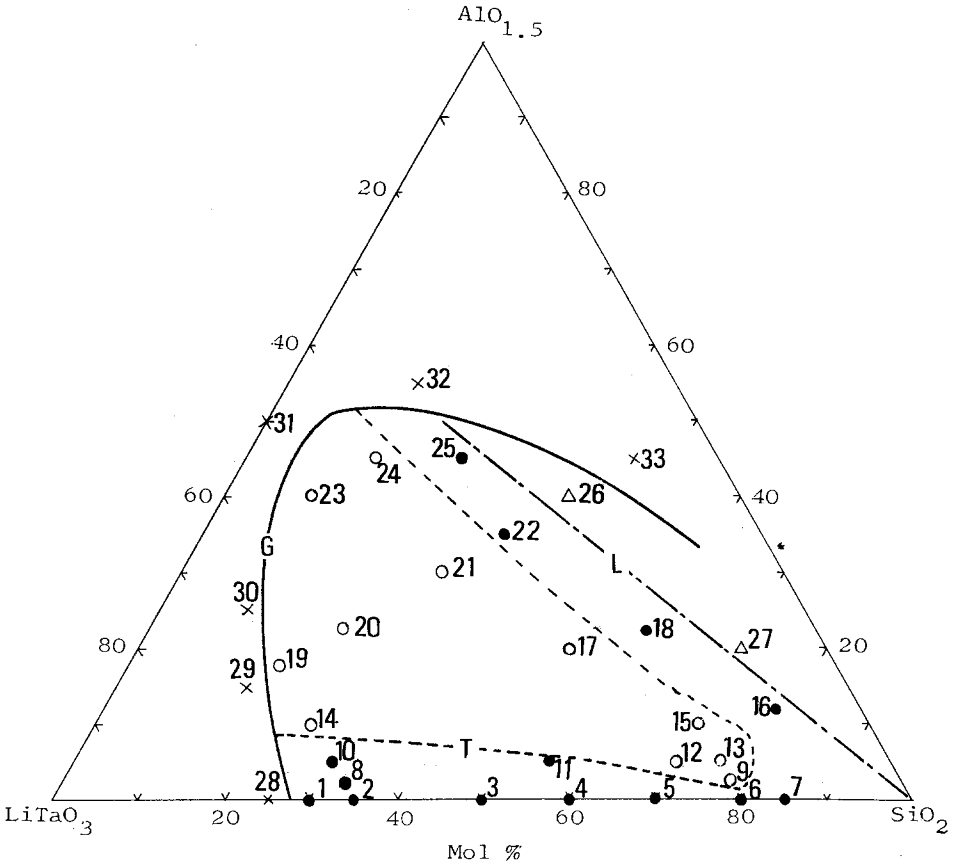

Figure 1 Region of glass formation (bounded by line G) and those from which transparent and opaque glass-ceramics were obtained: × imperfect melt; ○ transparent glass-ceramics containing $LiTaO_3$ crystals; ● opaque glass-ceramics containing $LiTaO_3$ crystals; △ glass-ceramics containing no $LiTaO_3$ crystals.

Fig. 2c, f and i are magnified reproductions of a portion of Fig. 2b, e and h, respectively, showing a microstructure near the boundary between a crystalline cluster and the surrounding glassy matrix. Fig. 2f and i for the composition Nos. 4 and 6 show that a spherical or interconnected structure produced by the metastable liquid phase separation remains in both of the crystalline cluster and the surrounding glassy matrix. This suggests that the crystallization of the glasses commenced while the metastable glassy two-phase structure was still present. In Fig. 2c for No. 2 no such metastable structure is observed, which indicates that the metastable structure disappeared before the crystallization commenced.
the crystallization commenced.

The micrographs in Fig. 3 represent the compositions containing Al_2O_3 (Nos. 8, 13, 19 and 21). Aluminum to silicon atomic ratios of Nos. 8 and 13 are both 1:15, whereas those of Nos. 19 and 21 are both 1:1. Of these compositions No. 8 has the smallest Al_2O_3 content. As noted previously, all of these glasses remained transparent even after they crystallized except for the glass No. 8 which became opaque by crystallization. Except for No. 8, all of these glasses showed a metastable liquid phase separation prior to their crystallization in the same way as observed for the Al_2O_3-free glasses. Big differences between the Al_2O_3-free and Al_2O_3-containing glasses lie in the scale of their phase-separated structure and the size of their crystal grains precipitated after the phase separation, i.e. for the Al_2O_3-containing glasses the scale of the phase-separated structure was about 10 nm and the size of the crystal grains was 10–20 nm both of which were much smaller than those for the Al_2O_3-free glasses, respectively. In the glass No. 8, the phase separation hardly

TABLE II Transparency of heat-treated specimens and crystalline phases precipitated

No.	Temperature (° C)						
	750	800	850	900	950	1000	1050
1	–[1]	–	–	*LT*[2,3]	*LT*	*LT*	
2	–	–	–	*LT*	*LT*	*LT*	
3	–	–	–	–	*LT*	*LT*	
4	–	–	–	–	*LT*	*LT*	
5	–	–	–	–	*LT*	*LT*	
6	–	–	–	–	–	*LT*	
7	–	–	–	–	–	–	*LT*
8	–	–	–	*LT*	*LT*	*LT*	
9	–	–	–	–	LT	LT	
10	–	–	–	(LT)[7]	*LT*	*LT*	
11	–	–	–	–	*LT · T*[4]	*LT · T*	
12	–	–	–	T	LT · T	LT · T	
13	–	–	–	T	LT · T	LT	
14	–	–	LT · (S)[5]	LT · (S)	LT · (S)	LT · (S)	
15	–	–	–	T	LT · T	LT · T	
16	–	–	–	–	T	T · (LT)	*T · (LT)*
17	–	–	T · S	T · S	T · S	LT · T · S	
18	–	–	T	T · S	T · S	T · S	*T · S · (LT)*
19	–	–	LT	LT	LT	LT	
20	–	–	LT	LT	LT	LT	
21	–	T	T · S	LT · T · S	LT · T · S	LT · T · S	
22	–	–	T · S	T · S	T · S · X[6]	S · T · X · (LT)	*S · T · X · LT*
23	(LT)	LT	LT	LT	LT	*LT*	
24	–	LT	LT · (S)	LT · (S)	*LT · (S)*	*LT · (S)*	
25	–	–	*S · LT · (X)*	*LT · S · (X)*	*LT · S · (X)*	*LT · S · (X)*	
26	–	–	–	T · S	T · S	T · S · X	
27	–	–	–	–	T · X	T · X	T · X

[1] – Transparent glass.
[2] Specimens in italics were opaque, whereas those not were transparent.
[3] LT $LiTaO_3$ crystal.
[4] T Ta_2O_5 crystal.
[5] S β-quartz solid solution crystal.
[6] X unidentified crystal.
[7] ( ) traces of crystal.

occurred and the size of the crystalline clusters formed was 3 μm, being almost equal to that for Al_2O_3-free glasses.

For all the specimens examined with an electronmicroscope, diameters of the $LiTaO_3$ crystal grains or crystalline clusters precipitated in each of the specimens, their numbers in a unit volume of the specimens, and their contents were determined and the results are given in Table III; the diameters of the $LiTaO_3$ crystal grains or crystalline clusters denoted by d and their number denoted by N were determined directly on the micrographs of Figs. 2 and 3. Since the crystallized specimen No. 21 contained crystals other than the $LiTaO_3$, the number of the $LiTaO_3$ crystal grains per unit volume of the specimen, N^*, was calculated by using the formula,

$$N^* = \frac{\rho W}{\rho_c \frac{4}{3} \pi (d/2)^3}$$

where ρ is the density of the crystallized specimens measured by Archimedean technique, W is the weight fraction of the $LiTaO_3$ crystal, ρ_c is the density of the $LiTaO_3$ crystal calculated from its lattice dimension determined by X-ray diffraction analysis, and d is the average diameter of the crystals determined on the electronmicrograph. The W values in the formula were determined by comparing the intensity of the (204) X-ray diffraction line of the $LiTaO_3$ crystal for the crystallized glasses with that for the standard mixtures of the $LiTaO_3$ crystal and glasses. Although the crystallized glasses Nos. 13 and 19 contained

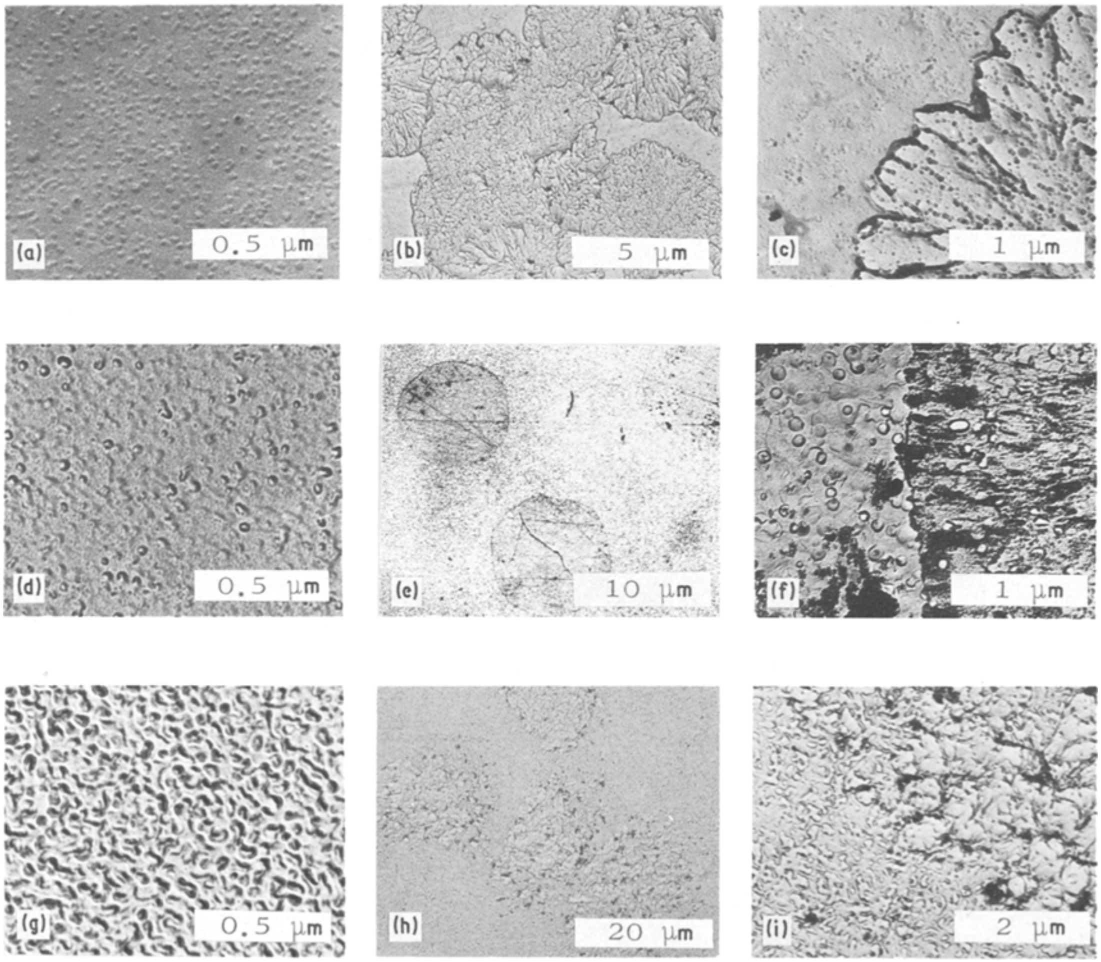

Figure 2 Electron micrographs of $LiTaO_3-SiO_2$ glasses before and after crystallization: (a) Specimen 2 heated to 850° C (phase-separated, transparent); (b) and (c) Specimen 2 heated to 900° C (partially crystallized, opaque; crystal phase $LiTaO_3$); (d) Specimen 4 heated to 900° C (phase-separated, transparent); (e) and (f) Specimen 4 heated to 950° C (partially crystallized, opaque; crystal phase $LiTaO_3$); (g) Specimen 6 heated to 950° C (phase-separated, transparent); (h) and (i) Specimen 6 heated to 1000° C (partially crystallized, opaque; crystal phase $LiTaO_3$). Photographs (c), (f) and (i) are part of the interface between the crystal and surrounding matrix magnified from the preceding photograph.

TABLE III Content (W), particle diameter (d) and particle number (N and N^*) of $LiTaO_3$ crystals precipitated in glass-ceramics

No.	Max. temp. of heat-treatment	ρ† ($g\,cm^{-3}$)	ρ_c† ($g\,cm^{-3}$)	W (wt. fraction)	d (nm)	N (grains cm^{-3})	N^*‡ (grains cm^{-3})
2	900			0.74	0.5×10^4	1.1×10^{10}	
4	950			0.27	1.0×10^4	2.5×10^8	
6	1000			0.23	1.5×10^4	1.3×10^8	
8	900			0.67	0.3×10^4	2.3×10^{10}	
13	1000	3.4	7.45	0.26	2.0×10	6.1×10^{16}	2.8×10^{16}
19	850	6.0	7.45	0.59	1.0×10	3.0×10^{17}	9.1×10^{17}
21	900	4.9	7.45	0.45	2.0×10		7.1×10^{16}

† ρ and ρ_c are the density of the crystallized specimens and $LiTaO_3$ crystal, respectively.

‡ N^* is calculated from $N^* = \rho W / \rho_c \frac{4}{3} \pi (d/2)^3$.

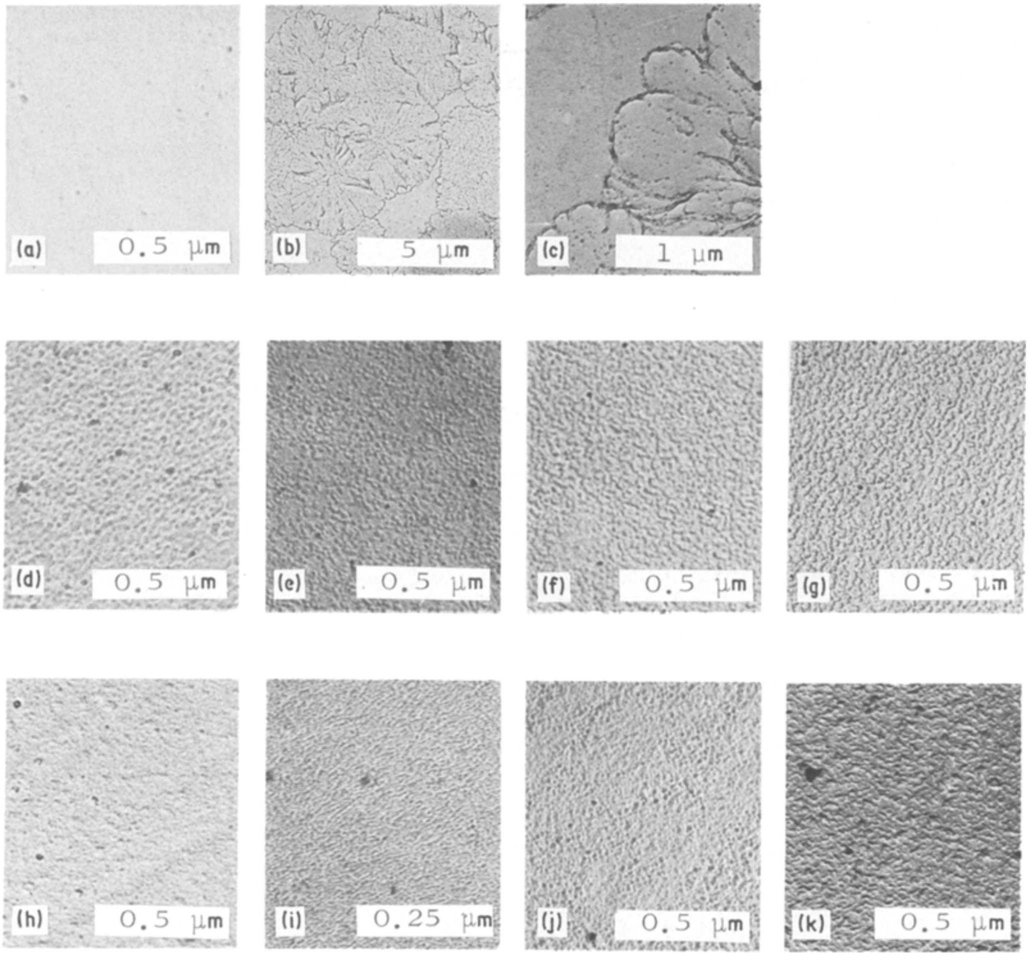

Figure 3 Electron micrographs of $LiTaO_3-SiO_2-Al_2O_3$ glasses before and after crystallization: (a) Specimen 8 heated to 850° C (transparent); (b) Specimen 8 heated to 900° C (partially crystallized, opaque; crystal phase $LiTaO_3$); (c) crystal–matrix interface of (b) magnified; (d) Specimen 13 heated to 850° C (phase-separated, transparent); (e) Specimen 13 heated to 900° C (partially crystallized, transparent; crystal phase Ta_2O_5); (f) Specimen 13 heated to 950° C (partially crystallized, transparent; crystal phase Ta_2O_5 and $LiTaO_3$); (g) Specimen 13 heated to 1000° C (partially crystallized, transparent; crystal phase $LiTaO_3$); (h) Specimen 19 heated to 800° C (phase-separated, transparent); (i) Specimen 19 heated to 850° C (partially crystallized, transparent, crystal phase $LiTaO_3$); (j) Specimen 21 heated to 750° C (phase-separated, transparent); (k) Specimen 21 heated to 900° C (partially crystallized, transparent; crystal phase $LiTaO_3$, Ta_2O_5 and β-quartz solid solution).

only the $LiTaO_3$ crystals, their N^* values were also calculated by using the above formula for comparison with the N values determined directly on the micrographs. They are in good agreement. Table III indicates that for the transparent crystallized glasses containing Al_2O_3 (Nos. 13, 19 and 21) the d values are 10–20 nm and the N or N^* values are $10^{16}-10^{18}$ grains cm^{-3}, whereas for the opaque crystallized glasses containing no or a minute amount of Al_2O_3 (Nos. 2, 4, 6 and 8) the d values are 3–15 µm and the N values are 10^8-10^{10} grains cm^{-3}.

2.5. Phase diagram of the system $LiTaO_3-SiO_2$

A phase diagram of the $LiTaO_3-SiO_2$ system was produced in which a region of metastable liquid phase separation was located. The liquidus line was determined by quenching pieces (0.1 g) of glasses with various $LiTaO_3/SiO_2$ mole ratios by dropping into water, after heating at various temperatures in the range of 1400°–1600° C for about 10 min, and then subjecting to X-ray diffraction analysis. The melting temperatures for the $LiTaO_3$ [7] and SiO_2 [8] were quoted from the literature. Stable

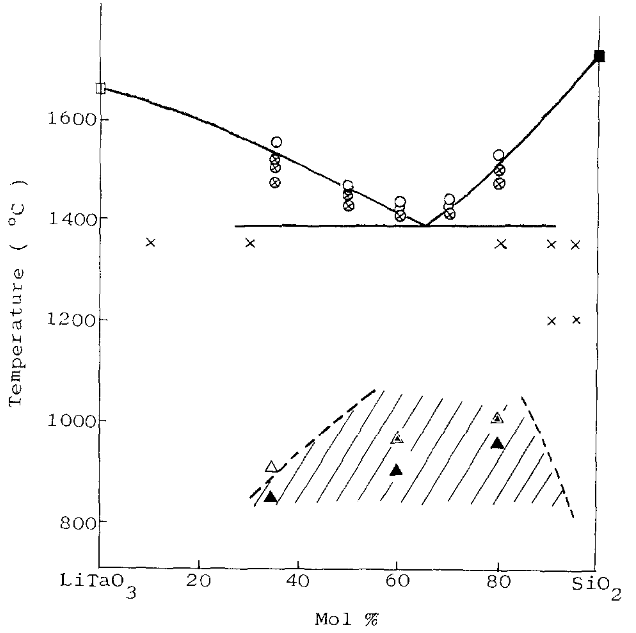

Figure 4 Phase diagram of the system $LiTaO_3-SiO_2$: ○ perfect melt; ⊗ melt containing crystals; × $LiTaO_3 + SiO_2$ crystals; △ homogeneous glass; ▲ phase-separated glass containing no crystals; △ phase-separated glass in which $LiTaO_3$ crystals were partially precipitated; □ and ■ taken from the data by A. A. Ballman [7] and by R. B. Sosman [8].

crystals existing below the solidus line were examined by X-ray diffraction analyses of the sintered masses obtained by heating the compacted mixtures (about 2 g) of chemical reagent grade Li_2CO_3, Ta_2O_5 and SiO_2 powders, with varying $LiTaO_3/SiO_2$ mole ratios in platinum crucibles at various temperatures below the solidus for 2 h. The results are shown in Fig. 4. Liquidus and solidus lines estimated from these data are indicated by solid lines. The temperatures at which the glasses of various compositions showed the metastable liquid phase-separation (see Fig. 2) are also plotted in Fig. 4. A liquid two-phase region, estimated from these data, is indicated by the oblique lines. Except for the composition No. 2, the sharp clearing temperatures could not be obtained since the glass specimens were liable to crystallize before the liquid two-phase structure disappeared.

3. Discussion

3.1. Transparency of crystallized glasses related to their network-former content

Layton *et al.* [6] reported that composite materials consisting primarily of titanates or niobates with a perovskite-type structure and formed by crystallization from glass are transparent, provided that the network-former content of the parent glass is very low. They also reported that glasses must contain *B* and *N* with $B/N > 1$ to yield well crystallized transparent materials, where *N* denotes the number of network-former cations such as Si^{4+} and Al^{3+} ions and *B* denotes that of network-substituting cations such as Ti^{4+} and Nb^{5+} ions. Since the $LiTaO_3$ phase precipitated in the present $LiTaO_3-SiO_2-Al_2O_3$ glasses has a similar crystal structure to that of the perovskite-type phase [9] and in addition the Ta^{5+} ion has the same valency and similar size [10] as the Nb^{5+} ion, it is expected that the rule of Layton *et al.* should be applicable to the present system. As Fig. 1 shows, however, the rule does not hold. For example, the transparent crystallized materials are obtained even from the Al_2O_3 containing glasses with B/N as small as 0.25 (e.g. Nos. 9, 13 and 15), whereas only opaque crystallized materials are obtained from the Al_2O_3-free glasses with B/N larger than 1.00 (e.g. Nos. 1, 2 and 3).

These facts indicate that the Al_2O_3-content of the glasses is a more important factor than the B/N ratio in determining the transparency of the crystallized glasses of the present system.

3.2. Crystallization process in Al_2O_3-free glasses

In the pseudo-binary system $LiTaO_3-SiO_2$, there is a metastable miscibility gap as shown in Fig. 4. Most of the glasses in this system, therefore, separate into glassy two-phases with SiO_2- and $LiTaO_3$-rich compositions when heated, as shown in Fig. 2. Of the two glassy phases formed, the one with a droplet or worm-like structure is estimated to be SiO_2-rich and the matrix phase surrounding the above structure to be $LiTaO_3$-rich, since at elevated temperatures the $LiTaO_3$ crystals precipitate from the latter phase (Fig. 2f and i). Nucleation of the $LiTaO_3$ crystals in the $LiTaO_3$-rich glass phase would be much easier than in the original homogeneous glass, since the free energy change associated with the bulk transformation of glass into crystal is higher [11], the free energy of the crystal–glass interface is lower, and the activation energy associated with the atomic rearrangement for the crystal nucleation is lower in the $LiTaO_3$-rich glass phase than in the original homogeneous glass. This means that the nucleation of the $LiTaO_3$ crystal in the original glasses is enhanced by the liquid phase separation. However, the fact that no transparent crystalline material was obtained from any glasses of the $LiTaO_3$–SiO_2 system, especially, even from the glass with the *B/N* ratio of as high as 1.86, suggests that besides the simple phase separation some other mechanism works in enhancing the rate of nucleation of the $LiTaO_3$ crystals in the glasses, thus making the resultant glass-ceramics transparent.

3.3. Crystallization process in Al_2O_3-containing glasses

Except for glass No. 8, the Al_2O_3-containing glasses in the $LiTaO_3$–SiO_2–Al_2O_3 system (bounded by lines G and T in Fig. 1) also exhibit phase separation prior to their crystallization. The scale of phase separation of these glasses, at least in its early stage, is, however, much finer than that of the Al_2O_3-free glasses; i.e. about 10 nm for the former whereas 30–40 nm for the latter. Furthermore, the size of crystals precipitated after phase separation in the Al_2O_3-containing glasses is 10–20 nm, being much smaller than that of the Al_2O_3-free glasses. The number of crystals is 10^{16}–10^{18} cm^{-3}, which is much larger than that of the Al_2O_3-free glasses. These facts suggest that the mechanisms of phase separation and crystallization in the Al_2O_3-free glasses would become distinctly changed by the addition of Al_2O_3.

3.4. Effect of addition of Al_2O_3 on crystallization

The present authors already reported elsewhere [12] that the Ta^{5+} ions in oxide glasses, when coexisting with alkali ions (R^+), tend to form TaO_6 octahedra using an extra oxygen ion accompanied by the R^+ ion together with the five oxygen ions originally surrounding it. These octahedra can link at their corners with each other or with other common glass-forming tetrahedra such as SiO_4, forming a random glass network with some flexibility in their bond angles. The Ta^{5+} ions would take such a position in the $LiTaO_3$-rich phase of the phase-separated $LiTaO_3$–SiO_2 glasses.

On the other hand, the Al^{3+} ions in oxide glasses, when coexisting with the R^+ ions, tend to form AlO_4 tetrahedra, using an extra oxygen ion accompanied by the R^+ ion [13]. When the Al_2O_3 is added to the $LiTaO_3$–SiO_2 glasses, the Al^{3+} ions, together with the Ta^{5+} ions, would approach the Li^+ ions to use the single-bonded oxygen ions accompanied by the Li^+ ions. Thus, when these glasses separate into Li_2O- and SiO_2-rich phases on heating, the Al^{3+} and Ta^{5+} ions would both shift to the Li_2O-rich phase. Sharp competition between the Al^{3+} and Ta^{5+} ions in the Li_2O-rich phase to acquire oxygen ions in accordance with their own coordination number would make this phase unstable; i.e., if single-bonded oxygen ions accompanied by the Li^+ ions are used by the Al^{3+} ions, the Ta^{5+} ions are forced to link with each other not on their corners but on their edges or faces, thus forming structurally ordered, inflexible regions sporadically in the random glass network of the Li_2O-rich phase. However, if the oxygen ions accompanied by the Li^+ ions are used by the Ta^{5+} ions, the Al^{3+} ions are forced to utilize the oxygens already binding two polyhedra, forming structural units named by Lacy [14] as "triclusters". These triclusters also form structurally more inflexible regions in the glass network than the AlO_4 tetrahedra consisting of extra oxygen ions accompanied by the R^+ ions and three oxygen ions originally accompanied by the Al^{3+} ion.

The structurally inflexible regions consisting of the edge- or face-shared oxygen octahedra of the Ta^{5+} ions or the Al^{3+}-tricluster, formed sporadically in the glass network of the Li_2O-rich phase, would become nucleation sites for crystallization and thus enhance the rate of nucleation of the $LiTaO_3$ crystals. This would be a reason why the Al_2O_3 introduced into the $LiTaO_3$–SiO_2 glass enhances the rate of nucleation, thus making the resultant glass-ceramics transparent.

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