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Effect of Al_2O_3 additions on the acid durability of a Li_2O–ZnO–SiO_2 glass and its glass-ceramic

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Abstract

The effect of Al_2O_3 substitution on the acid durability of a Li_2O–ZnO–SiO_2 glass and its glass-ceramic was investigated depending on the applied heat treatments, the type and concentrations of acid solutions, and leaching time. Satisfactory acid durability was obtained by using 6 wt.% Al_2O_3 for the glass and 11 wt.% for the glass-ceramic. The acid resistance of both glasses and glass-ceramics was found to be affected markedly by the presence of P_2O_5 or TiO_2 used as nucleating agent.

Keywords: D. Glass; D. Glass-ceramic; Acid durability

1. Introduction

The chemical stability of glasses and glass-ceramics determines their applications in different environments and is therefore of considerable practical importance. The mechanisms of reactions occurring between glasses and aqueous solutions, and the factors affecting chemical durability were studied in detail [1–6]. It is generally agreed that the chemical behaviour of silicate glasses is related to their composition. The structural role of Al_2O_3 in the silicate glasses and its beneficial effects on the chemical stability has been recognised for years [7–11]. The acid durability of glass-ceramics depends essentially on the nature and concentration of crystalline phases present, the composition and concentration of residual glassy phase and the microstructure, all of which is controlled by glass composition and applied heat treatments [7].

The effect of Al_2O_3 additions on the crystallization behavior, bending strength, and thermal expansion behavior of a Li_2O–ZnO–SiO_2 glass and its glass-ceramic was investigated in our previous works [12–15]. The aim of the present work is to determine the effect of Al_2O_3 additions on the acid durability of this glass and its glass-ceramic depending on the amount of Al_2O_3 substituted for ZnO up to 11 wt.%, and applied heat treatments.

2. Experimental procedures

Nominal compositions of the glasses studied are given in Table 1. All glasses were prepared from Merck quality raw materials by melting them in a Pt crucible at 1400–1450 °C for 14–16 h. The homogenised glass melts were poured into distilled water and after drying were crushed in an agate mortar. The crushed grains were then sieved using B.S sieves to obtain grains passing through a 2-mm sieve but retained on a 1.6-mm sieve. After washing several times with methyl alcohol, the grains were annealed between 480 and 500 °C for 4 h, cooled slowly to about 50 °C and stored in a desiccator. Glass-ceramic samples were prepared from these granular glasses by applying suitable heat treatments planned according to the DTA results of the glasses [12]. In addition to the granular samples, polished discs were prepared and leached under the same conditions applied to the granular materials. Crystalline phases developed were identified by X-ray diffraction (XRD) in the 2θ range 15–70° using a diffractometer (Philips PW 1820) employing CuK_α radiation. Satisfactory XRD patterns could not be obtained from the granular samples presumably because of the high absorption caused by high

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Table 1
Nominal compositions of the glasses (wt.%)

Glass code	Li_2O	ZnO	Al_2O_3	SiO_2	P_2O_5	TiO_2
A0P3	10	32	–	55	3	–
A4P3	10	28	4	55	3	–
A6P3	10	26	6	55	3	–
A8P3	10	24	8	55	3	–
A11P3	10	21	11	55	3	–
A11T3	10	21	11	55	–	3
A11T5	9.79	20.56	10.78	53.87	–	5
A11	10.31	21.65	11.34	56.70	–	–

surface irregularities. Therefore, the changes occurred upon leaching of glass-ceramics were determined by using glass-ceramic discs. All compositions studied showed volume crystallization, and the XRD patterns of both the powdered samples and the discs were determined to resemble the same phases before leaching. 2.03–2.07 g of glass and glass-ceramic grains were leached in 400 ml of boiling acid solutions for 8 h. The acid solutions were prevented from evaporating by using condensers. The leached samples were washed with ethyl alcohol and dried at 250 °C for 14 h, and after cooling to about 40 °C were reweighed. Each experiment was repeated at least twice and the percentage weight loss was taken as a measure of the relative magnitude of the acid resistivity. The reproducibility of the results was better than ±7% for glasses and glass-ceramics.

3. Results and discussion

The percentage of weight losses occurred on leaching of annealed glasses and glass-ceramics in boiling 0.625 M HCl solution for duration of 8 h are given in Table 2.

Acid durability of the original alumina-free A0P3 glass increased with the first 4% Al_2O_3 addition, reached a maximum around 6% and did not change remarkably with further Al_2O_3 additions. The observed increase in the acid durability of glasses with alumina additions is not an unexpected result because the beneficial effect of alumina on the acid resistance of alkali and alkali-free silicate glasses are well known from the literature [7–9]. In the presence of charge balancing oxides, such as Li_2O or P_2O_5, alumina can enter into the silicate network in the form of AlO_4 groups. This reduces the number of non-bridging oxygens, suppresses the tendency for amorphous phase separation and provides a denser and more stable structure especially when it combines with PO_4 groups already present in the glass structure.

As can be seen from Table 2, the acid durability of glass-ceramics is lower than their parent glasses and decreases with increasing crystallization temperature. An increase of crystallization time, from 3 to 6 h, did not lead to occur an important change in the acid resistivity of A0P3, A4P3, A6P3, and A11P3 glass-ceramics which suggests that the crystallization time of 3 h is suitable for comparing the acid durability of glass-ceramic compositions studied. Probably the most striking feature of the acid durability measurements is the effect of P_2O_5 and TiO_2 additions on the acid resistivity of glass-ceramics containing 11% Al_2O_3. Neither the addition of P_2O_5 alone, nor the addition of $AlCl_3.6H_2O$ and P_2O_5 together into the leaching solution in the amounts giving the equivalent P^{5+} and Al^{3+} concentrations existing in composition A11P3 increased the acid resistance of P_2O_5- and TiO_2-free A11 glass-ceramic.

Table 2
Effect of applied heat treatments on the acid resistance of glass-ceramics

Composition	Applied heat treatments (°C/h)	Crystallized phase(s)	Weight losses (%)
A0P3	Annealed	Amorphous	6.70
	650/3	γ_o-LZS$_{ss}$	40.25
	900/3	γ_o-LZS$_{ss}$ + cristobalite	62.39
	900/6	γ_o-LZS$_{ss}$ + cristobalite	61.45
A4P3	Annealed	Amorphous 1.10	
	660/3	γ_o-LZS$_{ss}$	6.08
	790/3	γ_o-LZS$_{ss}$ + virgilite	25.85
	875/3	γ_o-LZS$_{ss}$ + β-quartz$_{ss}$	53.10
	875/6	γ_o-LZS$_{ss}$ + β-quartz$_{ss}$ + β-spodumene$_{ss}$	52.85
A6P3	Annealed	Amorphous	0.24
	670/3	γ_o-LZS$_{ss}$	3.06
	770/3	γ_o-LZS$_{ss}$ + virgilite	17.10
	900/3	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$ + β-quartz	47.75
	900/6	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$ + β-quartz	49.10
A8P3	Annealed	Amorphous	0.29
	670/3	γ_o-LZS$_{ss}$	3.88
	755/3	γ_o-LZS$_{ss}$ + virgilite	11.85
	900/3	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$	29.32
A11P3	Annealed	Amorphous	0.37
	720/3	γ_o-LZS$_{ss}$	6.73
	790/3	γ_o-LZS$_{ss}$ + virgilite	11.21
	900/3	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$	4.72
	900/6	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$	6.85
A11	Annealed	Amorphous	7.16
	700/3	γ_o-LZS$_{ss}$ + virgilite	21.95
	750/3	γ_o-LZS$_{ss}$ + virgilite	25.73
	875/3	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$	18.81
	875/3	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$	18.53[a]; 15.15[b]
A11T3	Annealed	Amorphous	1.16
	710/3	γ_o-LZS$_{ss}$ + virgilite	30.71
	875/3	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$	15.14
A11T5	Annealed	Amorphous	0.23
	650/3	γ_o-LZS$_{ss}$	1.71
	750/3	γ_o-LZS$_{ss}$ + virgilite	1.44
	875/3	γ_o-LZS$_{ss}$ + β-spodumene$_{ss}$	8.36

[a] P_2O_5 was added into solution.

[b] P_2O_5 and $AlCl_3.6H_2O$ were added into solution.

The effect of leaching time on the acid durability of glass-ceramics held at the last crystallization temperatures is illustrated in Fig. 1 for 0.625 M HCl solution. It is clear that, the high leaching rates occurred in A0P3, A4P3, and A6P3 can be decreased markedly by additions of 8 and 11% Al_2O_3.

The effect of the type and concentration of leaching solutions used on the acid durability is given in Table 3 for glass-ceramics held at the last crystallization temperatures. Although a slight decrease in the weight losses occurs in A0P3 and A4P3 glass-ceramics with increasing acid concentration, the acid durability seems not to be affected markedly from the type and concentration of solutions used.

XRD patterns recorded before and after leaching of the glass-ceramics have provided useful information that can be used to explain the observed leaching behaviour. As can be seen from Fig. 2, the XRD reflections of γ_o-Li_2ZnSiO_4 solid solution (γ_o-LZS_{ss}) disappeared completely from the pattern of leached alumina-free A0P3 glass-ceramic leaving either glassy phase (leached after crystallization at 650 °C) or cristobalite (leached after crystallization at 900 °C). This result shows clearly that γ_o-LZS_{ss} is dissolved easily by acid solution, and is responsible for the high weight losses occurred upon leaching of A0P3 glass-ceramic. When alumina-bearing glasses are held at low temperatures, γ_o-LZS_{ss} is crystallized alone and Al_2O_3 remained in the residual glassy phase (except A11 and A11T3 compositions in which γ_o-LZS_{ss} and virgilite, $Li_xAl_xSi_{1-x}O_2$, crystallize together). In this case, the XRD reflections of γ_o-LZS_{ss} did not disappear upon leaching but shifted slightly, presumably as a result of small changes occurring in its composition. Examples of XRD patterns showing this situation are given in Fig. 3. It is obvious that the leachable γ_o-LZS_{ss} existing in the alumina-free composition becomes a less soluble phase in alumina-bearing compositions as the alumina remains in the residual glassy phase and results in the low weight losses illustrated in Table 2. When the alumina-bearing glasses are held at higher temperatures alumina begins to precipitate from the glass phase in the form of virgilite, ($Li_xAl_xSi_{1-x}O_2$), β-quartz$_{ss}$, or β-spodumene$_{ss}$ (β-$Li_2O.Al_2O_3.nSiO_2$). Upon leaching, the XRD reflections of the γ_o-LZS_{ss} disappeared completely from the patterns of A4P3 and A6P3, did not change remarkably in the pattern of A11P3, but could not be identified positively in those of A8P3, A11, A11T3, and A11T5 glass-ceramics. The XRD reflections of virgilite were found not to be affected from the acid attack in the patterns of A4P3, A6P3, A8P3, and A11P3. In the patterns of leached A11 and A11T3 glass-ceramics, on the other hand, β-quartz$_{ss}$ was identified instead of virgilite. The other phases, i.e. β-quartz, β-quartz$_{ss}$, and β-spodumene$_{ss}$ existing before leaching, were identified positively also in the patterns of leached samples, with the exception that β-spodumene$_{ss}$ was found to be replaced by keatite$_{ss}$ upon leaching of A11T5 glass-ceramic. Examples of the XRD patterns are given in Figs. 4 and 5. According to the XRD results, the changes observed on the XRD patterns of leached glass-ceramics are related essentially to the dissolution of γ_o-LZS_{ss} which is influenced by crystallization temperature, Al_2O_3 content, and by the nucleating agents used. The other phases are not affected markedly from the acid attack.

Table 3
Effect of the type and concentration of acid solutions on the acid resistance of glass-ceramics (weight losses,%)

Composition	0.25 M HCl	1.25 M HCl	0.37 M H_2SO_4	0.92 M H_2SO_4
A0P3	62.55	56.66	62.24	58.55
A4P3	52.32	49.03	53.25	50.21
A6P3	44.73	44.80	46.20	44.59
A8P3	24.75	31.88	25.84	27.95
A11P3	4.12	5.22	4.45	4.36

The equilibrium concentrations of the phases present in the glass-ceramics investigated were calculated by using available phase diagrams [13,14] and are listed in Table 4. These concentrations can be compared with the weight losses occurred upon leaching of glass-ceramics held at the last crystallization temperature. The calculated equilibrium concentrations of γ_o-LZS_{ss} existed in A0P3, A4P3, and A6P3 are 65.79, 57.80, and 53.73 wt.%, respectively, which are close to the weight losses determined for these glass-ceramics (Table 2) and consistent with the XRD results explained above. For compositions containing 8 and 11% alumina, on the other hand, the measured weight losses are well below the equilibrium concentrations of γ_o-LZS_{ss}. These results have shown that dissolution kinetics of γ_o-LZS_{ss} is changed markedly in compositions containing more than 6% Al_2O_3, and the leaching behavior of these glass-ceramics can not be explained simply in terms of the acid durability of the individual phases present. The changes occurred in the dissolution kinetics of γ_o-LZS_{ss}

Table 4
The calculated equilibrium concentrations of phases present in the glass-ceramics

Composition	Concentrations, wt.%		
	γ_o-LZS_{ss}	β-spodumene$_{ss}$	SiO_2
A0P3	65.79	–	34.21
A4P3	57.80	24.75	17.45
A6P3	53.73	37.18	9.09
A8P3	49.70	49.55	0.75
A11P3	43.70	56.30	–
A11	44.18	55.82	–
A11T3	43.70	56.30	–
A11T5	43.61	56.39	–

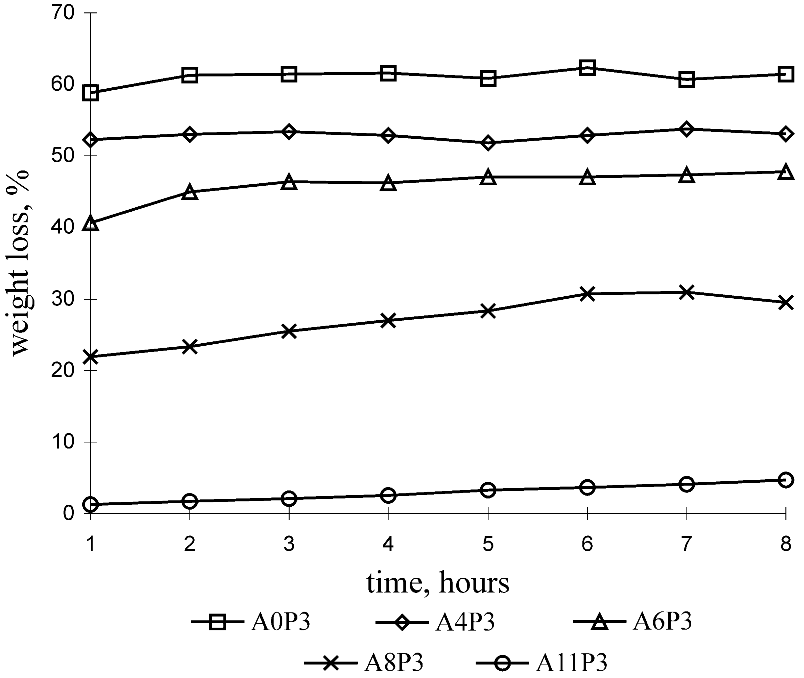

Fig. 1. Effect of leaching time on the acid durability of glass-ceramics.

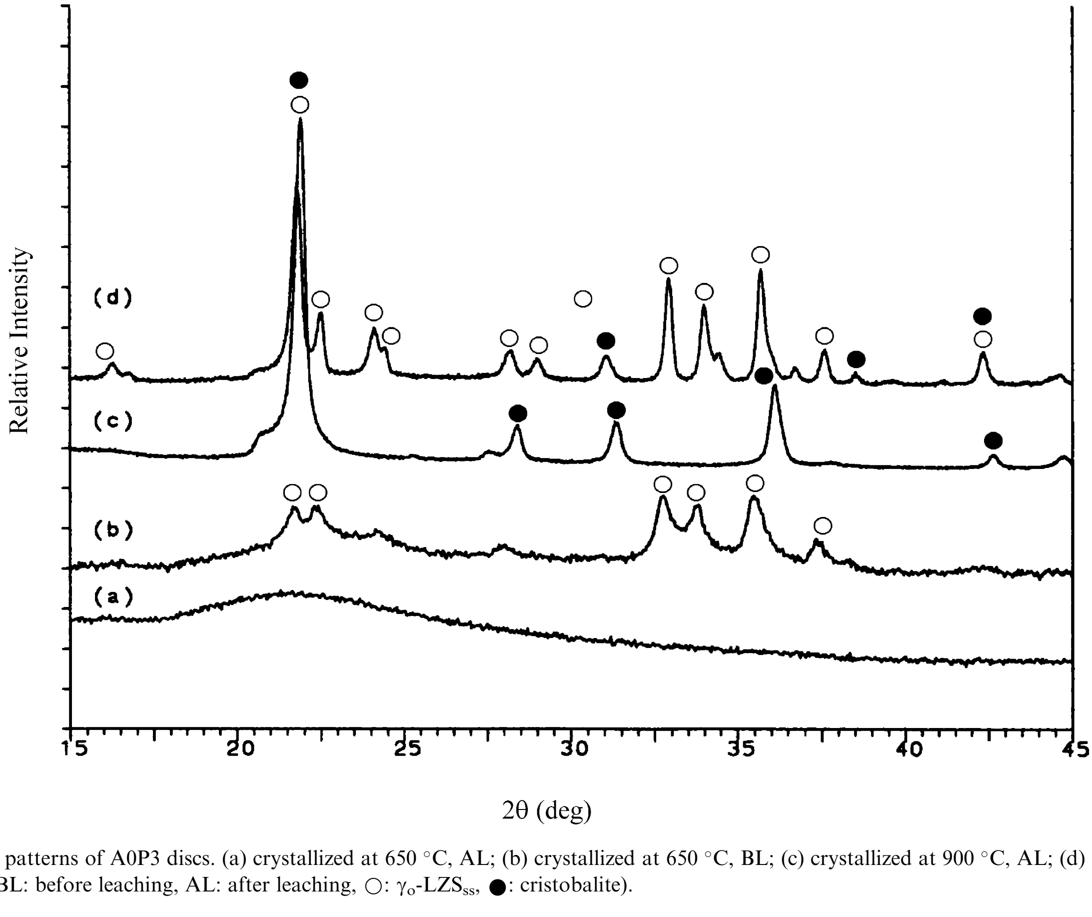

Fig. 2. XRD patterns of A0P3 discs. (a) crystallized at 650 °C, AL; (b) crystallized at 650 °C, BL; (c) crystallized at 900 °C, AL; (d) crystallized at 650 °C, BL (BL: before leaching, AL: after leaching, ○: γ_o-LZS$_{ss}$, ●: cristobalite).

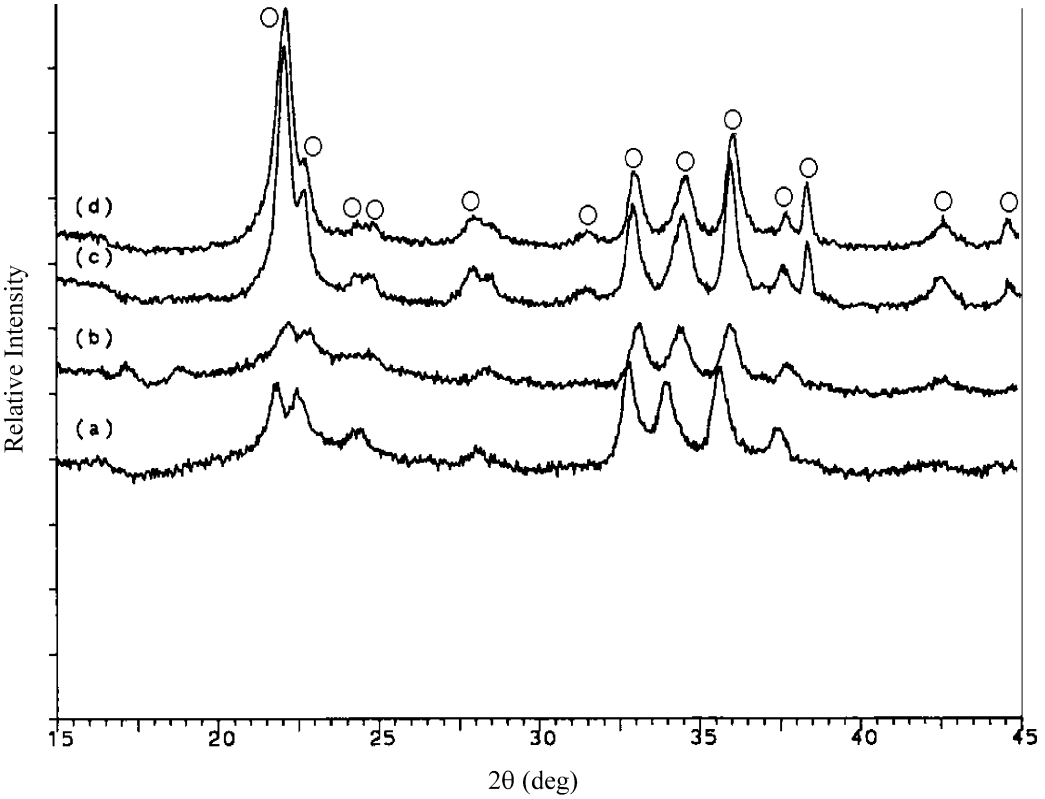

Fig. 3. XRD pattern of (a) A4P3, crystallized at 660 °C, BL; (b) A4P3, crystallized at 660 °C, AL; (c) A8P3, crystallized at 670 °C, BL; (d) A8P3, crystallized at 670 °C, AL (BL: before leaching, AL: after leaching, ○: γ_o-LZS$_{ss}$).

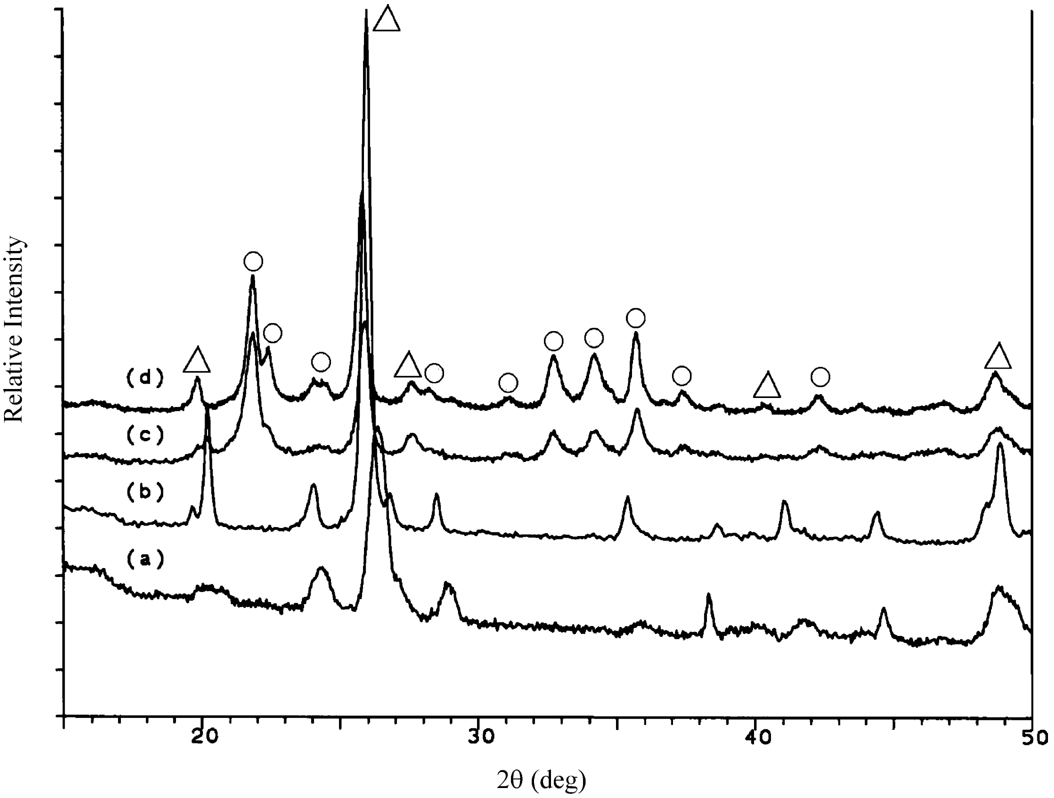

Fig. 4. XRD pattern of (a) A11, crystallized at 700 °C, AL; (b) A11T3, crystallized at 710 °C, AL; (c) A11P3, crystallized at 790 °C, AL; (d) A11P3, crystallized at 790 °C, BL (BL: before leaching, AL: after leaching, ○: γ_o-LZS$_{ss}$, △: virgilite).

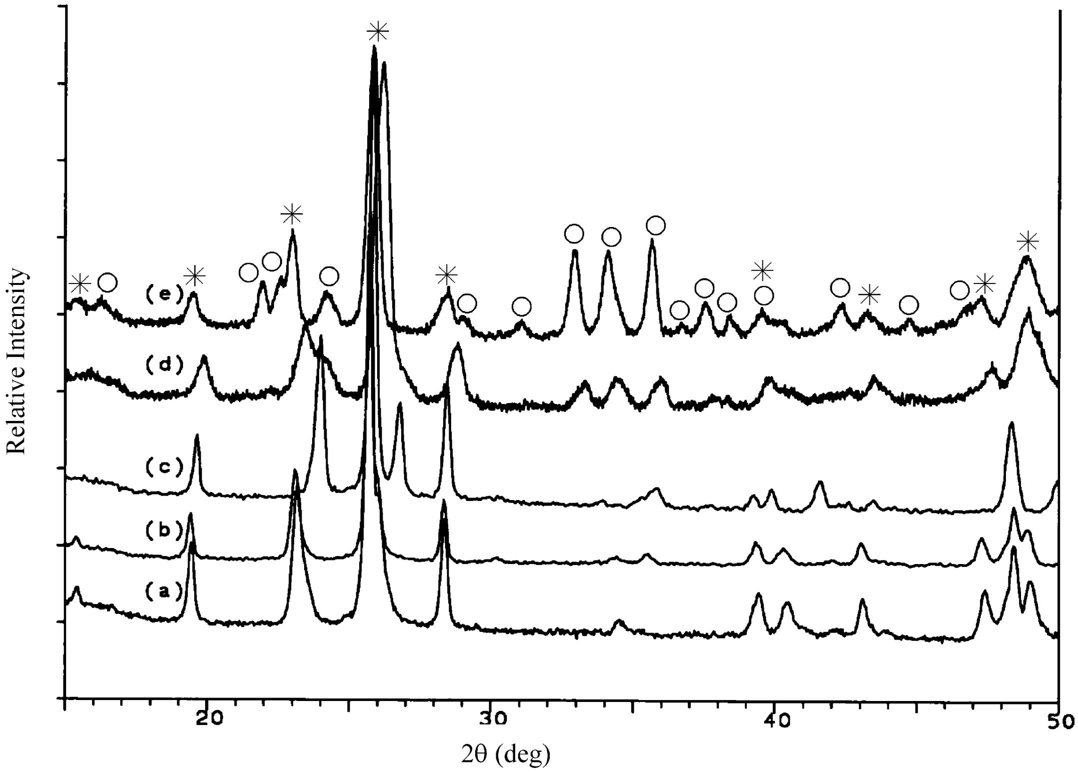

Fig. 5. XRD pattern of (a) A11,crystallized at 875 °C, AL; (b) A11T3, crystallized at 875 °C, AL; (c) A11T5, crystallized at 875 °C, AL; (d) A11P3, crystallized at 900 °C, AL; (e) A11P3, crystallized at 900 °C, BL (AL: after leaching, BL:before leaching, ○: γ_o-LZS_{ss}, ✱: β-spodumene$_{ss}$).

may be due to possible formation of an alumina-rich amorphous film on the leached glass-ceramic surface, the stability of which is affected markedly by the presence and concentration of nucleating agents. Such a protective film may be also responsible for the low weight losses occurred on leaching of glass-ceramics crystallized at low temperatures, where Al_2O_3 remained in the residual glassy phase.

4. Conclusions

The acid resistance of the original alumina-free glass and its glass-ceramic can be increased with partial replacement of ZnO by Al_2O_3. For glasses, satisfactory acid resistance can be obtained by using about 6% Al_2O_3. Acid durability of the glass-ceramics depends essentially on the acid resistance of γ_o-LZS_{ss} phase which in turn is controlled by crystallization temperature, alumina content and nucleating agents. The alumina-bearing crystals formed have a substantial self-protection property up to 6% Al_2O_3 additions above which they can suppress also the leaching of γ_o-LZS_{ss}. The efficiency of Al_2O_3 in the improvement of acid durability for compositions containing 11% Al_2O_3 can be increased markedly by using 3% P_2O_5 or 5% TiO_2. Gradual replacement of leachable γ_o-LZS_{ss} by high acid resistant alumina-containing phase and possible formation of a protective film on the surface of leached glass-ceramics are believed to account for the improvements in acid resistance.

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