Characterization of Glass–Ceramic Corrosion and Durability

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Abstract

The chemical durability of some selected glass–ceramic materials based on the Li_2O– $(MnO, CaO)MgO$–Al_2O_3–SiO_2 glass composition, has been determined by HCl, using the powder test.

The leachability of the glass–ceramic was gradually increased by replacing MgO with MnO, while it was decreased by addition of MnO instead of CaO. Calcium oxide had a retarding effect on the durability of the material when it was added instead of MgO and/or MnO. However, on the addition of Al_2O_3 in replacing Li_2O, the durability of the material was markedly improved. The leaching data were found to be dependent mainly on the proportion of the glass oxide constituents i.e. MgO/MnO, CaO/MnO and Li_2O/Al_2O_3 ratios present in the glasses.

The results were correlated to different views concerning the effect of various ions on the rate of interdiffusion between the crystalline-glass materials and leaching solution, the type, and proportions of the crystalline phases developed in glass–ceramics and residual glass phase.

Die chemische Dauerhaftigkeit einiger ausgewählter Glaskeramikmaterialien, basierend auf einer Li_2O–$(MnO, CaO)MgO$–Al_2O_3–SiO_2-Glasverbindung, wurde mit Hilfe von HCl und des Pulvertests bestimmt.

Die Auslaugfähigkeit der Glaskeramic konnte nach und nach erhöht werden, indem MgO durch MnO ersetzt wurde, während eine Abnahme beobachtet werden konnte, wenn MnO anstatt CaO zugegeben wurde. Kalziumoxyd erhöhte die Dauerhaftigkeit des Materials, wenn es anstelle von MgO und/oder MnO zugegeben wurde. Die Zugabe von Al_2O_3, um Li_2O zu ersetzen, erhöhte die Dauerhaftigkeit des Materials beträchtlich. Es zeigte sich, daß die Auslaugdaten hauptsächlich vom Anteil der Oxydbestandteile des Glases abhängen, d.h. von den MgO/MnO-, CaO/MnO- und Li_2O/Al_2O_3-Verhältnissen.

Die Ergebnisse wurden mit verschiedenen Betrachtungsweisen korreliert, die den Einfluß folgender Effekte beschreiben: den Einfluß unterschiedlicher Ionen auf die Interdiffusion zwischen den kristallinen Glasmaterialien und der Auslauglösung, den Effekt der Art und der Verhältnisse der sich entwickelnden kristallinen Phasen in der Glaskeramik und den Einfluß der Restglasphase.

On a déterminé la résistance à l'attaque chimique de quelques vitrocéramiques ayant pour base le verre de composition Li_2O– $(MnO,CaO)MgO$–Al_2O_3–SiO_2, à l'aide du test de poudres dans HCl.

Le lessivage de la vitrocéramique est augmenté lorsque l'on remplace MgO par MnO, il est par contre diminué si on remplace CaO par MnO. L'oxyde de calcium a un effet retardant sur la longévité du matériau lorsqu'il remplace MgO et/ou MnO. D'autre part, si l'on remplace Li_2O par Al_2O_3 la longévité du matériau est sensiblement améliorée. On a constaté que les résultats des tests d'attaque dépendent surtout de la proportion des oxydes contenus dans le verre, i.e. MgO/MnO, CaO/MnO et Li_2O/Al_2O_3.

On a corrélé ces résultats aux différentes interprétations expliquant l'effet de certains ions sur la vitesse d'interdiffusion entre les verres et la solution d'attaque, et l'effet du type et de la proportion entre phases cristalline et verre amorphe présents dans ces vitrocéramiques.

1 Introduction

The chemical durability of glass is a very important property for technical applications. Therefore, many authors have already investigated

possible reaction processes between the glass sur-
face and acids or aqueous media.[1] However, de-
spite these efforts, the corrosion mechanism of
glass–ceramic materials with aqueous solutions
has received little attention.

The processes of chemical corrosion of a
material by water or other reagents are often very
complex and glass–ceramics in general possess
good chemical stability and they compare
favourably in this respect with other ceramic-type
materials.[2] Many glass-ceramics contain crystals
which are far less durable in acid than their
residual glass or coexisting crystalline phases e.g.
lithium metasilicate crystals are more highly
soluble than their parent lithium silicate glass.[2]
However, in some other cases the intergranular
boundaries are more susceptible to attack than the
crystal particles themselves.[3]

In the present work, the leaching by 2N HCl of
the glass–ceramic materials based on the Li_2O–
$(MnO,CaO)MgO$–Al_2O_3–SiO_2 glass composition
was determined. Because of the wide range of
solid-solution phases which could be formed
within this multi-component system, glass-ceramic
materials with a broad range of properties could
be expected.

2 Experimental

2.1 Glass composition
Two ternary-base glass compositions belonging to
the Li_2O–MgO–SiO_2 and Li_2O–CaO–SiO_2 systems
containing various MnO/MgO and MnO/CaO
ratios together, in some cases, with various
Al_2O_3/Li_2O replacements have been investigated.

The mole percentages of the studies glass com-
positions are as follows:

(1) G_1–G_4; 23.12 Li_2O–$(13.28$-$X)$ MgO–$XMnO$–
    63.6 SiO_2,
(2) G_5–G_8; 23.12 Li_2O–$(13.28$-$X)$ CaO–$XMnO$–
    63.6 SiO_2,
    where $X = 3.32$, 6.64 or 9.96;
(3) G_9–G_{10}; 23.12 Li_2O–$[13.28$-$(X+Z)]$ MgO–
    XMn–$ZCaO$–63.6 SiO_2, where $X = 3.32$,
    $Z = 3.22$, 6.64;
(4) G_{11}–G_{13}; $(23.12$-$Y)Li_2O$–YAl_2O_3–$6.64MgO$–
    6.64 MnO–63.6 SiO_2, where $Y = 5.78$, 11.56,
    13.87;
(5) G_{14}–G_{17}; $(23.12$-$Y)Li_2O$–YAl_2O_3–$[13.28$-$(X+Z)]$
    MgO–$XMnO$–$ZCaO$–$63.6SiO_2$, where $Y =$
    11.56 or 13.87, $X = 3.32$, 6.64 or 9.96 and
    $Z = 3.32$ or 6.64.

2.2 Material preparation
The glasses were prepared from thoroughly mixed
purified silica sand, reagent grade Li_2CO_3,

$MgCO_3$, $CaCO_3$ and calcined Al_2O_3 together with
a highest purity of MnO_2 as a source of MnO.
They were melted in Buttersea-type fired clay
Morganite crucibles (UK) in a gas-fired furnace at
1300–1400°C for 3 h. It is worth mentioning that
attack by the melts on the inside walls of the fired
clay crucibles was negligible after the completion
of melting, with no contamination in the glass
samples being observed. Melting was continued
with stirring to ensure homogeneity. The homo-
geneity of the melts was achieved and ensured in
the resultant glasses by microscopic examination.
The melts were cast into discs which were prop-
erly annealed to minimize strain.

2.3 Thermal treatment process
To obtain glass–ceramics with a minimum resid-
ual glassy matrix, selected heat-treatment process
were applied to the glass. Therefore, the Al_2O_3-
free glasses were soaked at the nucleation temper-
ature in the range 500–550°C for 3 h, and then
crystallized at 780–850°C for 8 h, whereas the
Al_2O_3-containing samples were soaked at 600–
650°C for 3 h, and then at 800–950°C for 8 h. The
X-ray diffraction technique using a Ni filter and
Cu radiation was used to identify the crystal phase
constituents of the glass–ceramics (Table 1).

2.4 Preparation of samples for leaching
It is recognized that the chemical composition of
the glass surface is not necessarily identical to that
of the bulk.[4] Thermal treatment of the glasses gen-
erally induces surface or bulk crystallization. In
many cases[5] both types of crystallization are
formed in the material during thermal treatment.
Consequently, the crystalline phases developed on
the surface are not necessarily identical to those
encountered in the bulk. The grain test was sug-
gested to minimize the effect of such factors.
Therefore, the grain test[6] was applied in the pre-
sent work to assess the chemical durability of the
glass–ceramic materials obtained. The grain test is
thought to yield a true representation of the
leaching data of the materials. It provides reliable
information about the glass–ceramics as a com-
posite material and not about the surface, any
effect due to differences in phase composition of
the surface relative to the bulk are minimized.

2.5 Preparation of samples for leaching
The crystalline samples were crushed in an agate
mortar and then sieved using B.S. sieves to obtain
grains passing through a 0.6 mm sieve and being
retained on a 0.3 mm sieve. The grains were
washed several times with ether, dried at 110°C
for 2 h and then transferred to weighing bottles
and cooled in a desiccator.

Table 1. Components, phases developed, and leaching values of the glass–ceramics

Glass number	Components (mol%)					Phases developed	Loss (wt %) at different duration (h)		
							3	6	12
	MgO glass								
	Li$_2$O	MgO	SiO$_2$						
1	23·12	13·28	63·6			LS$_2$, C, Q	3·95	4·45	5·05
	MgO/MnO glasses								
	MnO								
2	3·32					LS$_2$, C, Q	4·15	4·65	5·22
3	6·64					LS$_2$, K	4·32	4·78	5·35
4	9·96					LS$_2$, Rh ss, Q	4·48	4·95	5·50
	CaO glass								
	Li$_2$O	CaO	SiO$_2$						
5	23·12	13·28	63·6			LS$_2$, W, Q	5·60	6·40	6·90
	CaO/MnO glasses								
	MnO								
6	3·32					LS$_2$, Mn W, Q	5·15	5·85	6·45
7	6·64					LS$_2$, B, Q	4·80	5·45	6·10
8	9·96					LS$_2$, (Mn,Ca)SiO$_3$, Q	4·55	5·15	5·75
	Mixed divalent oxide glasses								
	CaO	MgO	MnO						
9	3·32	6·64	3·32			LS$_2$, Dp ss, Q	4·42	4·87	5·45
10	6·64	3·32	3·32			LS$_2$, Mn P ss, Q	4·55	4·89	5·60
	Al$_2$O$_3$ glasses								
	Al$_2$O$_3$								
11	5·78					Sp ss, LS$_2$, LS, K	2·75	3·03	3·43
12	11·56					Sp ss, K	1·97	2·25	2·55
13	13·87					Sp ss, (Mn, Mg)SiO$_3$ ss	1·82	2·07	2·36
	Mixed divalent aluminosilicates								
	Li$_2$O	Al$_2$O$_3$	MgO	CaO	MnO				
14	11·56	11·56	3·32	6·64	3·32	Sp ss, Sch	1·92	2·25	2·50
15	11·56	11·56	—	6·64	6·64	Sp ss, B	2·45	2·82	2·96
16	9·25	13·87	3·32	3·32	6·64	Sp ss, MnSiO$_3$, An	2·32	2·70	2·85
17	9·25	13·87	—	3·32	9·96	Sp ss, An, MnSiO$_3$	2·55	2·91	3·08

LS = Lithium metasilicate; LS$_2$ = lithium disilicate; C = clinoenstatite; K = kanoite, Rh = rhodonite; W = wollastonite; Dp = diopside; P = pyroxene; Sp = β-spodumene; An = anorthite; Sch = schefferite; Q = α-quartz; B = bustamite; ss = solid solution.

2.6 Leaching procedure

One gram of the sample grains was accurately weighed in a sintered glass crucible (C4) and then placed in a 400 cm^3 polyethylene beaker. The sample was subjected to the static action of 200 cm^3 of 2N HCl for 3–12 h at boiling point using a contact thermometer water bath. The polyethylene beaker with its content was covered by a polyethylene cover to reduce evaporation. The volume of the leaching solution was made large enough relative to the weight of the sample grains in order to avoid the formation of saturated solutions which might prevent further leaching of grains. The reproducibility of the results for representative duplicate samples is better than ±5%. The percentage weight loss was taken as a measure of the relative magnitude of the leaching rate.

3 Results

The effect of MnO/MgO, MnO/CaO and Al$_2$O$_3$/ Li$_2$O replacements on the leachability of the

glass–ceramics based on the two ternary glass systems Li$_2$O–MgO–SiO$_2$ and Li$_2$O-CaO-SiO$_2$ was investigated. The data obtained are listed in Table 1 and represented in Figs 1–7.

3.1 Effect of MnO/MgO replacement

The leaching values given by samples of various MnO/MgO ratios were higher than that of MnO-free sample (C1). Figure 1 clearly indicates that the leachability of the MgO-containing glass–
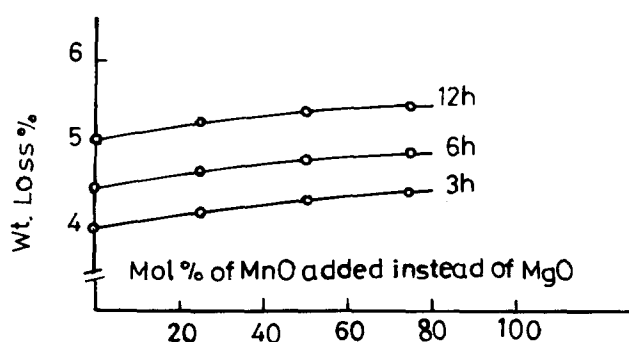

Fig. 1. Effect of MgO/MnO replacement on leaching of the samples at different duration.

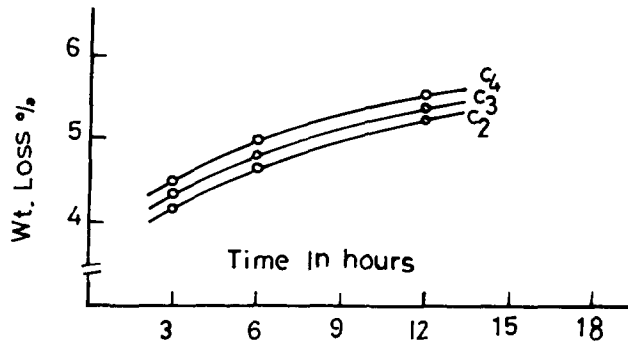Fig. 2. Leaching rate of MgO/MnO-containing samples.

Fig. 4. Leaching rate of CaO/MnO-containing samples.

ceramic was gradually increased by progressive addition of MnO instead of MgO. The leachability showed the highest values in the sample of MnO/MgO ratio equal to 3 (C4), i.e. it acquires the worst chemical durability. Applying the long-term action of acid, Fig. 2, revealed that the sample with the lowest MnO/MgO ratios (i.e. 0·33), C2, was more durable than that of the highest ratio (i.e. 3), C4.

3.2 Effect of MnO/CaO replacement

Unlike the MnO/MgO-containing samples, the addition of MnO in replacing CaO in Li_2O–CaO–SiO_2 glasses decreased the leachability of the glass–ceramics, i.e. it improved the chemical durability of the material. Figure 3 exhibits the weight-loss percentages in the samples attacked by acid solution as a function of MnO/CaO replacement in the glass, which indicates that the extent of corrosion of the crystalline material was decreased by gradual replacement of MnO instead of CaO in the glass.

With respect to the study the effect of long duration of action (Fig. 4), it was seen that the sample with the highest MnO/CaO ratio (i.e. C3), exhibited the most durability (Fig. 4, C8), while that with low MnO (i.e. MnO/CaO = 0·33, C6) was the least durable one (Table 1).

3.3 The mixed effect of divalent oxides

The experimental data revealed that the presence of CaO added in the glasses instead of either MnO
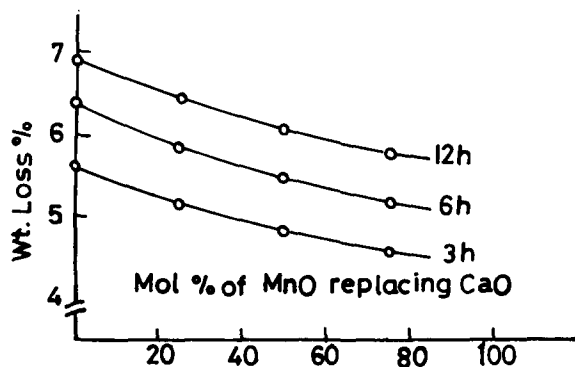
or MgO increased the leachability of the glass–ceramic. Table 1 showed that the leachability of sample C3 based on MnO/MgO glass (i.e. CaO-free glass) was less than that of sample C9 in which the MnO was partially replaced by CaO. However, the leachability of the latter sample (C9) is less than that of sample 10 in which the MgO was partially replaced by CaO.

3.4 Effect of Al_2O_3/Li_2O replacement

The chemical durability of the crystalline samples was markedly improved on addition of Al_2O_3 instead of Li_2O. Figure 5 clearly indicates that the leachability of the Al_2O_3-containing sample was progressively decreased by increasing the Al_2O_3 at the expense of Li_2O and reached a maximum when Al_2O_3/Li_2O was equal to 1·5.

From the study of the leaching rate of the samples (Fig. 6), it is evident that the highest rate of leaching was given by sample C11 (with low Al_2O_3 content). As the Al_2O_3 content was increased, the leaching rate given by the samples was decreased. Therefore, sample C13 (with an Al_2O_3/Li_2O ratio of 1·5) exhibited the lowest rate of leaching.

3.5 The mixed effect of divalent oxides in aluminosilicate glasses

With respect to the glasses of constant Al_2O_3 con-

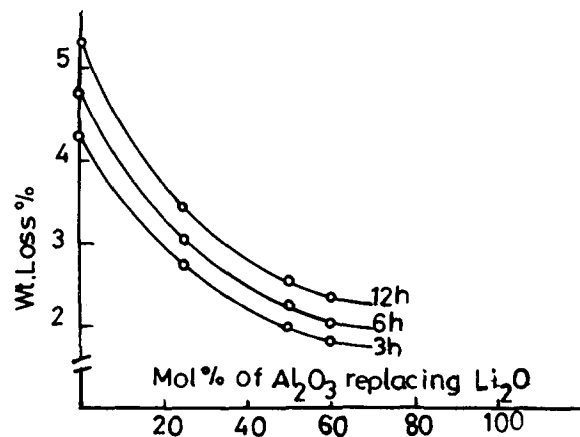Fig. 3. Effect of CaO/MnO replacement on leachability of the samples at different duration.

Fig. 5. Effect of Li_2O/Al_2O_3 replacement on leachability of the samples at different duration.
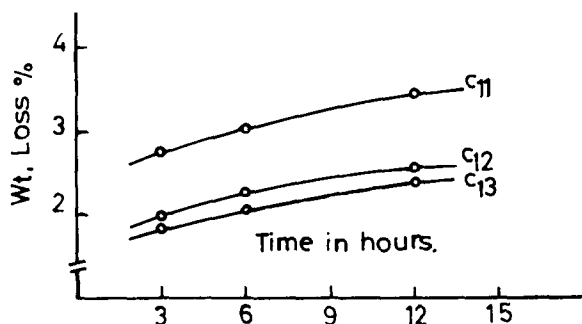
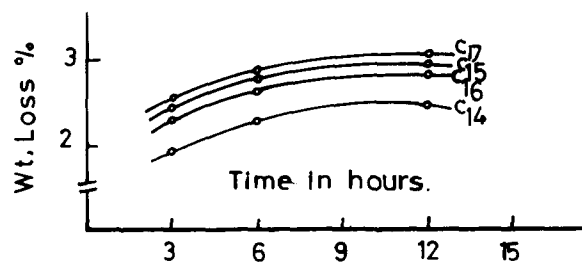**Fig. 6.** Leaching rate of Al_2O_3-containing samples.

Fig. 7. Leaching rate of mixed divalent alumino silicate samples.

tent with various MnO/MgO and/or MnO/CaO ratios (i.e. C14–C17), it is seen that the leachability of sample C14 (with 1 MgO : 2 CaO : 1 MnO) was less than that of sample C15 in which the MgO was replaced by MnO. Also, the leachability of sample C16 (with 1 MgO : 1 CaO : 2 MnO) was less than that of sample C_{17} in which the MgO was replaced by MnO, i.e. the durability exhibited by samples C14 and C16 (with MgO) were better than that of samples 15 and 17 (with MnO instead of MgO) respectively. For determining the leaching rate of the mixed divalent aluminosilicate samples (Fig. 7), it is evident that the highest rate of leaching was given by sample C17, while the lowest rate of leaching was given by sample C14.

4 Discussion

The ability of glass to withstand the attack of an aqueous solution depends primarily on its composition. In binary alkali silicate glasses, the extent of leaching decreases when the alkali content is decreased or when part of the silica or alkali is replaced by any other oxide.[7] As the third oxide is introduced into the glass, the rate of leaching rapidly decreases to a minimum and then, with an increase of the amount of the third oxide added, the rate of leaching begins to rise rapidly; this is mainly dependent on the nature of the third oxide added. The improvement of the leaching behaviour of alkali silicate glasses when alkaline earth oxides are added probably results from the reduction of the diffusion coefficient of the alkali

ion by the alkaline earth ion.[8] In alkali aluminosilicate glass, aluminium ions assume network-forming sites, AlO_4, and thereby hold positively charged alkali ions to maintain electrical neutrality. The number of non-bridging oxygens will also decrease or will be entirely eliminated.[9] In general, the primary process which takes place when alkali silicate glasses like lithium silicate come into contact with acids or water, is the exchange of alkali metal ions on the glass surface for hydrogen ions in solution. This ion-exchange reaction can be represented by the equation:

$$\text{Glass} \equiv Si-O-Li + H^+ \rightleftharpoons \text{glass} \equiv Si-O-H + Li^+$$
(1)
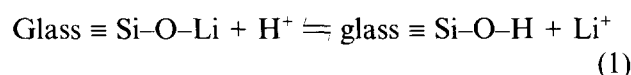
The rate of reaction (1) is controlled by interdiffusion of Li^+ and H^+ in the glass.[8] As the decomposition of silicate glasses by an aqueous solution involves the breakdown of Si–O–Si and Si–O–M (M = alkali ion), the bond strength between the various cations and oxygen and the field strength of these cations may be taken as a measure of the stability of the glass.[10]

The presence of Al^{3+} ions will retard the rate of ion exchange between the alkali and H^+ (or H_3O) ions. Dilmore *et al.*[11] established that the remarkable improvement in the corrosion caused by small additions of Al_2O_3 is due to the precipitation of a protective Al_2O_3-rich complex from the corrosion solution forming an aluminosilicate film on the silica-rich film which is formed on the glass surface.

Glass–ceramics, on the other hand, show, in most cases, good chemical stability which compares well with other ceramic materials. In glass–ceramic materials, several different crystalline compounds may be present together with a residual glassy phase. The relative resistance of these phases to the attack by water or other reagents will determine the chemical stability of the material.[2] The initial attack will be on the glass phase which is thought to play an important role in determining the resistance of a glass–ceramic to chemical attack.[2] This occurs because the early stage of attack involves ion exchange between H^+ (H_3O^+) ions and mobile cations (like alkali metal ions) in the glass. Therefore, the silica network structure can be attacked by a process of hydration. The greater mobility of alkali metal ions in the glass phase as compared with that of similar ions incorporated in crystal phases will lead to greater reactivity of the glass phase and hence to inferior resistance to chemical attack. However, the solubility of both the formed crystals and the residual glass phase in leaching solution have an almost equally important influence on the stability of glass–ceramics.[12] The dense

non-porous microstructure of the glass–ceramics makes it possible to count on better chemical stability as compared with porous ceramics, which have a more extensive surface and greater penetrability to liquids and vapours.[2] In glass–ceramics the chemical durability is considered a function of many factors, namely the nature and concentration of the crystalline phases, composition of the glass phases and microstructure.

With respect to the acid mineral stability, some minerals are very resistant to the action of acids (nearly insoluble). Others show weak resistivity and decompose or gelatinize on treatment with acid solutions.

Lithium aluminosilicate solid-solution phases (β-eucryptite and β-spodumene)[2,13] and silica[14] minerals show very high resistivity towards the action of HCl solution. It has also been reported[1] that a thermal shock resistant glass–ceramic (like lithium aluminosilicate) has high resistance to chemical attack. McMillan[2] pointed out that the lithium aluminosilicate glass–ceramics of medium thermal expansion are quite unaffected by exposure to chlorine or hydrogen chloride gases for a period of 6 h at 800°C. Kay & Doremus[15] suggested that the apparently high durability of the β-spodumene glass–ceramics was a result of the low reactivity of the crystalline phases. Partridge & McMillan[16] showed that the presence of a large proportion of crystalline silica in the form of cristobalite or quartz gives a better resistance to attack by boiling water than does the presence of lithium aluminosilicate crystals of spodumene type.

Varieties of pyroxene phases and their solid solutions, like Mn^{2+}-, Mg^{2+}- and/or Ca^{2+}-containing types, show variable resistivity towards acid attack. Diopside ($CaMgSi_2O_6$) for example, is insoluble in acid solution; enstatite, clinoenstatite ($MgSiO_3$), kanoite (($Mn^{2+}Mg)_2Si_2O_6$) and rhodonite ($MnSiO_3$) are slightly attacked by acids,[13] while bustamite (($Ca,Mn)(SiO_3$)) is partially soluble in HCl. Lithium metasilicate and disilicate,[14] wollastonite[13] and anorthite,[14] on the other hand, are decomposed by acid solution. Wollastonite is soluble in HCl and gelatinous silica separated out from the solution.[13,14] Anorthite is also decomposed by acids with a separation of gelatinous silica, or polysilicic acid ($H_5AlSi_2O_8$) may be formed.[14]

The present X-ray diffraction data (Fig. 8 and Table 1), revealed that clinoenstatite, lithium disilicate and minor amounts of α-quartz were crystallized from lithia magnesia silicate glass (C1). On partial MnO/MgO replacement, a series of synthesized Mn,Mg silicate solid-solution phases were formed. At low MnO/MgO ratio (C2) clinoen-
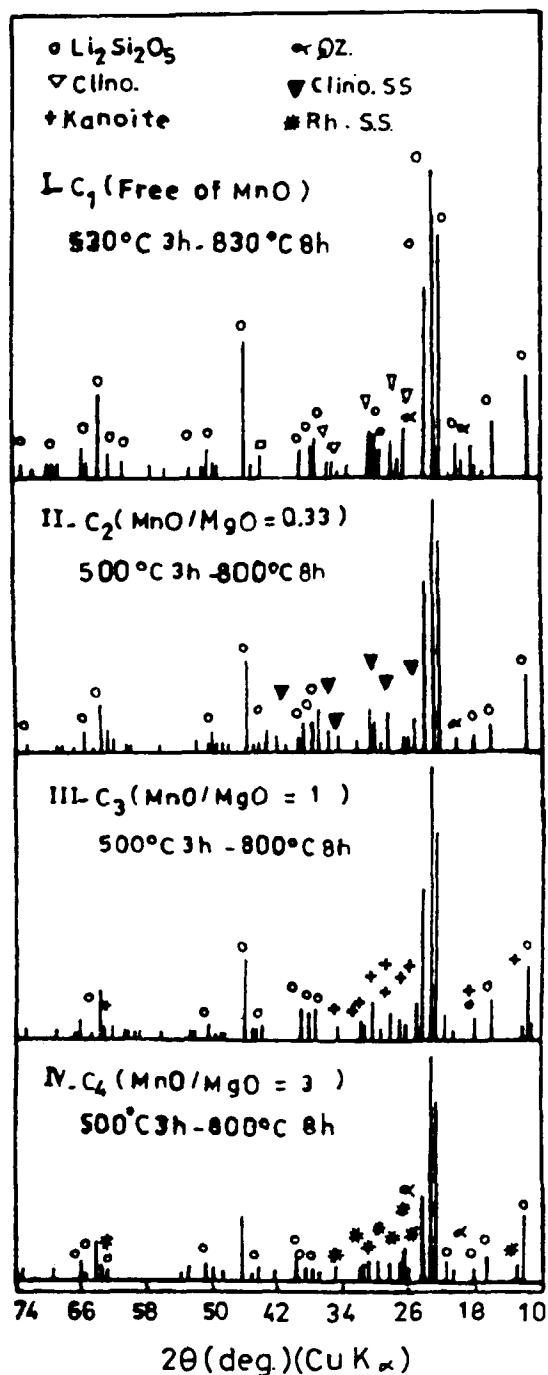

Fig. 8. XRD of crystallized glasses of various Mn/MgO ratios.

statite solid solution of the probable formula ($Mg_{0.75}$ $Mn_{0.25})SiO_3$[17] was formed. Kanoite, i.e. $Mn^{2+}Mg(Si_2O_6)$, was crystallized by increasing the MnO/MgO ratio in the glass up to unity (Fig. 8, C3) At higher MnO/MgO ratio, a rhodonite solid-solution phase ($Mn_{0.75}Mg_{0.25})SiO_3$ was developed (Fig. 8, C4). All the MnO/MgO pyroxene-like phases are slightly attacked by acid; however, Mg-containing pyroxene seemed to be less readily attacked by acid than the Mn-containing variety. Hence the higher the proportion of Mn^{2+}-containing pyroxene-like phase, the more readily it is attacked by the acid. Therefore, the leachability of MgO-containing samples was increased on the ad-
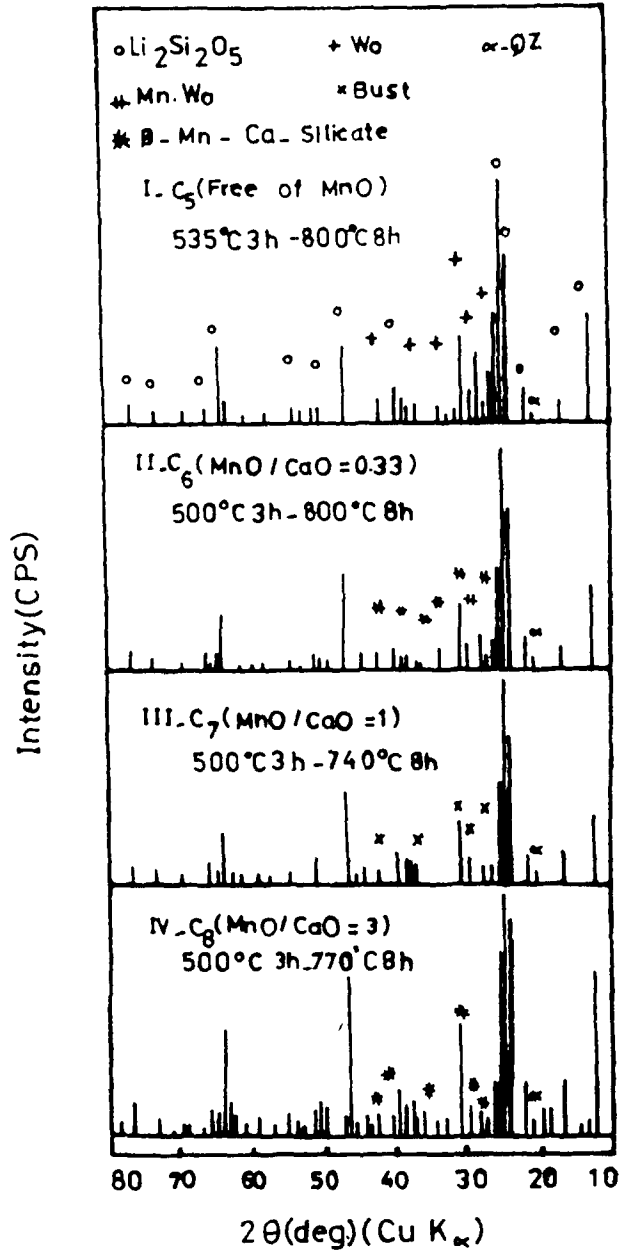
Fig. 9. XRD of crystallized glasses of various Mn/CaO ratios.

Fig. 10. XRD of crystallized glasses of various Al_2O_3/Li_2O ratios.

dition of MnO instead of MgO. Lithium disilicate and wollastonite ($CaSiO_3$), together with minor amounts of α-quartz, were formed in lithia calcia silicate glass–ceramics (C5, Fig. 9). However, varieties of Ca,Mn silicate solid solution were formed in the glass–ceramics as a function of MnO/CaO ratio in the glass. At low MnO/CaO ratio (C6) Mn wollastonite (($Ca_{0.75}Mn_{0.25}$)SiO_3) was developed. On increasing the MnO/CaO ratio up to unity (C7), bustamite ($CaMnSi_2O_6$) was developed. At higher MnO/CaO ratio (C8, Fig. 9), β-$Mn_{0.75}Ca_{0.25}SiO_3$ phase was crystallized. It is clear that as the MnO/CaO ratio present in the glass was increased, the wollastonite ($CaSiO_3$) phase content in the crystallized sample was decreased and $MnSiO_3$ phase content was increased instead. Actually, the wollastonite phase was easily decomposed by acid while $MnSiO_3$ was slightly attacked.
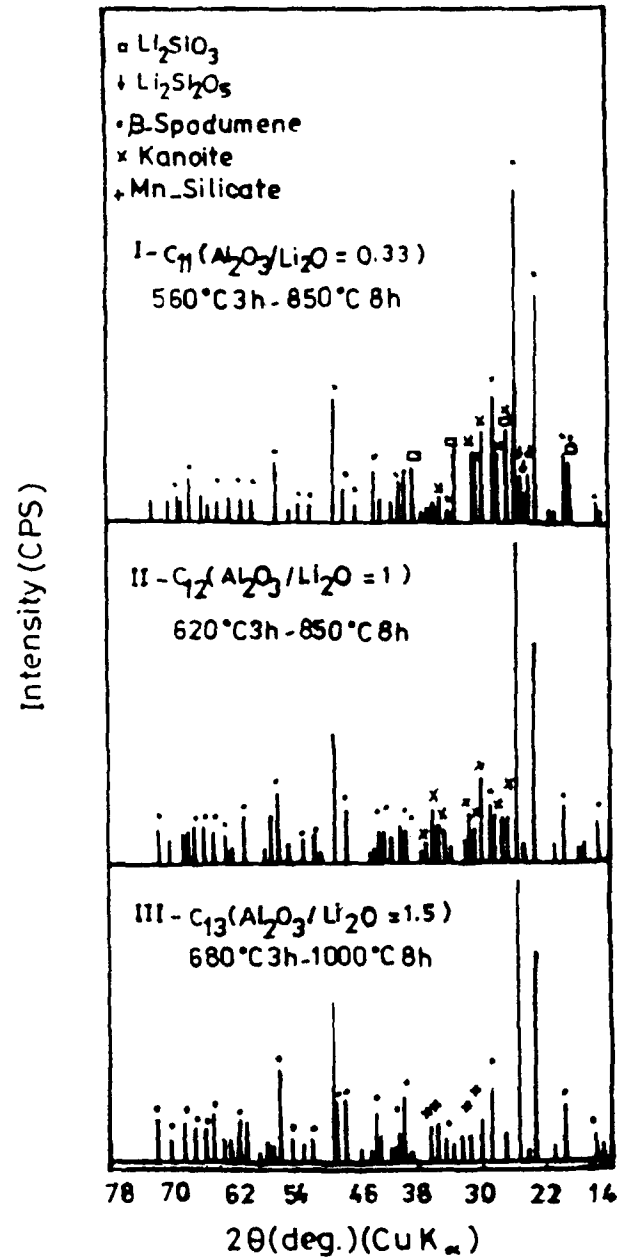
Therefore, the leachability of CaO-containing samples was decreased on the replacement of CaO by MnO.

On the basis of the X-ray data it could be expected that the formation of insoluble diopside pyroxene solid-solution phase in C9 may favour the better chemical durability rather than sample C10 in which Mn pyroxene phase of slightly attacked was formed.

The leachability of the Al_2O_3-containing samples was markedly improved on the addition of Al_2O_3 instead of Li_2O. This may be ascribed to the low reactivity of the lithium alumina silicate solid-solution phases, β-spodumene (nearly unattacked), which was formed as the dominant crystalline phase instead of the relatively easily decomposed lithium silicate phases (Fig. 10). Such a lower reactivity of the β-spodumene phase is

probably related to the structure of this crystal where it has a low positive expansion coefficient.[2] The Li ion in this crystalline phase probably occupies a stuffed position.[18] Kay & Doremus[15] showed that the volume of the crystals remains essentially constant with temperature as reflected in its low coefficient of thermal expansion. They suggested that the tendency of the lattice to maintain a constant volume reduces the rate of hydration reaction. It seems more likely that the lower reactivity of β-spodumene may be related to the lack of ion exchange and lack of enhancement of the reaction in which the breakdown of the Si–O–Si bond takes place. Exchange between Li^+ in the β-spodumene and H^+ for acid may not occur, but this would be surprising because crystals and glasses contain alkali ions. Whatever the reason, the β-spodumene phase appears to react more slowly with the acid solution than other crystals and glasses. Furthermore, the decrease in the amount of Li^+ ions in the glass matrix also favours the reduction of the leaching rate. This may account for the improvement of the chemical durability of Al_2O_3-containing samples as the Al_2O_3/Li_2O replacement is increased.

β-Spodumene solid-solution together with Mn-containing pyroxene phase, i.e. schefferite phase $((Ca^{2+})(Mn_{0.5}Mg_{0.5})Si_2O_6)$,[19] bustamite $((Ca_{0.5}Mn_{0.5})Si_2O_6)$ or β-$MnSiO_3$ were also crystallized in the aluminosilicate glasses containing mixed divalent oxides (C14–C17). Anorthite was exceptionally formed in these glasses in which the Al_2O_3/Li_2O ratio was greater than unity (C16, C17, Table 1).

It is clear therefore that at constant Al_2O_3/Li_2O ratio, as in the case of samples C14 and C15, the higher the MgO content, the lower the leachability of the sample (i.e. the higher the durability). This may be attributed to the formation of the most durable Mn pyroxene phase of schefferite in C14 instead of the partially attacked bustamite phase in C15. The same crystal phases were formed in both C16 and C17. However, the durability of sample C16 is better than that of C17; this may be attributed to the fine microstructure developed in sample C16 of three mixed divalent oxides, as compared with that of MnO/CaO-containing sample C17, of a relatively coarse-grained microstructure.

5 Conclusions

The corrosion behaviour of some glass–ceramic materials belonging to the Li_2O–(MnO, CaO)MgO–Al_2O_3–SiO_2 glass composition have been investigated by HCl using the powder test.

The chemical stability of glass–ceramics is

greatly dependent on the nature and concentration of crystalline phases, as well as the residual glass phase. The crystallization of a high proportion of pyroxene phases and their solid solutions either in the form of Mg- and/or Mn-containing varieties gives a better resistance to attack by HCl than does the crystallization of calcium silicate phases like wollastonite; the Mg pyroxene-containing variety exhibits the best results. The formation of lithium aluminosilicates like β-spodumene at the expense of lithium silicate greatly improved the durability of the materials.

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