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The crystallization process and chemical durability of glass-ceramics based on the Li_2O–B_2O_3 (Fe_2O_3)–SiO_2 (GeO_2) system

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Abstract

The effect of partial replacements of GeO_2 for SiO_2 and Fe_2O_3 for B_2O_3 on the crystallization process of a Li_2O–B_2O_3–SiO_2 glass-ceramic was followed by means of differential thermal analysis (DTA), X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The chemical resistance of the glass-ceramics toward the attack of acid media was also determined. Results showed a decrease in both transition (T_g) and softing (T_s) temperatures by the replacement processes. Varieties of crystalline phases including Ge–lithium disilicate ss, lithium diborate, lithium metasilicate as well as lithium iron silicate ss containing germanium were formed in the crystallized glasses. The crystallization of meta- and/or disilicate and their proportions depend on both temperature and duration of the process. The chemical durability of the crystallized glasses was improved by the replacement processes. The obtained durability data depend on the nature, concentration of the crystalline phases formed, the nature of glassy matrix, and the microstructure of the glass-ceramics. The role played by the glass oxide constituents in determining crystal phases, their solid solutions, microstructure, and the chemical durability of the glass-ceramics was discussed.

Keywords: D. Glass; Crystallization; Solid solution (ss); Microstructure; Chemical durability

1. Introduction

Borosilicate glasses are well-known materials due to their variety of technological applications [1]. Most borosilicate glasses are phase separable with the formation of a chemically durable silica rich and a less durable borate rich phase [2]. Studying the Li_2O–B_2O_3–SiO_2 system is very difficult because of the high volatility of B_2O_3 and Li_2O at high temperatures [3]. Fundamental studies of this system (glasses containing less than 25.6 mol% Li_2O) were performed by **Sastry and Hummel** [4]. They showed that depending on the samples behavior during quenching and annealing, all glasses can be divided into three groups: (a) colorless, transparent; (b) white, liquational, opaque; and (c) intermediate, which become liquational after repeated heating.

Nikulin et al. [5] showed that the properties of some alkali-borosilicate glasses can be improved substantially, by choosing the optimum composition of glass and using suitable heat treatments, causing phase separation with the formation of conducting chemically unstable phase enclosed in drops and a high-silica matrix.

Germanium is a semiconductor that has the properties of both metals and metalliods. This unique property makes it possible to obtain glass-forming compounds, based on germanium dioxide, with unusual properties by controlling the composition. Germanium dioxide is a strong candidate material for creating new matrices and optical media [6]. Germanate glasses are mostly of theoretical interest, since they are isostructural with silicate. They are studied for comparative purposes.

Błaszczak et al. [3] studied the Infrared of glasses in the Li_2O–B_2O_3–GeO_2 (SiO_2) systems and they revealed that the lithium borosilicate glasses are considered as important materials in the present technology. They are characterized by low thermal expansivity, good chemical resistance and

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considerable hardness. The studied systems differ in the presence of glass-forming oxides, GeO_2 and SiO_2. Their hexagonal forms (GeO_2 and high temperature quartz) are isostructural. Lithium borogermanate glasses melt at temperatures lower than those containing silica (bond energy of Ge–O is lower than that of Si–O) and because their properties are similar to those of lithium borosilicate glasses, they can be widely applied [3].

Salman and Salama [7] found that the presence of iron oxide in the CaO–MgO (Li_2O, Fe_2O_3)–SiO_2 glasses increases the crystallization centers and stimulates the crystallization of the glass during the reheating process giving rise to volume crystallization of medium to fine grained microstructure. Also, the state of iron, its coordination and concentration in the glasses mainly determined the nature of the phases formed especially at high $Li_2O+Fe_2O_3$ content.

Romero et al. [8] studied the effect of iron oxide content on the crystallization of a diopside glass-ceramic frit in the K_2O–ZnO–MgO–CaO–Al_2O_3–SiO_2 system and a granite waste glass. The measurements showed that the distribution of Fe^{3+} ions among different crystalline phases formed such as franklinite ($ZnFe_2O_4$) and hematite (Fe_2O_3) depend on the iron content in the original diopside mixture. Thus, the original glass crystallizes to franklinite or hematite when iron content is greater than 2% and 15%, respectively [8].

The structural and microstructure properties of ferrimagnetic glass/glass-ceramics from chemical composition $34SiO_2$–$(45-x)CaO$–$16P_2O_5$–$4.5MgO$–$0.5CaF_2$–xFe_2O_3 ($x=10$–20 wt%) were studied by **Sharma et al.** [9]. Results showed that the iron oxide behaves as a structural modifier. This is evident from the decrease in glass transition temperature. Glass-ceramic samples exhibited the formation of apatite, wollastonite, hematite, and magnetite as major crystalline phases. Higher Fe_2O_3 content creates more non-bridging oxygen and increases the surface activity (dissolution), which is conducive for the formation of silanol groups and thereby affecting the polymeric adhesion.

Present research aims to study the crystallization process of the lithium-borosilicate glass system with the object to follow the role played by the replacements of GeO_2 for SiO_2 and Fe_2O_3 for B_2O_3 on the crystallization characteristics, microstructure and chemical durability of the glass-ceramics obtained.

2. Experimental

2.1. Batch composition and glass preparation

Glass batches were prepared from reagent grade powders of Li_2CO_3, H_3BO_3, Quartz (SiO_2), GeO_2 and Fe_2O_3. The glass oxide constituents are given in Table 1. Glass batches were melted in Pt–2% Rh crucible, covered with Pt foil to minimize the evaporation, in an electric furnace with SiC heating elements at 1300–1400 °C for 3 h. The melt was swirled several times at about 30 min intervals to obtain clear homogeneous melt. The melt was cast into rods and as buttons, which were then properly annealed in a muffle furnace at 450–550 °C to minimize the strain.

Table 1
The compositions of the studied glass.

Glass no.	Oxide contents (mol%)				
	Li_2O	B_2O_3	SiO_2	GeO_2	Fe_2O_3
G_1	33	17	50	–	–
G_2	33	17	48	2	–
G_3	33	17	46	4	–
G_4	33	17	44	6	–
G_5	33	16	44	6	1
G_6	33	14	44	6	3
G_7	33	11	44	6	6

2.2. Differential thermal analysis (DTA)

Thermal behavior of the finely powdered glass samples was examined using a SETARAM LabSys™ TG-DSC16 under Ar gas atmosphere. About 50 mg of the powdered glass was heated in Pt-holder against another Pt-holder containing Al_2O_3 as a reference material. A constant heating rate of 10 °C/min was adopted. Data were recorded using a computer driven data acquisition system. Results were used as a guide for determining the heat-treatment temperatures required to induce crystallization of the glasses.

2.3. Crystallization and glass-ceramic formation

For crystallization, a suitable controlled heat-treatment schedule was applied to the glass to obtain thermally treated glass-ceramic materials of holocrystalline mass with minimum residual glassy phase without deformation. To prepare the glass-ceramic materials, controlled thermal treatment of the glasses was carried out at the main DTA exothermic peak temperature determined for each glass sample. The glass samples were subjected to double stage heat-treatment regimes, therefore, at endothermic temperature of each glass composition, the glass sample was soaked for 5 h and then the temperature was raised up to the exothermic temperature for 10 h. After crystallization, the muffle furnace was switched off and the samples were allowed to cool down to room temperature.

2.4. Material investigation

X-ray diffraction analysis (XRD) was used to identify the crystal phases formed. This was obtained by using a Bruker-AXS D8 Advance with Ni filtered Cu-Kα radiation. The reference data for the interpretation of the X-ray diffraction patterns was obtained from ASTM X-ray diffraction card files. The crystallization characteristics and internal microstructures of fractured surfaces of the crystalline samples, coated with gold, were examined by using scanning electron microscopy (SEM). Representative electron micrographs were obtained by using Jeol, JXA-840 Electron Probe Microanalyzer.

2.5. Chemical durability test

The powdered test was applied to assess the chemical durability of the obtained glass-ceramics. The selected samples were crushed in an agate mortar and then sieved using B.S. sieves to obtain particles with diameters ranging between 0.63 and 0.32 mm. The grains were washed by ethyl alcohol then with pure dry ether three times and then dried at 100 °C in an oven. The dried sample was accurately weighed (1.0 g) in a sintered glass crucible (G4), and then placed in 400 ml polyethylene beaker.

The samples were tested in 0.1 N HCl solution; 200 ml of the acid solution was introduced into the polyethylene beaker. This quantity was sufficient to cover the sintered glass crucible. The polyethylene beaker was covered by the polyethylene cover to reduce evaporation. The beaker was placed in a water bath regulated at 95 °C. After 3 h, the beaker was removed from the bath and the sintered glass crucible was fitted on a suction pump and the whole solution was pumped through it. The sintered crucibles were dried in an oven at 110 °C for 1 h, and then transferred to a desiccator to cool to room temperature. The chemical durability was expressed as the loss in weight of the glass-ceramic samples after immersion. Therefore, the sintered glass crucible was reweighed and the total weight loss was calculated.

3. Results

3.1. Crystallization characteristics

The progress of crystallization in the glasses, the type, and the proportions of the resulting crystalline phase assemblages were markedly dependent on the variation of the glass oxide constituents, the extent of GeO_2/SiO_2 and Fe_2O_3/B_2O_3 replacements as well as the effect of the applied thermal treatment. The crystallization characteristics including thermal behavior of the glass, formation of crystalline phases and microstructure of the resulting glass-ceramics were studied.

3.1.1. Differential thermal analysis (DTA)

The DTA data (Fig. 1) of the investigated glasses show endothermic effects at the 445–495 °C temperature range. This represents the proceeding phenomena of the glass crystallization. Exothermic effects at the 575–775 °C temperature range indicated to the crystallization reactions were also recorded.

The DTA data (Fig. 1) also reveal the addition of GeO_2 at the expense of SiO_2 in the base glass, i.e. G_2–G_4, and replacing Fe_2O_3/B_2O_3 in GeO_2-containing glasses, i.e. G_5–G_7, has led to shifting of both the endothermic dips and the onset of the crystallization exothermic peaks to lower temperatures.

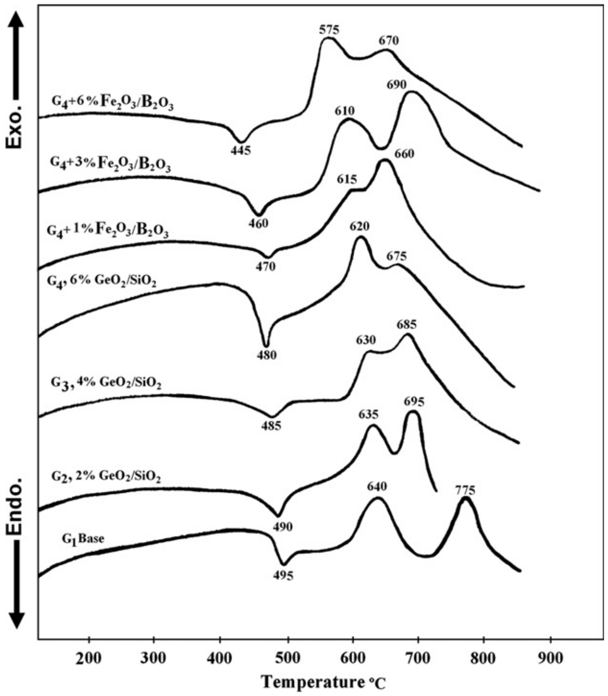

Fig. 1. DTA curves of the studied glasses.

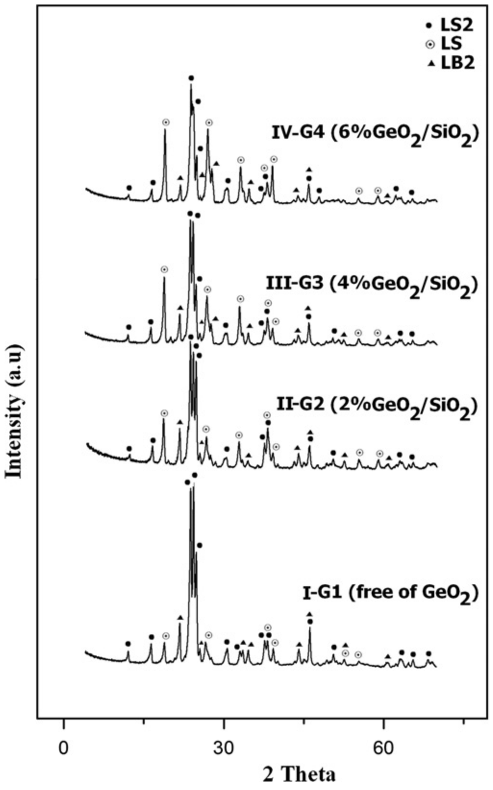

Fig. 2. X-ray diffraction patterns of the crystallized glasses (G_1–G_4). LS lithium metasilicate—Li_2SiO_3, LS_2 lithium disilicate—$Li_2Si_2O_5$, LB_2 lithium diborate—$Li_2B_4O_7$.

Table 2
The crystalline phases formed of the glass-ceramics and their leachability values as weight loss by 0.1 N HCl.

G. no.	Replacement (mol%)	Heat-treatment (°C/h)	Crystalline phases formed	Wt. loss (g)
G_1	**–**	**495/5–775/10**	**LS_2, $Li_2B_4O_7$, LS**	**0.1435**
G_2	**$2GeO_2/SiO_2$**	**490/5–695/10**	**LS_2ss, LS, $Li_2B_4O_7$**	**–**
G_3	**$4GeO_2/SiO_2$**	**485/5–685/10**	**LS_2ss, LS, $Li_2B_4O_7$**	**–**
G_4	**$6GeO_2/SiO_2$**	**480/5–675/10**	**LS_2 ss, LS, $Li_2B_4O_7$**	**0.1370**
G_5	**$6GeO_2/SiO_2+1Fe_2O_3/B_2O_3$**	**470/5–660/10**	**LS, $Li_2B_4O_7$, LS_2 ss, Li $FeSi_2O_6$**	**–**
G_6	**$6GeO_2/SiO_2+3Fe_2O_3/B_2O_3$**	**460/5–690/10**	**LS, Li $FeSi_2O_6$, $Li_2B_4O_7$, LS_2ss**	**0.1091**
G_7	**$6GeO_2/SiO_2+6Fe_2O_3/B_2O_3$**	**445/5–670/10**	**LS, Li $FeSi_2O_6$ ss, $Li_2B_4O_7$**	**0.0605**

LS_2 lithium disilicate, **LS** lithium metasilicate, **ss;** solid solution.

3.1.2. XRD analysis

X-ray diffraction analysis (Fig. 2, Pattern I) shows that the base glass ,i.e. G_1, treated at 495 °C/5 h–775 °C/10 h, has crystallized to lithium disilicate—$Li_2Si_2O_5$ as major crystalline phase (major lines 3.74, 3.65, 3.58 and 2.39, card no. 17-447), lithium di-borate—$Li_2B_4O_7$ (major lines 4.08, 3.91, 3.48 and 2.66, card no. 18-717), and lithium metasilicate—Li_2SiO_3 (major lines 4.69, 3.35, 2.71 and 2.35, card no. 29-828) phases (Table 2).

Partial replacements of GeO_2 at the expense of SiO_2 (2, 4 and 6 mol%) in the glass (i.e. G_2, G_3 and G_4, heat-treated at 490 °C/5 h–695 °C/10 h, 485 °C/5 h–685 °C/10 h and 480 °C/5 h–675 °C/10 h, respectively) led to the formation of the same phases as those obtained from the base glass (G_1) and no GeO_2-containing phases could be identified (Fig. 2, Patterns II–IV). When the glasses G_1 and G_4, treated at higher temperature, i.e. 825 °C/10 h, they crystallized to lithium disilicate and lithium di-borate phases and no lithium metasilicate could be detected as shown from the XRD analysis (Fig. 3).

The partial replacement of Fe_2O_3 (1 mol%) at the expense of B_2O_3 in GeO_2-containing glass, i.e. G_5 crystallized at 470 °C/5 h–660 °C/10 h, has led to the crystallization of lithium iron silicate phase, of pyroxene family, (major lines 6.32, 4.44, 2.99 and 2.87, card no. 89-255) together with lithium metasilicate, lithium di-borate, and lithium disilicate ss as indicated from the XRD analysis (Fig. 4, Pattern II). By increasing the Fe_2O_3/B_2O_3 replacements in GeO_2-containing glass (3 and 6 mol% Fe_2O_3), i.e. G_6 and G_7 treated at 460 °C/5 h–690 °C/10 h and 445 °C/5 h–670 °C/10 h, respectively, the X-ray diffraction analysis (Fig. 4, Patterns III and IV) revealed that, the crystallization of lithium metasilicate and lithium iron silicate phases were increased at the expense of lithium disilicate ss and lithium diborate phases (Table 2).

It should be mentioned that, as the iron content in the studied glasses was increased, the lithium iron-pyroxene ss and lithium metasilicate phases were increased, while lithium disilicate ss phase was decreased (Fig. 4).

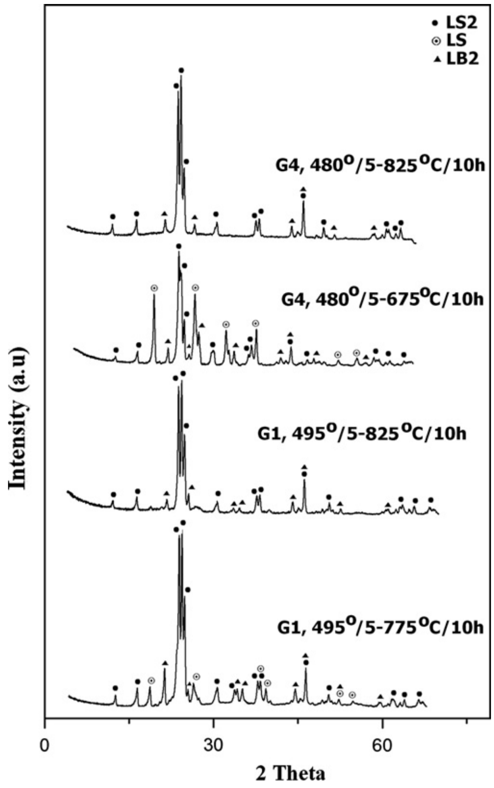

Fig. 3. X-ray diffraction patterns of the glasses (G_1 and G_4) crystallized at different temperatures.

Scanning electron micrographs (Fig. 5) show the effect of GeO_2/SiO_2 and Fe_2O_3/B_2O_3 replacements on the microstructure of some selected glass-ceramics. SEM micrograph of fractured surface of the crystallized base glass, G_1, clearly shows volume crystallization of rounded-like growths (Fig. 5A). The GeO_2/SiO_2 replacement in the base glass up to 6 mol% GeO_2, i.e.G_4, has led to the formation of volume crystallization of fine grained microstructure (Fig. 5B). The addition of Fe_2O_3 at the expense of B_2O_3 up to 6 mol% in GeO_2-containing glass (i.e. G_7) has led to the formation of volume crystallization of tiny aggregates of fine grained microstructure (Fig. 5C).

3.2. Chemical durability

The test of the chemical durability was carried out by the weight loss technique in acid solution (0.1 N HCl) at 95 °C for 3 h for some selected glass-ceramics (i.e. G_1, G_4, G_6 and G_7). The obtained data are given in Table 2 and graphically represented in Fig. 6.

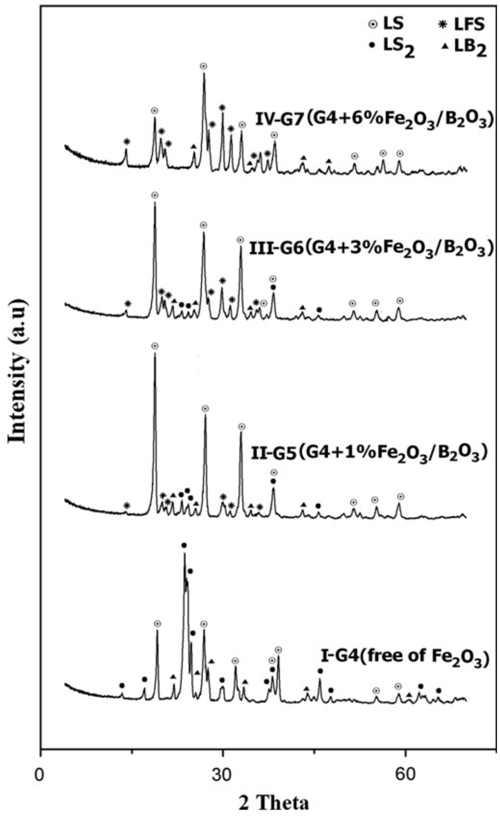

Fig. 4. X-ray diffraction patterns of the crystallized glasses (G_4–G_7). LFS; Lithium iron silicate—$LiFeSi_2O_6$.

Present results indicated that the addition of GeO_2 at the expense of SiO_2 decreased the leaching value of the crystalline glasses (Fig. 6, Table 2), i.e. the chemical durability value of sample G_4 (with 6 mol% GeO_2) was better than that of the base crystalline glass, i.e. G_1 (free of GeO_2). Also the chemical durability of the GeO_2-containing glass-ceramics was greatly improved by the addition of Fe_2O_3 at the expense of B_2O_3, i.e. G_6 and G_7, therefore, the leachability of the sample was decreased by progressive addition of iron oxide compared with that free of Fe_2O_3, i.e. G_4 (Fig. 6, Table 2).

4. Discussion

4.1. Crystallization characteristics.

The crystallization behavior of the glass during the reheating process is known to be connected with the nature and proportions of the glass oxide constituents. The ability of some cations to build glass forming units or to be housed as modifiers in interstitial positions in the glass structure should also be considered [10].

Addition of GeO_2 at the expense of SiO_2 in the base glass, i.e.G_2–G_4, led to shifting both the endothermic and exothermic peak temperatures toward lower temperatures (Fig. 1, Table 2). Ge and Si cations carry the same charge (4+) and are, therefore, electrostatically equivalent. Because the Ge–O bond is weaker than that of Si–O bond, an oxygen vacancy can produce more easily near a Ge cation by trapping an electron [6]. Thus the GeO_2-containing glasses were crystallized easier than those free of it. Also, the glass transition temperatures (T_g) were decreased as the iron content increased by the Fe_2O_3/B_2O_3 replacements in the GeO_2-containing

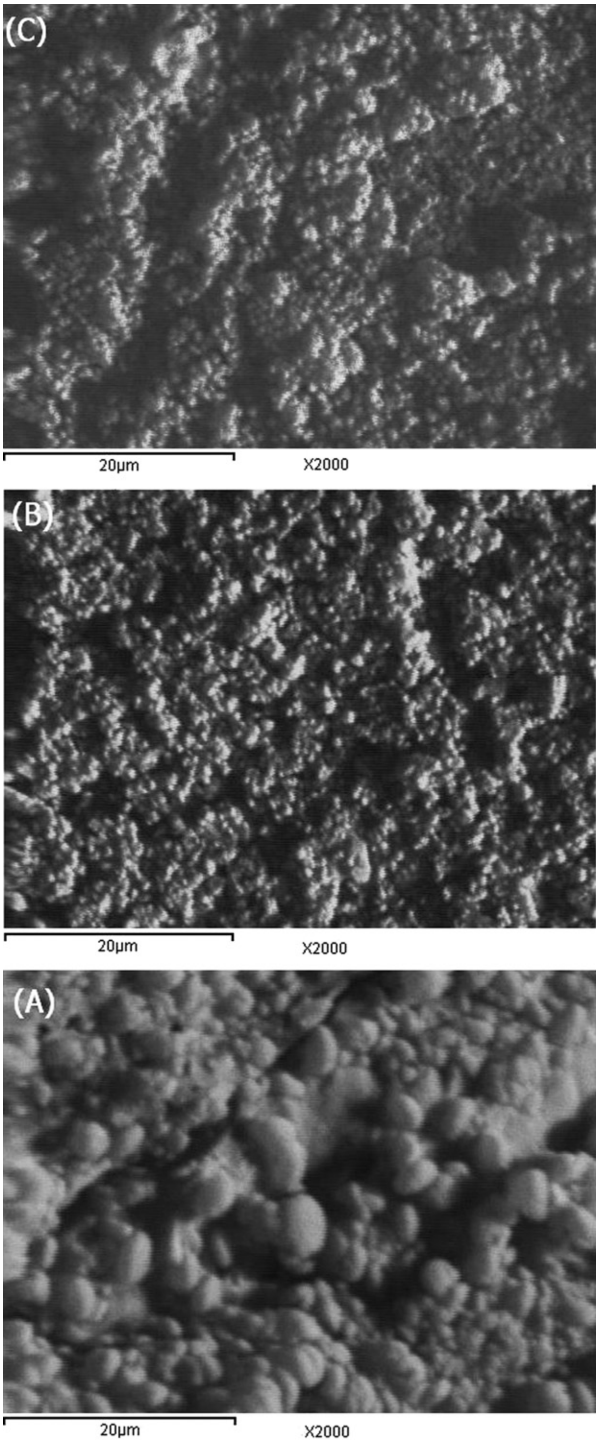

Fig. 5. SEM micrographs of fractured surface of the glasses; (A) G_1 crystallized at 495 °C/5 h – 775 °C/10 h showed volume crystallization of rounded-like growths. (B) G_4 crystallized at 480 °C/5 h – 675 °C/10 h showed volume crystallization of fine grained microstructure. (C) G_7 crystallized at 445 °C/5 h – 670 °C/10 h showed crystallization of tiny aggregates of fine grained microstructure.

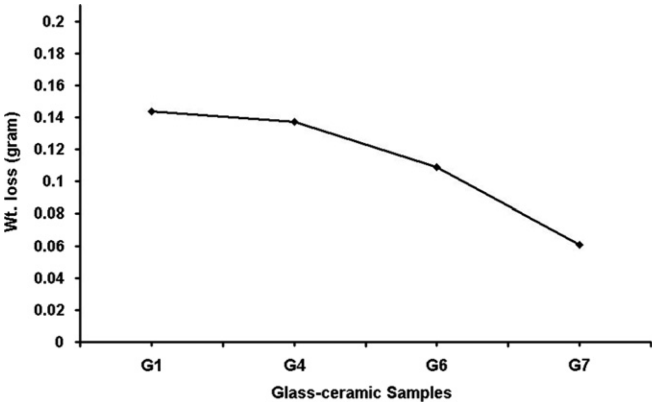

Fig. 6. Chemical stability of the glass-ceramic samples.

glasses (Fig. 1, Table 2). This could be attributed to the introduction of Fe_2O_3 inducing several structural modifications in the glasses. The glass-transition temperature is closely related to the strength of glass network. An increase in modifier content is expected to decrease the connectivity of the network, creating non-bridging oxygens (NBOs). Consequently the network becomes less rigid and requires less energy to break. Thus, when iron oxide is added to glass network, it acts as a modifier [9].

The X-ray diffraction analysis (Fig. 2, Pattern I) indicated that the glass G_1 crystallized into lithium disilicate, as predominant phase, together with lithium diborate and a minor constituent of lithium metasilicate was crystallized as well. Crystallization of meta- and disilicate, and their ratios, was depending on the heat-treatment temperatures and duration of the process. Lithium metasilicate is formed almost exclusively by low temperature treatment of glasses, while at higher temperature, lithium disilicate appears. However, **Hench and others** [11,12] revealed that a lithium metasilicate phase appears as a precursor to crystallization of the equilibrium lithium disilicate in the 33 mol% Li_2SiO_3 glasses.

Mineralogically, lithium disilicate—$Li_2Si_2O_5$ was formed first, as a predominant phase, among the crystallization products of the glasses G_1–G_4 as a result of the combination between one mole of Li_2O together with double quantity of SiO_2 to form $Li_2Si_2O_5$ molecules. The lithium metasilicate—Li_2SiO_3 was detected as a secondary phase among the crystallization products of the glasses containing GeO_2 at temperatures between 675 °C and 775 °C for 10 h (Fig. 2). However, the crystallization of the glasses G_1 and G_4 treated at higher temperatures (e.g. 825 °C for 10 h.), no lithium metasilicate could be detected (Fig. 3). **Tulyaganov et al.** [13] reported that the predominant crystallization of lithium disilicate—$Li_2Si_2O_5$ occurs via the precursor lithium metasilicate (Li_2SiO_3). The growth of lithium disilicate increases at 680 °C, due to the solid-state reaction of the chemical equation:

$$\mathbf{Li_2SiO_3(crystal) + SiO_2(glass) \rightarrow Li_2Si_2O_5(crystal)}$$

Theoretically, on the basis of the petrochemical calculation [14] of the present lithium-borosilicate glass composition into normative molecules, only predominant lithium disilicate and lithium diborate could be formed. The presence of B_2O_3 in the glass seemed to affect the ordering toward the metasilicate formation. Therefore, a remainder of Li-metasilicate in the crystalline base glass was encountered [15].

Structurally, in both lithium and disilicate crystals, the Li^+ ions are tetrahedrally bonded with oxygen ions and are represented by triangles **Hench et al.** [11]. He stated that, if alternate Li_2O groups, at the interface between the crystals, are removed from the metasilicate lattice, a small displacive shift will be sufficient to produce the disilicate lattice. Therefore, it seemed that the metasilicate phase was precipitated metastably at lower temperature by an ordering of extremely small regions in the glass containing randomly distributed Li_2O SiO_2 chains. With additional heating or long duration Li_2O groups apparently diffuse out of the metasilicate crystallites, probably as ionic species, producing the complex layered disilicate structure from the SiO_2-rich matrix at the metasilicate interface.

The GeO_2/SiO_2 replacements in the glasses G_2 and G_3 have led to increasing the formation of lithium metasilicate phase together with lithium disilicate ss (major) and lithium diborate, however no GeO_2-containing phases could be identified (Fig. 2, Patterns II and III).

At higher GeO_2/SiO_2 replacement up to 6 mol%, i.e. G_4, lithium disilicate solid solution phase was formed as indicated from the shift of d-spacing lines of XRD characteristics for the lithium disilicate phase (Fig. 2, Pattern IV). **Kolesova and Kalinina** [16] showed that GeO_2 can combine with SiO_2 to form solid solutions. The concentration of SiO_2 in the solution is 60–70 mol%. **Urnes** [17] proved that Ge replaced Si isostructurally in lithium aluminum germanosilicate glasses. Monovalent cation, such as Li^+ may be incorporated in the pyroxene structure together with trivalent cations like Fe^{3+} in the form of isomorphous phase like $LiFe^{3+}Ge_2O_6$ [18]. **Hasdemire et al.** [19] showed that lithium disilicate has a wide range of solid solution formation. He stated that the lithium disilicate ss composition ranges to ≈ 39 mol% Li_2O for temperatures below 550 °C. Therefore, according to the petrochemical calculation of the glass composition into normative mineral molecules [14], it seems more likely that germanium may be accommodated in the lithium disilicate structure forming lithium germanium silicate phase of the probable formula—$Li_2(Ge_{0.11}Si_{0.89})_2O_5$.

It is well known that compositions crystallizing to give solid solution series are important to control the properties of the resultant materials, and offer an excellent opportunity to the glass-ceramic study [20].

The replacement of Fe_2O_3 at the expense of B_2O_3 in GeO_2-containing glasses, i.e.G_5 and G_6, favors the formation of lithium iron silicate, of pyroxene family, at the expense of lithium disilicate ss phase while, lithium metasilicate was crystallized as predominant phase together with lithium diborate (Fig. 4, Patterns II and III, Table 2).

It should be mentioned that during the increase of iron content in the GeO_2-containing glasses, the crystallization of lithium iron silicate and lithium metasilicate phases were increased, while the lithium disilicate phase was decreased. This may be illustrated according to the following schematic [21] equation:

$$Li_2Si_2O_5 + Fe_2O_3 \rightarrow 2LiFeSi_2O_6 + 2Li_2SiO_3$$

Lithium iron pyroxene was described by **Salman** [21] as $LiFe^{3+}Si_2O_6$ among the crystallization products of lithium silicate, lithium borosilicate, calcium lithium magnesium silicate and calcium lithium magnesium aluminum silicate with addition of iron oxide. He showed that iron oxide prefers to be accommodated in the lithium silicate structure rather than lithium borate.

On further increasing of the Fe_2O_3/B_2O_3 replacements in GeO_2-containing glasses, up to 6 mol%, i.e. G_7, the X-ray diffraction analysis (Fig. 4, Patterns IV) revealed that the lithium iron silicate solid solution phase, of the probable formula—$LiFe(Si_{0.75},Ge_{0.25})_2O_6$, could be formed [19,21] instead of lithium disilicate solid solution phase, together with lithium metasilicate (as major) and lithium diborate phases. The germanium oxide seemed to be incorporated in the iron pyroxene silicate structure since the Ge^{4+} is isostructurly with silicon forming solid solution. A wide variety of ionic substitution occurs in the members of the pyroxene group, and there is complete replacement between some of the group components [22].

4.2. *Chemical durability*

One of the characteristic properties of the material is its ability to resist the corrosive action of water, aqueous solution of acids, alkalies and salts etc. This resistance is known as chemical durability which depends on the structure, composition of the material, laboratory conditions, and environment [23].

In the glass ceramic materials, the chemical durability is a function of many factors such as the ratios of the glass oxides added and consequently the nature and the concentration of the crystalline phases formed, composition of the present residual glassy phase, all of which are controlled by the glass composition and applied heat treatments [24]. Microstructure can also be taken into considerations. The 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 vapors [25]. The chemical stability of glass-ceramics determines their applications in different environments and is therefore of considerable practical importance. The mechanism of reactions occurring between glass-ceramics and aqueous solutions, as well as the factors affecting the chemical durability, was studied. It is generally agreed that the chemical behavior of glass-ceramics is related to their phases formed and the residual glassy matrix [26].

The effect of acidic solutions on the different types of mineral phases was studied by many authors [25,27]. 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 under treatment with acid solutions. **McMillan** [24] showed that the presence of a large proportion of crystalline silica in the form of cristobalite or quartz gives better chemical durability. In glass-ceramic materials, several different crystalline compounds may be present together with a residual glassy phase. The relative resistance of these phases to acid attack will determine the chemical durability of the material. Varieties of pyroxene phases and their solid solutions show high resistance toward the acid attack. Lithium metasilicate and disilicate phases, on the other hand, are decomposed by acids [22].

Studies on corrosion of glass-ceramics indicated that the chemical durability cannot be solely deduced from the durability of the separate phases but also interfaces have to be taken into account. The phase boundary attack was assumed to be due to stresses or minor compositional gradients at the interface [28]. It was stated that the initial attack will be on the residual glassy phase which is thought to play an important role in determining the resistance of glass ceramic to chemical attack [27]. The solubility of both the formed crystals and the residual glass phase in leaching solution has almost an equally important influence on the chemical stability of glass-ceramics.

The present results revealed that, the leaching value of the investigated glass-ceramic G_1 was the highest value than those in other studied samples (Table 2). This may be attributed to the formation of lithium disilicate, lithium diborate and lithium metasilicate phases as the crystallization products, which are slightly decomposed by acidic solution [29].

The addition of GeO_2, at the expense of SiO_2, up to 6 mol% in the glasses, i.e. G_4, has led to decreasing the weight loss value (Fig. 6, Table 2). This may be due to that the germanium cation tends to accommodate in the lithium disilicate structure instead of silicon cation and this led to increasing the Si/O ratio in the glassy matrix and improved the chemical durability [30]. **Wei Deng et al.** [31] stated that high silica content has a tendency to improve glass-network interconnectivity and enhance chemical resistance by increasing the ratio of bridging oxygens and nonbridging oxygens.

The leachability of the GeO_2-containing glass-ceramics was greatly decreased by the replacement of Fe_2O_3 at the expense of B_2O_3 (G_6 and G_7) as compared with that of crystalline sample free of Fe_2O_3 (G_4), i.e. the chemical durability was markedly improved (Fig. 6, Table 2). This may be ascribed to the formation of the more durable lithium iron pyroxene phase of pyroxene family [22] among the crystallization products at the expense of the relatively decomposed lithium disilicate phase [24]. In addition to the formation of fine microstructure without pores led to improve the chemical durability of the obtained glass ceramics by GeO_2/SiO_2 and Fe_2O_3/B_2O_3 replacements [25].

5. Conclusions

The effect of GeO_2/SiO_2 and Fe_2O_3/B_2O_3 replacements on the crystallization characteristics and the chemical durability of the glass composition $33Li_2O–17B_2O_3–50SiO_2$ (mol%) were investigated. The transition (T_g) and softening (T_s) temperatures were decreased by the replacement processes. Heat-treatment temperatures and duration of the process played an important role in the crystallization of lithium meta and/or disilicate phases. A series of solid solution phases, including lithium germanium silicate [$Li_2(Ge_{0.11}Si_{0.89})_2O_5$] and lithium iron germanium silicate [$LiFe(Ge_{0.25}Si_{0.75})_2O_6$], could be obtained together with lithium disilicate, lithium iron silicate, lithium metasilicate, and lithium diborate phases. A combination of fine grained microstructure and good chemical durability were obtained by increasing the germanium and/or iron oxide content in the lithium borosilicate glass-ceramic.

References

[1] S.M. Liu, G.L. Zhao, Y. Hao, J.X. Wang, G.R. Han, Effects of mixed alkaline earth oxides additive on crystallization and structure changes in borosilicate glasses, Journal of Non-Crystalline Solids 354 (10–11) (2008) 956–961.

[2] M. Arbab, V.K. Marghussian, H. Sarpoolaky, M. Kord, The effect of RO oxides on microstructure and chemical durability of borosilicate glasses opacified by P_2O_5, Ceramics International 33 (6) (2007) 943–950.

[3] K. Błaszczak, W. Jelonek, A. Adamczyk, Infrared studies of glasses in the $Li_2O–B_2O_3–GeO_2$ (SiO_2) systems, Journal of Molecular Structure 511–512 (1999) 163–166.

[4] B.S. Sastry, F.A. Hummel, Studies in Lithium Oxide Systems: VII, $Li_2O–B_2O_3–SiO_2$, Journal of American Ceramic Society 43 (1960) 7–17.

[5] V.K.H. Nikulin, O.S. Viktorova, L.M. Prusakova, R.I. Ainetdinova, M.G. Meshcher Yakova, Effect of liquidation on the properties of low-alkali-borosilicate glasses, Glass and Ceramics 48 (1991) 145–150.

[6] A. Margaryan, M.A. Piliavin, Germanate Glasses: Structure, Spectroscopy and Properties, Artech House Inc, Boston, London, 1993, pp. 6–82.

[7] S.M. Salman, S.N. Salama, Pyroxene solid solution crystallized from CaO–MgO (Li_2O, Fe_2O_3)–SiO_2 glasses, Ceramic International 12 (1986) 221–228.

[8] M. Romero, J.M. Rincon, A. Acosta, Effect of iron oxide content on the crystallization of a diopside glass-ceramic glaze, Journal of the European Ceramic Society 22 (2002) 883–890.

[9] K. Sharma, S. Bhattacharya, C. Muralic, K.G. Bhushanb, G.P. Kothiyala, Interactions of ferrimagnetic glass/glass-ceramics with bovine serum albumin, Applied Surface Science 258 (2012) 2356–2361.

[10] L. Stoch, Structure and crystallization of multi component glasses, in: Proceedings of the XIX International Congress on Glass, Invited Papers, vol. 1, Edinburgh, Scotland, 1–6 July 2001, pp. 62–73.

[11] L.L. Hench, S.W. Freiman, D.L. Kinser, The early stages of crystallization in Li_2O $2SiO_2$ glass, Physics and Chemistry of Glasses 12 (1971) 58.

[12] D.L. Kinser, L.L. Hench, Effect of metastable precipitate on the electrical properties of a Li_2O SiO_2 glass, Journal of American Ceramic Society 51 (1968) 378–382.

[13] D.U. Tulyaganov, S. Agathopoulos, I. Kansal, P. Valério, M.J. Ribeiro, J.M.F. Ferreira, Synthesis and properties of lithium disilicate glass-ceramics in the system $SiO_2–Al_2O_3–K_2O–Li_2O$, Ceramics International 35 (2009) 3013–3019.

[14] T.F. Barth, Theoretical Petrology, 2nd ed., Wiley, NY, 1962.

[15] S.N. Salama, S.M. Salman, H. Darwish, Crystallization characteristics of some lithia calcia magnesia borosilicate glasses, Ceramics International 21 (1995) 159–167.

[16] V.A. Kolesova, A.M. Kalinina, Physics and Chemistry of Glasses, vol. 1, USSR, 1975.

[17] S. Urnes, X-ray diffraction studies of glasses in the system $Li_2O–AI_2O_3–SiO_2–GeO_2$, Physics and Chemistry of Glasses 12 (1971) 83–84.

[18] M. Behruzi, E. Banerjea-Appel, F.D. Scherberich, Th. Hahn, Proceedings of the XVIIth Congress and General Assembly of the International Union of Crystallography, Washington, USA, 1996, pp. 8–17.

[19] I. Hasdemire, R. Bruckner, J. Deubener, Crystallisation of lithium di- and metasilicate solid solutions from $Li_2O–SiO_2$ glasses, Physics and Chemistry of Glasses 39 (1998) 253–257.

[20] P.S. Rogers, The initiation of crystal growth in glasses, Mineralogical Magazine 37 (1970) 741–758.

[21] S.M. Salman, Crystallization of alkali iron pyroxene $LiFeSi_2O_6$ in $Li_2O–SiO_2$ glasses containing iron oxide, Interceram 30 (1981) 48–51.

[22] W.A. Deer, R.A. Howie, A. Zussman, An Introduction To The Rock Forming Minerals Third ELBS Impression, Printing Press Ltd., Hong Kong, Common Wealth, 1992.

[23] Z. Jasenka, L. Dragutin, C. Lidija, J. Marko, Estimation of chemical resistance of dental ceramics by neural network, Dental Materials 24 (2008) 2719.

[24] P.W. McMillan, Glass-Ceramics, Academic Press, London, NY, 1979.

[25] A.J. Berezhnoi, Glass-Ceramics and Photositalls, Plenum Press, NY, London, 1970.

[26] E. Demirkesen, G. Goller, Effect of Al_2O_3 additions on the acid durability of a $Li_2O–ZnO–SiO_2$ glass and its glass-ceramic, Ceramic International 29 (2003) 463–469.

[27] A. Lodding, in: D.E. Clark, B. Zoitos (Eds.), Corrosion of Glass, Ceramics and Ceramic Superconductors, Noyes Publications, Park Ridge, New Jersey, 1992.

[28] S.V. Golubev, O.S. Pokrovsky, J. Schott, Experimental determination of the effect of dissolved CO_2 on the dissolution kinetics of Mg and Ca silicates at 25 °C, Chemical Geology 217 (2005) 227–238.

[29] S.M. Salman, S.N. Salama, H. Darwish, Effect of some divalent and trivalent oxides on the chemical stability of lithium borosilicate glasses and their crystalline solids, Glass Technology 43 (2002) 138–144.

[30] P. Pisciella, S. Crisucci, A. Karamanov, M. Pelino, Chemical durability of glasses obtained by vitrification of industrial wastes, Waste Management 21 (2001) 1–9.

[31] Wei Deng, Jin-shu Cheng, Pei-jing Tian, Mi-tang Wang, Chemical durability and weathering resistance of canasite based glass and glass-ceramics, Journal of Non-Crystalline Solids 358 (2012) 2847–2854.