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Crystallization characteristics and physico-chemical properties of indium-containing lithium iron aluminosilicate glasses

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Abstract

The crystallization characteristics, microhardness and chemical durability of glasses based on the Li_2O–Al_2O_3–Fe_2O_3 (In_2O_3)–SiO_2 system were investigated. The present work aims to study the effect of In_2O_3/Fe_2O_3 replacements on the crystallization and the resulting microstructure of the glass-ceramics. Very fine grained microstructure was mostly developed by In_2O_3/Fe_2O_3 replacements in the glass-ceramics. The crystalline phases formed after controlled heat-treatment of the glasses were β-eucryptite ss, lithium meta- and di-silicate as well as two forms of pyroxene phases ($LiFeSi_2O_6$ and $LiInSi_2O_6$). The microhardness values of the resulting glass-ceramics were decreased with In_2O_3/Fe_2O_3 replacements while the chemical durability was improved. The obtained data were correlated to the type of the crystalline phases formed and the resulting microstructure. Promising glass-ceramic materials of fine microstructure and good chemical durability could be obtained.

Keywords: Crystallization; Microhardness; Solid solution (ss); Chemical durability

1. Introduction

Glass-ceramics are polycrystalline solids produced by controlled crystallization of glasses [1]. Their properties depend on microstructure, the thermal history and the composition of phases developed during the manufacturing process. The ability to control these parameters depends on the original composition as well as the heat-treatment regime [2].

Aluminosilicate glass-ceramics are important commercial materials because of the combination of their exceptional thermal shock resistance, thermal stability, and outstanding chemical durability. In particular, glass-ceramics based on the β-eucryptite or β-spodumene solid solutions in the Li-aluminosilicate system have exceptionally low thermal expansion coefficients [3].

The behavior of iron-containing oxide glasses with heat-treatment to form glass-ceramics has been a subject of considerable importance, especially in determining the properties of the resultant materials [4]. If iron containing phases and related solid solution could be crystallized in a controlled way from an iron-rich glass composition, it could offer a unique method for the control of the magnetic, electric and other properties of the resultant materials [5].

Transition metal oxides like iron oxide are known to affect both nucleation and crystallization of silicate glasses [6]. The presence of Fe_2O_3 even in small amounts has a considerable influence on the crystallizability and nucleation of the glass during the heating process. Williamson et al. [7] found that the crystal growth rates were dependent not only on the amount of iron oxide added to glass but also on the ferrous/ferric ratio of the iron in the glass.

On the crystallization of semiconductive oxides, the indium oxide has a special potential because of its large solubility in convenient silicate and borate melts. In_2O_3 is a large band gap n-type semiconductor. Recently, indium oxide has been predominantly used as coating material for transparent electric conductors. Glassy substrates can easily be coated by In_2O_3 using sputtering or sol–gel techniques [8].

The present work aims to study the crystallization behavior, the phase relation and the extent of solid

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solution phases formed by controlled crystallization of lithium indium iron aluminosilicate glasses. The role of In_2O_3/Fe_2O_3 replacements in determining the microstructure and some properties like chemical durability and hardness of the glass-ceramic are also considered.

2. Experimental

2.1. Batch composition and glass preparation

The glass batches were prepared from reagent grade powders of Li_2CO_3, Al_2O_3, Quartz (SiO_2), Fe_2O_3 and In_2O_3. The glass oxide constituents are given in Table 1. The glass batches were melted in a 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 glass melt. The melt was cast into rods and as buttons, which were then properly annealed in a muffle furnace at 500–550 °C to minimize the strain.

2.2. Differential thermal analysis (DTA)

The thermal behavior of the finely powdered glass samples was examined using a SETARAM LabSys^{TM} 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. The results obtained were used as a guide for determining the required heat-treatment temperatures applied to induce crystallization of the glasses.

2.3. Thermal-treatment

The progress of crystallization in the glasses was followed using double stage heat-treatment regimes. Crystallization was carried out at temperatures in the region of the main DTA exothermic peak determined for each glass. The glasses were first heated according to the DTA results at the endothermic peak temperature for 5 h, which was followed by another thermal treatment at the exothermic peak temperature for 10 h.

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 were 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. Microhardness measurements

The microhardness values of the crystallized samples were measured by using Vicker's microhardness indenter (SHIMADZU, HMV-2 Series, Japan). The specimens were cut using a low speed diamond saw, with a dry ground and polished carefully to obtain smooth and flat parallel surfaces of the glass-ceramic samples before indentation testing. At least six indentation readings for each sample were made under normal atmospheric conditions. Testing was made using a load of 100 g, with fixed loading time 15 s.

2.6. Chemical durability test

The powdered test was applied to assess the chemical durability [9] 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 with ethyl alcohol and then with pure dry ether three times and finally dried. The dried sample was accurately weighed (1.0 g) in a sintered glass crucible (G4), which was 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 with its contents was covered by the polyethylene cover to reduce evaporation. The beaker was placed in a water bath regulated at 95 °C. After 1 h, the beaker was removed from the bath

Table 1
The compositions of the glass oxides.

Glass no.	Oxide contents (mole%)				
	Li_2O	Al_2O_3	Fe_2O_3	SiO_2	In_2O_3
G_1	24.56	3.32	4.95	67.17	–
G_2	24.56	3.32	3.95	67.17	1
G_3	24.56	3.32	2.95	67.17	2
G_4	24.56	3.32	1.95	67.17	3
G_5	24.56	3.32	0.95	67.17	4

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 characteristic

The crystallization characteristics including thermal behavior of the glasses, crystalline phases formed and microstructure of the resulting glass-ceramics were investigated.

3.1.1. Differential thermal analysis (DTA)

The DTA data of the glasses (Fig. 1, Table 2) shows endothermic peaks in the 495–540 °C temperature range. These endothermic peaks may be attributed to the glass transition (Tg) at which the atoms begin to arrange themselves in preliminary structural elements subsequent to crystallization. Various exothermic reactions in the 620–765 °C temperature range, due to crystallization reaction characteristics of the glasses, were also detected.

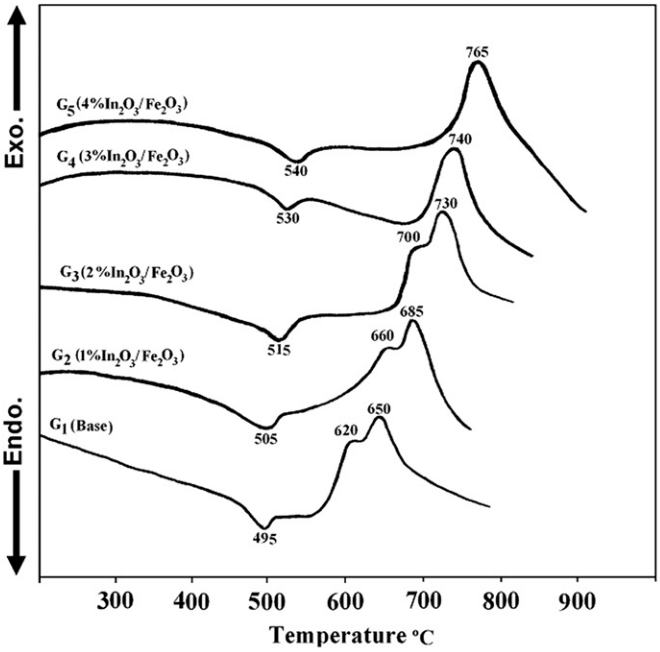

Fig. 1. DTA curves of the studied glasses (G_1–G_5).

3.1.2. XRD analysis

The XRD patterns of the glass-ceramic samples shown in Fig. 2 indicate evidence of crystallization that occurred in the glasses. Peaks corresponding to major crystalline phases are marked with symbols. All peaks were analyzed with ASTM card files.

The X-ray diffraction analysis (Fig. 2, Pattern I) shows that the base glass, G_1, crystallized to β-eucryptite ss phase (rich in silica) as major phase (major lines 4.44, 3.45, 2.53, 1.86 and 1.61, card file [10]), together with lithium disilicate—$Li_2Si_2O_5$ (major lines 5.42, 3.73, 3.65, 3.59 and 2.36, card no. 40-376), lithium iron silicate—$LiFeSi_2O_6$, of pyroxene family, (major lines 6.23, 4.44, 2.99, 2.86 and

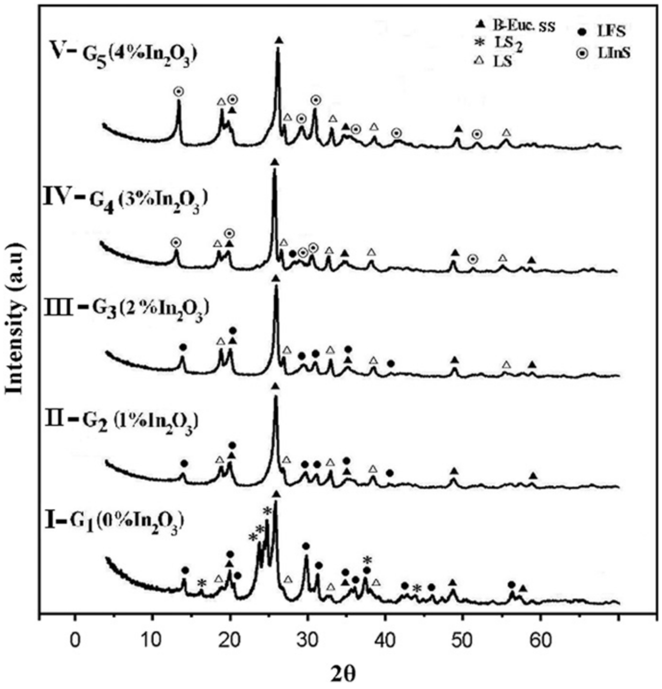

Fig. 2. X-ray diffraction patterns of the crystallized glasses (G_1–G_5). β-Euc, β-eucryptite—$LiAlSiO_4$; LFS, Lithium iron silicate—$LiFeSi_2O_6$; LS, Lithium metasilicate—Li_2SiO_3; LS_2, Lithium disilicate—$Li_2Si_2O_5$; LInS, Lithium indium silicate—$LiInSi_2O_6$; SS, solid solution.

Table 2
Crystalline phases developed, microhardness and chemical durability data.

Glass no.	Heat-treatment (°C/h)	Developed phases	Microhardness (MPa)	Wt. loss (gram)
G_1	495/5–650/10	β-euc. ss, LS_2, LFS, LS	764	0.0600
G_2	505/5–685/10	β-euc. ss, LFS ss, LS	722	0.0421
G_3	515/5–730/10	β-euc. ss, LS, LFS ss	701	0.0340
G_4	530/5–740/10	β-euc. ss, LS, LInS, LFS	–	–
G_5	540/5–765/10	β-euc. ss, LInS ss, LS	668	0.0203

β-euc, β-eucryptite—$LiAlSiO_4$; LFS, Lithium iron silicate—$LiFeSi_2O_6$; LS, Lithium metasilicate—Li_2SiO_3; LS_2, Lithium disilicate—$Li_2Si_2O_5$; LInS, Lithium indium silicate—$LiInSi_2O_6$; ss, solid solution.

2.50, card no. 89-225) and lithium metasilicate—Li_2SiO_3 (major lines 4.70, 3.31, 2.72 and 2.36, card no. 29-828) phases (Table 2).

The partial addition of In_2O_3 at the expense of Fe_2O_3 in the base glass (i.e. 1 and 2 mol%, G_2 and G_3) led to the crystallization of β-eucryptite ss (major), lithium iron silicate ss (probably Li[Fe, In]Si_2O_6), and lithium metasilicate—Li_2SiO_3 phase. No lithium disilicate—$Li_2Si_2O_5$ phase could be detected (Fig. 2, Patterns II and III, Table 2).

The increase of In_2O_3 at the expense of Fe_2O_3 in the glass up to 3 mol% (i.e. G_4) led to the crystallization of β-eucryptite ss (major), lithium iron silicate ss and lithium metasilicate—Li_2SiO_3 phases together with lithium indium silicate—$LiInSi_2O_6$ phase, of pyroxene family, (major lines 6.41, 3.02, 2.89, 2.10 and 1.60, card no. 33-799) (Fig. 2, Pattern IV, Table 2).

On further increase of the In_2O_3/Fe_2O_3 replacement (up to 4 mol% In_2O_3 i.e. G_5) the X-ray diffraction analysis (Fig. 2, Pattern V) revealed that, the crystallization of lithium indium silicate ss (probably Li[In, Fe]Si_2O_6) phase was increased, instead of lithium iron silicate—$LiFeSi_2O_6$, β- eucryptite ss (major), and lithium metasilicate—Li_2SiO_3 phases were also formed (Table 2).

The SEM micrographs of fractured surface of the crystallized glasses are represented in Fig. 3. The glass-ceramic of G_1, exhibited the formation of volume crystallization of fine grained microstructure (Fig. 3a). The partial substitution of indium oxide instead of Fe_2O_3 in the base glass (1 mol% In_2O_3 i.e. G_2) led to the formation of volume crystallization of tiny aggregates of crystals (Fig. 3b). However, on increasing In_2O_3/Fe_2O_3 replacement (4 mol% In_2O_3, i.e. G_5), the microstructure changed to fine crystals with aggregates of prismatic-like growths (Fig. 3c).

3.2. Microhardness

The microhardness property of the resulting glass-ceramics was determined by Vicker's microhardness. Table 2 exhibits the summary of the microhardness values (764–668 MPa) of the crystalline materials which are also graphically represented in Fig. 4. The microhardness value of the base crystalline material (free of In_2O_3) was 764 MPa. The addition of In_2O_3 at the expense of Fe_2O_3 in the base glass led to the decrease of the microhardness values of the investigated crystalline glasses (Fig. 4, Table 2).

3.3. Chemical durability

The chemical durability of the prepared glass-ceramics in acidic media (0.1 N HCl) at 95 °C for 1 h was determined. The obtained data are given in Table 2 and graphically represented in Fig. 5.

The present results revealed that, the In_2O_3-containing glass-ceramics were more durable than that free of it (the base glass-ceramics), i.e. the chemical durability of the glass-ceramics was improved by In_2O_3/Fe_2O_3 replacement in the glasses.

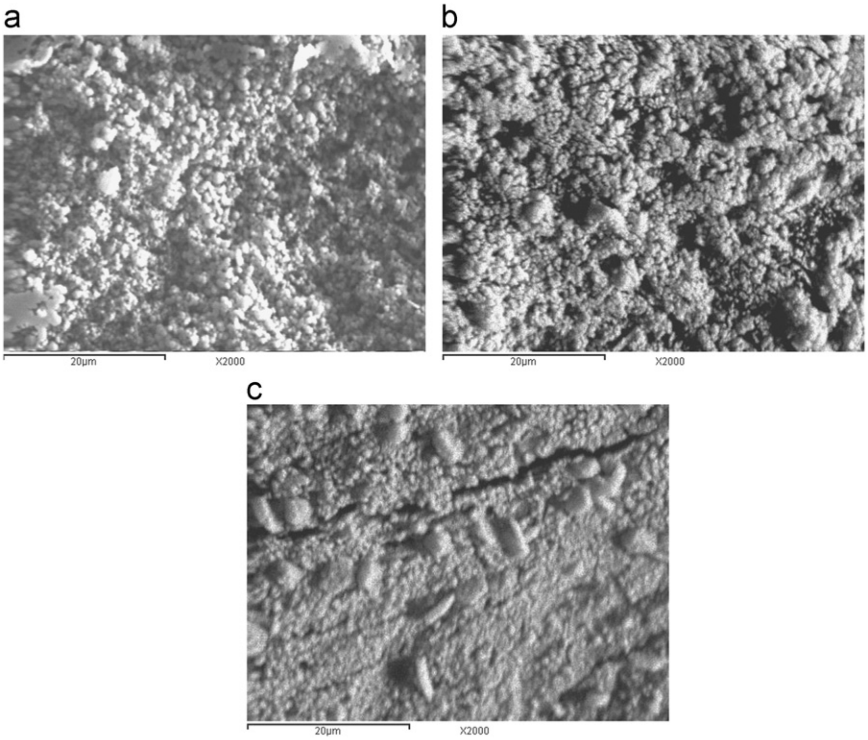

Fig. 3. SEM micrograph of fractured surface of the glasses. (a); G_1 crystallized at 495 °C/5 h–650 °C/10 h, showed volume crystallization of fine grained microstructure. (b); G_2 crystallized at 505 °C/5 h–685 °C/10 h, showed volume crystallization tiny aggregates-like growths. (c); G_5 crystallized at 540 °C/5 h–765 °C/10 h, showed crystallization of fine grained with prismatic microstructure.

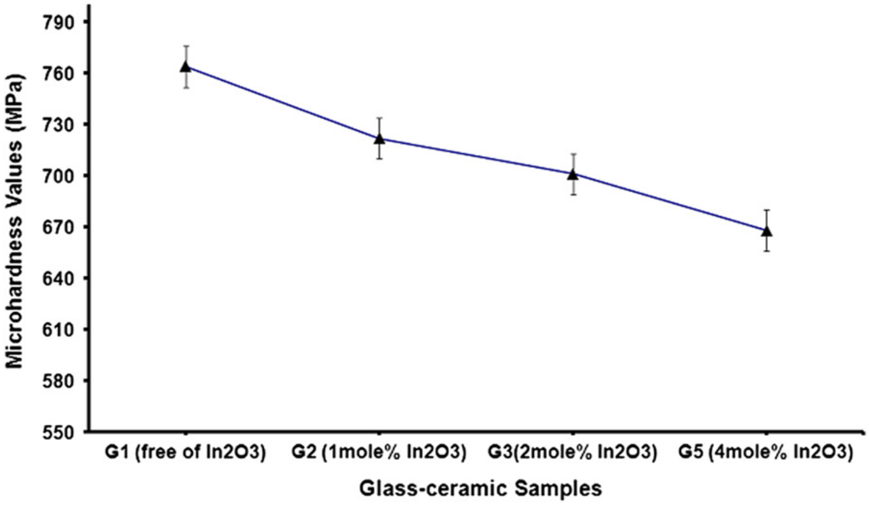

Fig. 4. Microhardness values of the glass-ceramic samples.

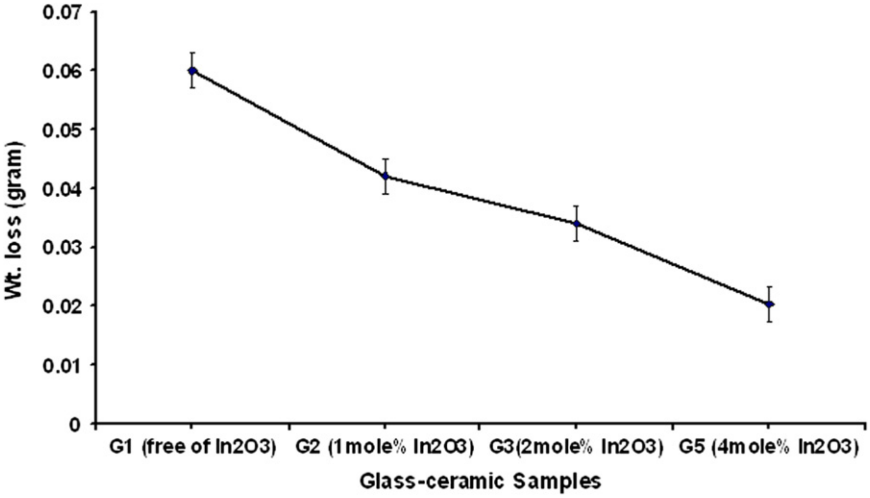

Fig. 5. Chemical stability of the glass-ceramic samples.

4. Discussion

4.1. Crystallization characteristics

The progress of crystallization in the glasses, the type and proportions of the crystalline phases formed were markedly dependent on the variation of the glass oxide constituents and the extent of oxides replacements [11].

The crystallization of the base glass, G_1, had high crystallization tendency upon heat-treatment and the crystallization occurred without great difficulty. This due to the presence of iron oxide which increases the crystallization centers and stimulates the crystallization of the glass during the reheating process [12].

The addition of In_2O_3 instead of Fe_2O_3 in the Al_2O_3-containing glasses increases the temperature at which the nucleation starts. The DTA data (Fig. 1) reveals that the endothermic and exothermic peak temperatures were shifted to higher temperatures by In_2O_3/Fe_2O_3 replacement in the studied glasses. This could be attributed to the role played by In_2O_3 in the glass structure; the field strength of In^{3+} (4.73) is higher than that of Fe^{3+} (3.54) [13]. It is expected, therefore, that the addition of In_2O_3 at the expense of Fe_2O_3 led to the increase of both the coherency of the glass structure and the nucleation temperature of these glasses.

Iron oxide can be present in the glass as ferrous and ferric ions, and their ratio depends upon the glass composition and melting conditions. In silicate glasses, the ferric cation may occupy octahedral FeO_6 and tetrahedral FeO_4 sites [14]. While, the ferrous cations occupy only octahedral sites which decrease by increasing the iron content [15].

The X-ray examination of the crystalline products of the present glasses showed that the crystallization of lithium indium-pyroxene and lithium meta-silicate phases was increased by In_2O_3/Fe_2O_3 replacement, while that of alkali iron-pyroxene and lithium disilicate phases was decreased (Fig. 2, Table 2).

The X-ray diffraction analysis (Fig. 2, Pattern I) revealed that the base glass, G_1, was crystallized to β-eucryptite ss

($LiAlSiO_4$-rich in silica) phase as major crystalline phase together with lithium disilicate—$Li_2Si_2O_5$, lithium iron silicate—$LiFeSi_2O_6$ and lithium metasilicate—Li_2SiO_3 phases. The crystallization of lithium aluminosilicate glasses generally, produces crystalline phases such as β-eucryptite and/or β-spodumene with low expansion coefficients, high thermal stability, and high chemical durability. The properties of a particular crystalline phase of a glass-ceramic may also be modified if the crystal enters into solid solution with another phase [16].

β-Eucryptite is the phase most likely to be formed first even from glasses of stoichiometric spodumene composition, due to the fact that the symmetry of the hexagonal β-eucryptite lattice is closer to the spherically symmetric glass structure than that of the tetragonal β-spodumene [17].

Li_2O exhibits a great affinity to combine with Al_2O_3 and SiO_2 to form lithium aluminosilicate. Based on the petrochemical calculation of normative mineral molecules [18] from the chemical composition, it was observed that, when Al_2O_3 is present it should be first combined with an equivalent amount of Li_2O and SiO_2 to form lithium aluminosilicate (β-eucryptite-silica rich). If there is an excess of Li_2O over Al_2O_3 in molar ratios, it can then combine with silica to form lithium silicate.

The XRD analysis (Fig. 2, Pattern I) reveals that, both lithium disilicate and metasilicate phases were detected. Mishima et al. [19] reported that the lithium metasilicate crystals grew linearly with heating time and the rate of crystal growth increased with temperature. Tulyaganov et al. [20], reported that in Al_2O_3-containing glass-ceramics, the predominant crystallization of lithium disilicate—$Li_2Si_2O_5$ occurs via the precursor lithium metasilicate—Li_2SiO_3 phase.

The $LiFeSi_2O_6$ phase is a new variety of clinopyroxene [21]. The clinopyroxene consists of a group of minerals of variable composition which crystallize fairly readily. These groups of minerals are closely related in crystallographic and other physical properties, as well as in chemical composition. 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], e.g. between diopside ($CaMgSi_2O_6$) and hedenbergite minerals from a continuous chemical series with augite and ferroaugite [$(CaMgFe^{2+})SiO_3$]. The complexity of this group is exhibited by the wide isomorphism of the various elements in the expandable pyroxene:

$$W_{1-p}(X, Y)_{1+p}Z_2O_6$$

where: W = Ca Na; X = Mg, Fe^{2+}, and Mn, Zn, Li; Y = Al, Fe^{3+}, Cr, Ti, In and p = number of ions

The wide range of replacement in the (X, Y) group commonly involving substitution of ions of different charge necessitates compensatory replacement in either the W or Z group, and the replacement must be such that the sum of the charges in the W, X, Y and Z group is 12.

The partial additions of In_2O_3 at the expense of Fe_2O_3 in the base glass (up to 2 mol% i.e. G_2, G_3) led to the crystallization of lithium iron silicate, β-eucryptite ss (as major) and lithium metasilicate phases (Fig. 2, Patterns II and III). While, no In_2O_3-containing phases could be detected. The indium oxide seems to be accommodated in the lithium–iron pyroxene structure and form pyroxene solid solution of the probable formula $Li(Fe,In)Si_2O_6$ as indicated from the shift of d-spacing lines of the XRD characteristics for the $LiFeSi_2O_6$ phase towards higher 2θ values. Glass compositions crystallizing to give solid solutions should be of importance from the point of view of improvement the physical properties of the material [6].

The lithium silicate phase was calculated as lithium disilicate—$Li_2Si_2O_5$ phase. However, the XRD analysis (Fig. 2, Patterns II and III) indicated that, lithium metasilicate phase was detected in appreciable amounts and no lithium disilicate phase could be detected. This may be attributed to the tendency of β-eucryptite to capture $n SiO_2$ in its structure and form β-eucryptite ss phase, rendering the residual glass to be relatively poor in silica i.e. it was relatively unsaturated [23]. Therefore, lithium metasilicate phase could be formed instead of the disilicate phase.

The increasing of In_2O_3 at the expense of Fe_2O_3 in the base glass, i.e. G_4,(up to 3 mol%) led to the crystallization of β-eucryptite ss (major) and lithium metasilicate phases in addition to the formation of lithium indium silicate—$LiInSi_2O_6$ phase, as new product, at the expense of lithium iron silicate phase (Fig. 2, Pattern IV, Table 2). On the basis of the petrochemical calculation into normative mineral molecules [18] from the chemical composition, it was revealed that Li_2O can combine with equivalent amount of In_2O_3 and SiO_2 to form lithium indium silicate—$LiInSi_2O_6$ phase. $LiInSi_2O_6$ phase is one of mineral phases related to the pyroxene family.

On further increase of In_2O_3/Fe_2O_3 replacement i.e. G_5, the crystallization of lithium indium silicate—$LiInSi_2O_6$ phase was increased, instead of lithium iron silicate phase together with β-eucryptite ss (major) and lithium metasilicate phases. However, no Fe_2O_3-containing phases could be detected; this may be attributed to the fact that the iron oxide might accommodate in the lithium–indium pyroxene structure and form pyroxene solid solution of the probable formula $Li(In,Fe)Si_2O_6$.

The scanning electron microscope revealed that the grain microstructures were changed from very fine and tiny to aggregates of prismatic growths on decreasing the iron content in the investigated samples. This is attributed to the fact that the iron is able to change its valence in the glass matrix. A transfer of valence electrons between the ions creates regions of local energy difference, which accelerating the nuclei formation [14].

4.2. Microhardness

The microhardness of material is often equated with its resistance to abrasion or wear and this characteristic is of practical interest since it may determine the resistivity of a material during use and it may also decide the suitability of the material for special applications.

Hardness is not a fundamental physical property of a material but it rather depends on several properties. Its interpretation varies considerably depending on the nature of the material under examination and the method of test under consideration [13]. According to Miska [24] the microhardness of crystallized glasses depends not only on the type of precipitating phases but also on their size, shape, and natural wetting as well on the emergence or absence of internal cracks. However, the degree of crystallinity should be also taken into consideration.

The obtained data revealed that, high microhardness value of the base crystalline glass (free of In_2O_3) is due to the formation of fine grained microstructure (G_1, Fig. 3a). On the other hand, the decreasing effect determined by In_2O_3/Fe_2O_3 replacement in the base glass on the microhardness value of the corresponding crystalline products may be attributed to the formation of fine crystals with aggregates of prismatic-like growths (G_5, Fig. 3c). Henry and Hill [25] reported that the microstructure mostly represents the major influence on the mechanical properties of the glass ceramic materials. The mechanical properties of glass-ceramics, among other variables, depend on volume fraction, grain size, crystal phase and shape of crystals [2].

4.3. Chemical durability

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 crystalline phases formed and the residual glassy matrix [26].

The acid durability of glass-ceramics depends essentially on the nature and content of crystalline phases present, the composition and content of residual glassy phase [13], all of which are controlled by glass composition and applied heat-treatments. Microstructure can also be taken into consideration.

In general, the additions of In_2O_3 at the expense of Fe_2O_3 in the glasses resulted into the improvement of the durability of the corresponding glass-ceramics. This may be attributed to the formation of the durable lithium indium pyroxene phase among the crystallization products instead of lithium iron silicate phase of pyroxene variety.

5. Conclusions

The crystallization characteristics and some physico-chemical properties of the glass-ceramics based on Li_2O–Al_2O_3–Fe_2O_3–SiO_2 system with In_2O_3/Fe_2O_3 replacements were investigated. The addition of In_2O_3 in the glasses led to increase in the structural rigidity and tended to increase both glass transition (Tg) and softening (Ts) temperatures. The presence of iron oxide increased the crystallization centers and the In_2O_3/Fe_2O_3 replacements led to the change of the microstructure from very fine grained texture to prismatic-like growths in the glass-ceramics. Lithium aluminosilicate phases have great affinity to form solid solution with silica. β-eucryptite ss, could be obtained with two pyroxene family phases as lithium iron silicate—$LiFeSi_2O_6$ and lithium indium silicate—$LiInSi_2O_6$ together with lithium meta- and di-silicate phases in the crystallized glasses. The obtained Vicker's microhardness values (764–668 MPa) were decreased by In_2O_3/Fe_2O_3 replacements while the chemical stability of the glass-ceramics improved.

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