CRYSTALLIZATION CHARACTERISTICS OF ALKALI-IRON GERMANATE CONTAINING SILICATE GLASSES

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The crystallization characteristics of the glasses based on stoichiometric composition of diopside (CaMgSi₂O₆)-lithium iron germanate (LiFeGe₂O₆) have been investigated. The effect of the compositional variation of the two pyroxene members CaMgSi₂O₆-LiFeGe₂O₆ on the thermal history of the glasses and type of the solid solution phases formed as well as the resulting microstructure formed by crystallization are traced by differential thermal analysis, X-ray diffraction analysis and scanning electron microscopy. In most cases intense uniform volume crystallization of fine-grained microstructure are achieved by increasing the LiFeGe₂O₆ content at the expense of CaMgSi₂O₆ in the glasses. Varieties of pyroxene ss of the two components are mostly detected by XRD from the high CaO, MgO-containing glasses, however, both LiFeGe₂O₆ and diopside are crystallized in the high iron-GeO₂-containing variety. The object of the present work was to understand the role of the glass oxide constituents in determining the type of the solid solution phases formed and the microstructure of the resulting material.

INTRODUCTION

It is well established that the structure and properties of glasses containing transition metal ions depend critically on the relative proportions of the different valence states of the particular transition metal [1].

The behaviour of iron-containing oxide glasses with heat-treatment to form glass-ceramics has been a subject of considerable importance, especially in determining the magnetic, electric and other properties of the resultant materials [2]. The use of XPS to study the oxidation states of iron in silicate [3], phosphate [4], borate [5] and germanate [1] glasses is well established. It has been found that, in case of silicate, germanate and phosphate glasses, iron exists in both Fe²⁺ and Fe³⁺ oxidation states and that the concentration of Fe³⁺ increases with increasing Fe₂O₃ content.

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 [6]. Germanium dioxide is a strong candidate material for creating new matrices and optical media. Germanium dioxide ability to transmit light in the infrared (IR) region makes it a desirable material for applications in this wavelength region. A need exists for the development of IR waveguiding media; this would be a significant step in the direction of creating applications that employ optical fibers and integrated optics [6].

Glass compositions crystallizing to give solid solutions should be of importance from the point of view of improvement the physical properties of the material [7]. The casting properties of the glass-ceramics are also improved by the presence of a high content of pyroxene phases. Minerals capable of wide isomorphous substitution in their crystal structure and having the necessary physical and chemical characteristics, such as pyroxenes, may form the basis for production of many crystalline and glass-ceramic materials [8].

The purpose of this work is to study the crystallization behaviour, phase relation and the extent of solid solution phases formed by controlling heating of some alkali iron germanium silicate glasses. The role of Fe_2O_3 and GeO_2 in determining the microstructure of the resultant material are also considered.

EXPERIMENTAL

Batch composition

Four glass compositions were calculated to give different proportions of stoichiometric diopside-CaMgSi₂O₆ and lithium iron germanate-LiFeGe₂O₆ molecules. The calculated weight percentage of LiFeGe₂O₆ molecules in the glasses was gradually increased from 10 % up to 50 % at the expense of diopside molecule (CaMgSi₂O₆). Details of the glass oxide constituents are given in table 1.

Glass preparation

The glasses were prepared from purified quartz and reagent grade powders of CaCO₃, MgCO₃, Li₂CO₃, GeO₂ and Fe₂O₃. The batch materials were melted in Pt-2 % Rh crucibles in an electric furnace with SiC heating elements in the temperature range 1350-1450°C for 4 hours. The glass melts were stirred during melting to ensure homogeneity. The melts were cast into discs and then annealed in a muffle furnace at about 500°C for 30 min. to minimize the strain.

Differential thermal analysis

The DTA technique was used to investigate the thermal behaviour of the glasses. DTA was carried out using the computerized Perkin Elmer DTA-7 series under dynamic N_2 purging gas atmosphere. About 70 mg of the powdered samples, which were sieved using B.S. sieves to obtain grains, passes through a 100-mesh sieve. Heating rate of 10°C/min. and corundum as a reference material were maintained for all the DTA runs.

Heat-treatment

The glasses were heated according to the DTA data. At the endothermic temperature of each glass composition, the glass sample was kept for 5 hrs and then was raised up to the exothermic peak temperature recorded on the DTA of each glass for 10 hr duration. Identification of crystal phases precipitating due to the course of crystallization was conducted by the X-ray diffraction analysis. The X-ray diffraction patterns were obtained by using a Philips-type diffraction (P.W.1730) with Ni-filtered Cu-k α radiation. The crystallization characteristics and internal microstructure of the fractured surfaces of the crystalline samples, coated with gold spray, were examined by scanning electron microscopy using a Jeol JSM-T20 scanning electron microscope.

RESULTS

Differential thermal analysis

The DTA curves of the glasses are shown in figure 1. Endothermic effects in the temperature range 576-657°C were recorded on the DTA of the glasses. These endothermic peak onsets correspond to the glass transition temperatures. Various exothermic effects at 693-877°C temperature range, which indicate the crystallization characteristics of the glasses, are also recorded.

Appearance of crystallized glasses

All the glasses changed colour upon heating. The glass of 10 % LiFeGe₂O₆ molecule content (G₁) turned yellowish brown, the 20 % glass turned brown on the surface and green in the bulk (G₂). As the iron content was increased (i.e., at higher LiFeGe₂O₆ molecule content) the samples of G₃ and G₄ turned deep brown.

Crystallization characteristics

The partial replacement of LiFeGe₂O₆ at the expense of diopside (CaMgSi₂O₆) stimulated the crystallization of the glass during the heat-treatment and markedly decreased the remaining glassy matrix. The DTA traces (figure 1) revealed that both of endothermic and exo-thermic peak temperatures were shifted to lower values by increasing the percentage of LiFeGe₂O₆ content. Experimentally, the crystallization tendency of the studied glasses was greatly increased by increasing the LiFeGe₂O₆ content.

Table 1. Theoretical phase constitution and the respective oxide components of the glasses

Glass	Theoretical phase	e molecule (wt.%)	Oxide components (wt.%)					
No.	LiFeGe ₂ O ₆	CaMgSi ₂ O ₆	CaO	MgO	SiO ₂	Li ₂ O	Fe_2O_3	GeO ₂
1	10	90	23.31	16.75	49.94	0.49	2.63	6.88
2	20	80	20.72	14.89	44.39	0.98	5.26	13.76
3	30	70	18.13	13.03	38.84	1.47	7.89	20.64
4	50	50	12.95	9.31	27.75	2.45	13.14	34.41



Figure 1. DTA thermograms of the investigated glasses.

The Scanning electron micrographs (figures 2-5) show the effect of increasing LiFeGe₂O₆ contents on the grain microstructure of the materials. Iron oxide acts as a crystallization catalyst, accelerates the crystallization process and increases the rate of nucleation. SEM micrograph of fractured surface of G_1 , clearly showed that volume crystallization of fibrous pyroxene solid solution was developed (figure 2). In the G_2 volume crystallization of prismatic like growths was formed (figure 3). On increasing the LiFeGe₂O₆ content in the material, volume crystallization of fibrous growths was developed in the crystalline glass G_3 (figure 4). At high content of LiFeGe₂O₆ (up to 50 %) tiny aggregates intergrowths with fine fibrous growths were developed (G_4 , figure 5)



Figure 2. SEM micrograph of fractured surface of G_1 crystallized at 660°C/5hr - 875°C/10 hr showing volume crystallization of fibrous growths of pyroxene solid solution 1. Magnification 1000×.



Figure 4. SEM micrograph of fractured surface of G_3 crystallized at 615°C/5hr - 760°C/10 hr showing volume crystallization of fine fibrous growths of pyroxene solid solution 3. Magnification 1000×.



Figure 3. SEM micrograph of fractured surface of G_2 crystallized at 650°C/5hr - 820°C/10 hr showing numerous prismatic growths of pyroxene solid solution 2. Magnification 1000×.



Figure 5. SEM micrograph of fractured surface of G_4 crystallized at 580°C/5hr - 700°C/10 hr showing tiny aggregates and fine fibrous growths of diopside and lithium iron germanate phases. Magnification 1000×.

Crystal phases formed and solid solution developed

The phases developed in the glasses (G_1 - G_4) over the investigated 675 - 850°C temperature range as indicated by the x-ray diffraction analysis (figures 6-7, table 2), were varieties of iron pyroxene solid solution of diopside and lithium iron germanate phases. The nature and concentration of the various phases developed were a function of the LiFeGe₂O₆/CaMgSi₂O₆ ratio present in the glasses and the condition of the heat-treatment applied.

At low LiFeGe₂O₆/CaMgSi₂O₆ (i.e., 10 / 90), G₁, the X-ray diffraction analysis (figure 6, pattern I) revealed that the crystallization at low temperature (i.e., $660^{\circ}C/5$ hr - $800^{\circ}C/10$ hr) developed only pyroxene solid solution phase 1 of diopsidic type. The *d*-spacing lines detected are greatly similar to that of diopside phase (Card No. 19-239). At higher temperature (i.e., $660^{\circ}C/5$ hr - $875^{\circ}C/10$ hr) the same crystalline phase of diopside nature appears with increasing the d-spacing line intensities, as indicted by the XRD (pattern II).

On increasing the LiFeGe₂O₆/CaMgSi₂O₆ ratio (i.e., 20/80), G₂, the XRD analysis (pattern III) revealed that the crystallization of the glass at 650° C/5 hr - 725° C/10 hr led to the formation of pyroxene ss phase 2 of diopside type. On heating the glass at 750° C/10 hr, 820°C/10 hr and 850°C/10 hr, the same type of solid phase could be detected with increasing the intensity of their characteristic d-spacing lines (figure 6, patterns III, IV, V & VI).

For glass G_3 with higher LiFeGe₂O₆/CaMgSi₂O₆ ratio (30/70) crystallized at 615°C/5 hr - 675°C/10 hr, the XRD analysis (figure 7, pattern I) revealed that the d-spacing lines of the solid solution phase formed were greatly identical to that of the diopsidic-augite solid solution pyroxene phase 3 (lines 4.69, 3.00, 2.95, 2.89, 2.56, 2.54, 2.51). However, no other phases could be traced by crystallization at high temperature (figure 7, patterns II & III).

Table 2. The crystalline phases developed in the studied glasses.

Glass No.	Heat-treatment (°C/hr)	Phases developed	
G ₁	650/5 - 800/10	Pyroxene ss 1	
G ₂	<u>660/5 - 875/10</u> 650/5 - 725/10	Pyroxene ss 2	
	650/5 - 750/10 650/5 - 800/10		
	650/5 - 850/10		
G ₃	615/5 - 675/10 615/5 - 760/10	Pyroxene ss 3 (Diopsidic-augite)	
G ₄	<u>615/5 - 850/10</u> <u>580/5 - 700/10</u>	CaMgSi ₂ O ₆ , LiFeGe ₂ O ₆	
	580/5 - 800/10 580/5 - 850/10		

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With the LiFeGe₂O₆/CaMgSi₂O₆ ratio equals unity i.e., G₄, crystallized at different temperatures e.g. 580° C/5 hr - 700°C/10 hr (pattern IV), 580° C/5 hr - 800° C/10 hr (pattern V) and 580° C/5 hr - 850° C/10 hr (pattern VI), the XRD analysis clearly showed that both lithium iron germanate phase (LiFeGe₂O₆, lines 6.46, 4.74, 4.54, 4.39, 4.00, 3.03, 2.73, card No. 26-1439) together with diopside phase were developed. The intensities of the d-spacing lines characteristic of both phases were increased by increasing the temperature as indicated from the XRD (figure 7, patterns IV, V & VI).

DISCUSSION

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 [9]. Kolesova et al [10] showed that GeO₂ can combine with SiO₂ to form solid solutions. The concentration of SiO₂ in the solution is 60-70 mol.%. Urnes [11] proved that Ge replaced Si isostructurally in lithium aluminium germanosilicate glasses. Monovalent cation, such as Li⁺ may be incorporated in the pyroxene structure together with trivalent cations like Fe³⁺ in the form of isomorphous phase like LiFe³⁺Ge₂O₆ [12].

The addition of alkali oxide to GeO₂ produces changes in germanate network which have been interpreted as the formation of 6-fold coordinated germanate polyhedra $[Ge^{4+}(GeO_3)_3]^{2-}$, which are charge balanced by alkali oxide [1, 13]. EXAFS and X-ray diffraction studies show an increase in Ge-O bond length and coordination number up to ~20 mole % Alkali oxide, after which a constant value for all higher concentrations could be obtained [1]. The combined presence of Li_2O_1 , Fe₂O₃ and GeO₂ are more effective than CaO and MgO in inducing crystallization of the glasses. Lithium ions are known to reduce the viscosity of glass (more so than Ca²⁺ and Mg²⁺ ions); therefore, the diffusion of the different ions of the glass during the crystallization process will markedly increase [14]. The efficiency of Li₂O in inducing homogeneous crystallization may be attributed to the combination of high mobility and high field strength of the Li⁺ ion. On the same time the increase of the percentage of GeO_2 at the expense of SiO_2 leads to increase the number of non-bridging oxygens (NBO) this was due to the fact that Ge-O bond is weaker than the Si-O bond [6]. And this can explain the ease of crystallization process of glasses by increasing the amount of lithium iron germanate at the expense of calcium magnesium silicate as indicated by the DTA data.

The change in nucleation rate is indicated by increasing the crystallization centers in the glass, as shown by SEM of the samples with different iron content nucleated for the same time, and is evidence that iron oxide favours nucleation. Salman et al., [15] pointed out that the presence of iron oxide increases the crystallization centers and stimulates the crystallization of the glass during the reheating process giving rise volume crystallization of medium to fine grained textures. By Scanning electron microscope it is clear that the grain microstructures were changed from fine fibrous, prismatic to tiny growths on increasing the iron content in the investigated samples. This is attributed to the fact that the iron is able to change its valency in glass matrix [16]. A transfer of valence electrons between the ions creates regions of local energy difference, thus accelerating the nuclei formation. Salman et al., [17] revealed that 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.



Figure 6. XRD analysis of crystallized glasses G_1 and G_2 heated at different temperatures.

Iron oxide can be present in the glass as ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, and their ratio depends upon the glass composition and melting conditions. In silicate glasses, the ferric cations may occupy octahedral FeO₆ and tetrahedral FeO_4 sites [16], while the ferrous cations occupy only octahedral sites which decrease by increasing the iron content [18]. The presence of an appreciable amount of Li₂O together with Fe₂O₃ in the present glasses greatly favour the formation of non-bridging oxygen atoms. The high concentration of non-bridging oxygen atoms in silicate glass will favour Fe²⁺ in the network-forming position as Fe²⁺O₄²⁻ [19]. As the number of non-bridging oxygen atoms was greatly increased, the Fe²⁺ ions were oxidized to Fe³⁺, a large percentage of which would favour network forming position as Fe³⁺O₄.



Figure 7. XRD analysis of crystallized glasses G_3 and G_4 heated at different temperatures.

Information relating to the redox state of iron in a series of alkali germanate glasses has been obtained from the X-ray photoelectron spectroscopy (XPS) [1]. Mekki et al., [1] indicted that oxygens in Ge-O-Fe²⁺ and Ge-O-Fe³⁺ sites both contributed to the non-bridging oxygens (NBO) signal possibly indicated that both Fe²⁺ and Fe³⁺ behave as network modifiers, but glass forming ability and physical properties are more typical of intermediate oxides.

Pyroxene consists of a group of minerals of variable composition, which crystallize fairly readily. They are closely related in crystallographic and other physical properties, as well as in chemical composition [20].

A wide variety of ionic substitutions occurs in the members of the pyroxene group, and there is complete replacement between some of the group components [15], e.g., between diopside-CaMgSi₂O₆ and hedenbergite-CaFe²⁺Si₂O₆ minerals which form a continuous chemical series with augite and ferroaugite (CaMgFe)SiO₃. A great extent of solid solution could be formed also between the two members diopside and LiFeSi₂O₆ [17]. Lithium containing pyroxenes are very rare in nature. Lithium iron pyroxene was described by Salman and coworkers [15, 17, 21& 22] as LiFe³⁺Si₂O₆ among the crystallization products of lithium silicate, lithium borosilicate, calcium lithium magnesium silicate and calcium lithium magnesium aluminium silicate with addition of iron oxide. He showed that iron oxide prefers to be accommodated in the lithium silicate structure rather than lithium borate [15].

The clinopyroxene have a wide range of chemical composition. The complexity of this group is exhibited by the wide isomorphism of the various elements in the expandable pyroxene formula:

$$W_{1-p}(x, y)_{1+p} Z_2O_6$$

where W = Ca, Na; x= Mg, Fe²⁺, Mn, Zn, Li; y = Al³⁺, Fe³⁺, Cr, Ti; Z= Si, Al, Fe³⁺ and p = number of ions [20].

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

The pyroxenes LiMGe₂O₆, where, M= Fe, Al, Ga, Cr; and NaMGe₂O₆, where, M= Fe, Cr, were prepared and crystallized in the monoclinic modification. However, the LiMGe₂O₆ pyroxenes are easier to synthesize than the corresponding Na compounds [12].

The present study revealed that the crystallization of the investigated glasses (G_1-G_4) generally developed pyroxene ss, diopside and lithium iron germanate phases, this is greatly dependent on the glass oxide components rather than the heat-treatment conditions.

In case of G_1 (with 10 % LiFeGe₂O₆) crystallized at 875°C/10 hr, the XRD analysis detected only the

d-spacing lines which were very similar to that of diopside. Salman et al. [17, 21], showed that diopside can accommodate considerable amounts of LiFeSi₂O₆ phase in its structure forming a series of pyroxene solid solutions up to 50 % LiFeSi₂O₆. It seems therefore, likely that during the crystallization of G₁ all the components of LiFeGe₂O₆ pyroxene phase are accommodated in the diopside structure, where in the presence of such structure as a host crystal lattice, it is assumed that the Li⁺ and Fe³⁺ in eightfold and sixfold coordination replace Ca²⁺ and Mg²⁺, respectively [17]. Also, Ge⁴⁺ replaces Si⁴⁺ isostructurally in fourfold coordination [6, 11]. The resulting pyroxene solid solution 1 phase had probably the following formula:

(Ca_{0.93}, Mg_{0.07})₁ (Mg_{0.86}, Fe_{0.07}, Li_{0.07})₁ (Ge_{0.07}, Si_{0.93})₂O₆

On increasing the lithium iron germanate component up to 20 % i.e., G_2 , the component of LiFeGe₂O₆ seemed also to be incorporated in the diopside structure giving rise to the probable pyroxene formula (Pyroxene ss 2):

$$(Ca_{0.85}, Mg_{0.15})_1 (Mg_{0.7}, Fe_{0.15}, Li_{0.15})_1 (Ge_{0.15}, Si_{0.85})_2O_6$$

On the same basis, the results of the crystallizing phase in G_3 (with 30 % LiFeGe₂O₆) can be explained, where only one pyroxene solid solution 3 phase which is greatly similar to the diopsidic augite nature of the probable formula:

$$(Ca_{0.77}, Mg_{0.23})_1 (Mg_{0.54}, Fe_{0.23}, Li_{0.23})_1 (Ge_{0.23}, Si_{0.77})_2O_6$$

At 50 % LiFeGe₂O₆ i.e., G₄, lithium iron germanate-LiFeGe₂O₆ together with diopside-CaMgSi₂O₆ pyroxene phases were developed. The LiFeGe₂O₆ phase is called a lithium germanate pyroxene which is crystallized in a monoclinic modification of clinoenstatite type, it is a low temperature form, reversible phase transforms to a high temperature form at about 1050°C [12].

CONCLUSIONS

Diopside can accommodate considerable amounts of LiFeGe₂O₆ phase in its structure forming series of pyroxene solid solutions. Lithium iron germanate enhanced the crystallization tendency of the glasses. The characteristic d-spacing lines of iron pyroxene solid solution phases vary with the gradual increase in lithium iron germanate contents in the glass and led to the formation of fine grain microstructure. The state of iron, its coordination and concentration in the glasses mainly determined the nature of the phases formed especially at high LiFeGe₂O₆ content. However, when LiFeGe₂O₆/ /CaMgSi₂O₆ ratio equals unity the two phases appear together i.e., the diopside together with lithium iron germanate phases could be crystallized.

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KRYSTALIZACE SILIKÁTOVÝCH SKEL S OBSAHEM GERMANIČITANU LITHNO-ŽELEZITÉHO

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Byla studována krystalizace skel se stechimetrií odpovídající směsi diopsidu (CaMgSi₂O₆) a germaničitanu lithnoželezitého (LiFeGe₂O₆). Vliv změny poměru těchto dvou koncových členů pyroxenové řady, teplotní historie, typ vytvořených tuhých roztoků a rovněž mikrostruktury vzniklé krystalizací byly studovány diferenční termální analýzou, RTG difrakcí a řádkovací elektronovou mikroskopií. Ve většině případů bylo dosaženo stejnoměrné objemové krystalizace s jemnou mikrostrukturou při rostoucím obsahu LeFeGe2O6 ve sklech. Typy pyroxenových tuhých roztoků LiFeGe2O6 a CaMgSi₂O₆ jsou většinou detekovatelné RTG difrakcí ve sklech s vysokým obsahem CaO a MgO, a jak LiFeGe₂O₆ tak diopsid krystalují ve formách s vysokým obsahem Fe a GeO2. Předmětem práce je pochopení úlohy složek skel při určení typu vytvořených tuhých roztoků a mikrostruktury vzniklého materiálu.