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Formation of glass-ceramic materials based on pyroxene solid solution—fluorapatite phases and their thermal expansion properties

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Abstract

The crystallization characteristics of some calcia–magnesia–alumino–silicate glasses containing P_2O_5 and CaF_2 have been investigated by differential thermal analysis (DTA), X-ray analysis (XRD) and scanning electron microscope (SEM).

Pyroxene solid solution and fluorapatite were the main phases crystallized by the controlled heat treatment of the glasses. The crystallization tendency of glasses was improved by increasing ($CaO + P_2O_5 + CaF_2$) at the expense of ($Al_2O_3 + SiO_2$) and also improved by adding minor additives of ($Na_2O + B_2O_3 + TiO_2$). Pyroxene solid solution is diopside-Ca-Tschermak's type solid solution.

There was no solid solution phase formed between pyroxene and fluorapatite phase, therefore fluorapatite phase was increased by increasing its components in the glasses.

Fine microstructure of fibrous growth was developed by increasing the fluorapatite in the glass-ceramic materials obtained.

The thermal expansion coefficients (α-values) of the glasses and glass-ceramics were determined. The α-values of the studied glasses ranged between 78×10^{-7} and $99 \times 10^{-7}\ {}^\circ C^{-1}$ in the (25–500 °C) temperature range and those of crystalline products ranged from 66×10^{-7} to $100 \times 10^{-7}\ {}^\circ C^{-1}$ in the (25–700 °C) temperature range. The data of the glasses were correlated to the internal structure of the glasses, nature and role played by glass forming cations. However, the expansivity of the crystalline glasses was mainly attributed to different factors including the crystalline phases formed and residual glassy phase.

Keywords: C. Thermal expansion; D. Glass; D. Glass-ceramics; Crystallization; Pyroxene solid solutions; Fluorapatite

1. Introduction

Glass-ceramics prepared by controlled nucleation and crystallization of glasses can be used in widely different applications depending on their microstructure, mechanical, physical and chemical properties. These properties are changing with composition and heat-treatment conditions [1], which can usually be tailored to produce glass-ceramics of specific properties.

Different varieties of glass-ceramics have been developed during the last years for biomedical and dental applications [2]. Natural bones and teeth are multiphase materials, their combination properties probably can be simulated only by multiphase materials [3]. There is a considerable interest in fluorapatite, hydroxyapatite or fluoride-substituted hydroxyapatite based glass-ceramics for medical applications [1]. Apatite structures $Ca_{10}(PO_4)_6F_x(OH)_{2-x}$ (where [x] is the fraction of OH^- replacement by F^-) are the basic composition for a variety of important bioactive ceramics [4,5].

A part of the glass-ceramics developed in the last years for biomedical applications are based on the CaO–MgO–P_2O_5–SiO_2 system [3,6]. Small amounts of other components like CaF_2 [7] or TiO_2 [8] have been added to the initial composition to facilitate the process. Yoshida and Nakagawa [9] prepared high strength glass-ceramics containing apatite, tricalcium phosphate and prosthetic material.

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The system $Ca_5(PO_4)_3F$–$CaMgSi_2O_6$ provides fundamental knowledge for the development of new kinds of ceramics, glasses and bioglass–ceramics. Furthermore, the high temperature relationships between apatite and diopside are very important from the geoscience point of view, since the components of the binary system are widespread rock forming minerals [10]. Pyroxene may form the basis for productions of many melt casts and ceramic-like materials [11].

It is claimed that the $Ca_5(PO_4)_3F$–$CaMgSi_2O_6$ glass-ceramics show a combination of high mechanical strength, a good chemical resistance and a good biocompatibility. Such materials are used as artificial implants in orthopedic surgery [12].

The aim of the present work was to focus on the crystallization characteristics, solid solutions formed and the microstructure of glass-ceramics based on CaO–MgO–Al_2O_3–SiO_2–P_2O_5–CaF_2 system with minor additions of Na_2O, B_2O_3 and TiO_2 with the object to provide fundamental knowledge for the type of multiphase solid solutions and the microstructure formed in the glass-ceramic materials and their thermal expansion property.

2. Experimental techniques

2.1. Glass composition and preparation

In the present work, six glass compositions based on the CaO–Al_2O_3–MgO–P_2O_5–CaF_2–SiO_2 system were investigated. The base glass composition (i.e., G_1) was modified by adding ($CaO + P_2O_5 + CaF_2$) contents instead of ($Al_2O_3 + SiO_2$) (on mole basis). Na_2O, B_2O_3 and TiO_2 were also added to the batch as minor additives in amounts of 2.0, 0.5 and 1.0 g, respectively, over 100 g glass oxides, i.e., G_1a–G_5a. The chemical compositions of the glasses prepared (in mol%) are given in Table 1.

Appropriate weight of reagent grade powders of $CaCO_3$, SiO_2 (quartz), $MgCO_3$, $Al(OH)_3$, $NH_4H_2PO_4$, CaF_2, Na_2CO_3, H_3BO_3 and TiO_2 were thoroughly mixed and melted in Al_2O_3 crucible in an electric furnace with SiC heating elements at 1450–1550 °C for 4 h. Melting was continued until clear homogeneous melt was obtained; this was achieved by swirling the melt several times at about 30-min intervals. The melt was cast into rods and as buttons, which were then properly annealed in a muffle furnace at 550 °C to minimize the strain.

2.2. Differential thermal analysis (DTA)

The thermal behaviour of the finely powdered glass sample was examined using a NETZSCH Geratebau GmbH Sleb Bestell-Nr. 348, 472 C. The powdered sample was heated in Pt holder against another Pt holder containing $\propto$-Al_2O_3 as a standard material. A uniform heating rate of 10 °C min^{-1} was adopted up to the appropriate temperature of the glasses. The results obtained were used as a guide to determine the temperatures for the heat treatment applied to induce crystallization.

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, and was then followed by another thermal treatment at the exothermic peak temperature for 10 h.

2.4. Textural and structural characterization

Identification of crystal phases precipitating during the course of crystallization was done by examining X-ray diffraction patterns obtained by using Philips diffractometer (P.W. 1730) with Ni-filtered Cu Kα radiation. The crystallization characteristics and internal microstructures of the resultant materials were examined by using scanning electron microscopy (SEM), where electron micrographs of representative samples were obtained using a Joel, JSM-T20 scanning electron microscope.

2.5. Thermal expansion measurements

The coefficients of thermal expansion of the investigated samples were carried out on 1.5–2.0-cm long rods

Table 1
The glass oxide constituents (mol%)

Glass no.	Oxides in mol%						Mole ratio of ($CaO + P_2O_5 + CaF_2$)/($Al_2O_3 + SiO_2$)
	CaO	P_2O_5	CaF_2	MgO	Al_2O_3	SiO_2	
G_1	26.65	–	–	20.05	6.63	46.67	0.50
G_1a	26.65	–	–	20.05	6.63	46.67	0.50
G_2a	27.96	0.86	0.29	20.05	5.32	45.52	0.57
G_3a	29.30	1.73	0.57	20.05	4.00	44.35	0.66
G_4a	30.62	2.6	0.87	20.05	2.67	43.19	0.80
G_5a	31.98	3.47	1.16	20.05	1.34	42.00	0.85

using Linseis L76/1250 automatic recording multiplier Dilatometer with a heating rate of 5 °C/min. The linear thermal expansion coefficient was automatically calculated using the general equation:

$$\alpha = \frac{\Delta L}{L}\frac{1}{\Delta T}$$

where ΔL is the increase in length, ΔT is the temperature interval over which the sample is heated and L is the original length of the specimen.

3. Results

3.1. *Differential thermal analysis*

The DTA curves of the glasses are shown in Fig. 1. Endothermic reactions at the temperature range of 705–775 °C were recorded on the DTA of the glasses. These endothermic effects are attributed to the glass transition (T_g), at which the atoms begin to rearrange themselves in preliminary structural elements prior to crystallization. Various exothermic effects at 926–985 °C indicating crystallization reaction in the glasses were also recorded. The endothermic dips as well as the onset of crystallization are shifted to lower temperatures with increasing ($CaO + P_2O_5 + CaF_2$) at the expense of ($Al_2O_3 + SiO_2$). Also, both the endothermic dip and exothermic peak temperatures were shifted to lower values (e.g., G_1a) by the addition of ($Na_2O + B_2O_3 + TiO_2$) as shown from Fig. 1.

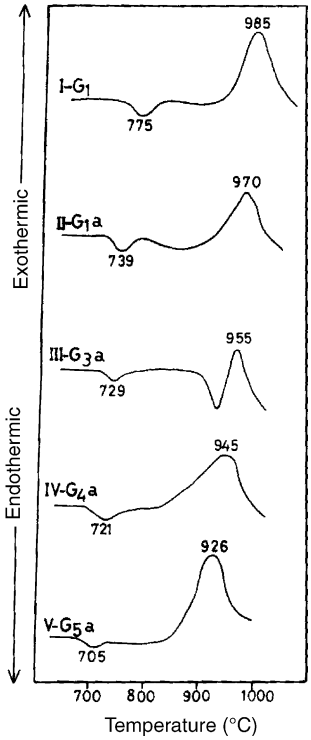

Fig. 1. DTA data of the investigated glasses.

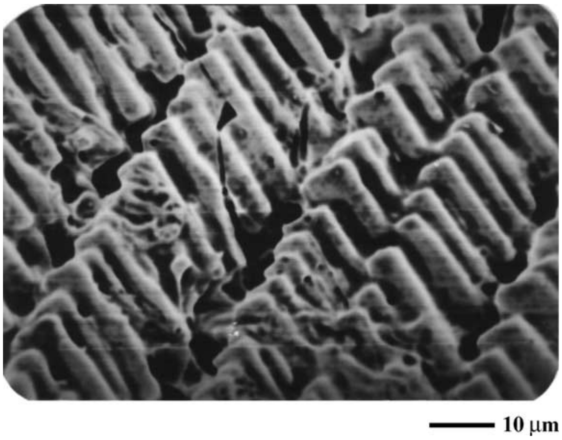

Fig. 2. SEM micrograph of fractured surface of G_1a crystallized at 740 °C/5 h–970 °C/10 h showing skeletal-like growths of pyroxene solid solution (X = 1500).

3.2. *Crystallization characteristics*

The DTA (Fig. 1) revealed that the temperatures of the endotherms and the exotherms of the glasses were decreased by increasing of ($CaO + P_2O_5 + CaF_2$) instead of ($Al_2O_3 + SiO_2$), i.e., a lower energy is needed to induce crystallization in such glasses. XRD analysis revealed that the addition of ($Na_2O + B_2O_3 + TiO_2$) as minor additives enhanced also the crystallization in the glasses, i.e., the crystallization tendency of the glasses was greatly improved by adding these additives.

SEM micrographs of the fractured surfaces of the crystallizing glasses G_1a and G_4a (Figs. 2 and 3) showed that skeletal-like growths were developed in G_1a (base glass, Fig. 2), while fine fibrous microstructure was formed by increasing the amount of ($CaO + P_2O_5 + CaF_2$), G_4a, Fig. 3.

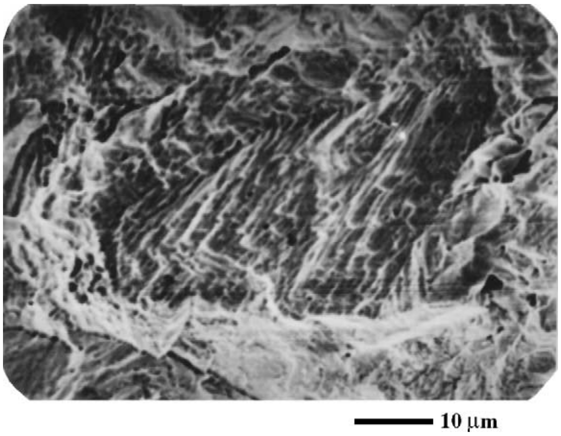

Fig. 3. SEM micrograph of fractured surface of G_4a crystallized at 720 °C/5 h–945 °C/10 h showing fine fibrous-like growths of pyroxene solid solution and fluorapatite phases (X = 1500).

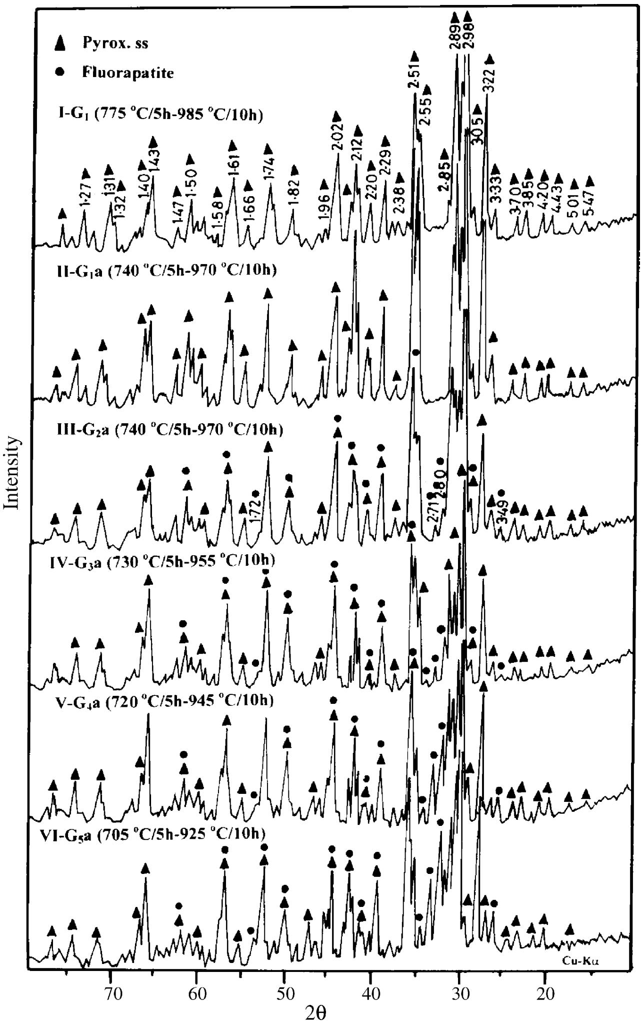

Fig. 4. XRD analysis of the crystallized glasses heated at different temperatures.

3.3. Crystal phases and solid solution developed

Pyroxene solid solution of diopsidic type and fluorapatite phases were detected by the X-ray diffractogramm (Fig. 4, Table 2). X-ray diffraction analysis (Fig. 4, pattern I) revealed that predominant aluminous pyroxene solid solution (lines 3.22, 2.98, 2.94, 2.89, 2.55, 2.53, 2.50) was developed by heating G_1 at 775 °C/5 h–985 °C/10 h.

The pyroxene solid solution phase amount was greatly increased by the addition of the minor additives (pattern II). However, when adding ($CaO + P_2O_5 + CaF_2$) (i.e. G_2a) minor amount of fluorapatite phase–$Ca_5(PO_4)_3F$–(lines 3.05, 2.80, 2071, card no., 15–876) was also detected (pattern III). On further addition of ($CaO + P_2O_5 + CaF_2$) instead of ($Al_2O_3 + SiO_2$) up to a ratio of 0.85 the amount of fluorapatite phase increases on G_3, G_4 and G_5 as shown from the diffractogramm (Fig. 4).

Fine microstructure of fibrous-like growths was developed by increasing the fluorapatite in the glass-ceramics obtained.

3.4. Thermal expansion

The data obtained clearly indicated that the thermal expansion coefficients (i.e., α-values) were increased by addition of ($CaO + P_2O_5 + CaF_2$) instead of ($Al_2O_3 + SiO_2$). The T_g and T_s temperature values of the glasses were decreased (Table 3, Fig. 5).

Generally, the addition of ($B_2O_3 + Na_2O + TiO_2$) as minor additives increased the expansion coefficient values of the studied glasses and also decreased both the T_g and T_s values as compared with those free of them, Table 3.

The present results also revealed that the addition of ($CaO + P_2O_5 + CaF_2$) instead of ($Al_2O_3 + SiO_2$) increased the expansion coefficients of the crystalline materials (Table 3, Fig. 6).

It should be mentioned that the presence of the minor additives in the glasses generally increased the α-values of the corresponding glass-ceramics, Table 3.

4. Discussion

The present results revealed that the endothermic temperatures (T_g) and the crystallization peak temperatures were shifted to lower values by adding the ($CaO + P_2O_5 + CaF_2$). This can be explained on the basis that the temperature of the glass transition was reduced with increasing the P_2O_5 and CaF_2 content in the glasses [2]. The CaF_2 was more effective in this sense. The dominant effect with fluorite is due to the fluorine rather than the calcium and it is thought that fluorine replaces bridging oxygen in the glass structure by non-bridging fluorine. Fluorine, therefore, serves to disrupt the glass network. Increasing the phosphate content, generally, reduces the glass transition temperature, which is consistent with

Table 2
Phases developed after heat treatment

Glass no.	Heat treatment (°C/h)	Phases developed arranged according to their abundance
G_1	775/5–985/10	Pyroxene solid solution
G_1a	740/5–970/10	Pyroxene solid solution (increase)
G_2a	740/5–970/10	Pyroxene solid solution + fluorapatite (minor)
G_3a	730/5–955/10	Pyroxene solid solution + fluorapatite (little)
G_4a	720/5–945/10	Pyroxene solid solution + fluorapatite (increase)
G_5a	705/5–925/10	Pyroxene solid solution + fluorapatite (increase)

Table 3
The thermal expansion coefficient values of various investigated glasses and their corresponding crystalline products

Glass no.	*R	Expansion coefficient $\times 10^{-7}$ °C^{-1}					T_g	T_s	Phases developed
		25–300	25–400	25–500	25–600	25–700			
G_1	0.5	78	81	81	–	–	705	733	Amorphous
		66	67	69	72	79	–	–	Pyrox. ss
G_1a	0.5	83	85	85	–	–	679	707	Amorphous
		76	80	81	83	85	–	–	Pyrox. ss
G_2a	0.57	85	88	89	–	–	671	699	Amorphous
		80	82	83	85	87	–	–	Pyrox. ss + FA
G_3a	0.66	90	92	93	–	–	662	690	Amorphous
		83	87	89	90	92	–	–	Pyrox. ss + FA
G_4a	0.80	92	97	98	–	–	659	684	Amorphous
		87	88	89	91	93	–	–	Pyrox. ss + FA
G_5a	0.85	96	98	99	–	–	650	672	Amorphous
		91	95	95	98	100	–	–	Pyrox. ss + FA

Pyrox. ss, pyroxene solid solution; FA, fluorapatite.

* R = ($CaO + P_2O_5 + CaF_2$)/($Al_2O_3 + SiO_2$) mole ratio.

the weaker phosphorous–oxygen bond strength relative to the silicon–oxygen and aluminium–oxygen bond strengths and also the lower transition temperature found for the phosphate glasses [13]. Furthermore, the fluorine content of the glass generally enhances amorphous phase separation, leading to bulk crystal nucleation. It may be concluded therefore that on increasing the ($CaO + P_2O_5 + CaF_2$)/($Al_2O_3 + SiO_2$) ratios may enhance the crystallization characteristics of the present glasses. Bulk crystal nucleation is a prerequisite for a successful castable glass-ceramic [14]. The addition of ($Na_2O + B_2O_3 + TiO_2$) as minor additives also relieves the rigidity of the glass structure and results in facilitating the melting process and increasing the crystallization tendency of the glasses.

It is well known that the 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 [15].

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

A wide variety of ionic substitutions occur in the members of the pyroxene group and there is a complete replacement between some of the group components [16].

The clinopyroxenes 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^{2+}, Fe^{2+}, Mn, Zn, Li, . . .; Y = Al, Fe^{3+}, Cr, Ti, . . . and Z = Si, Al, Fe, . . ., $P \approx 1$.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 charges in the W, X, Y and Z group is 12 [16].

XRD analysis revealed that only predominant pyroxene solid solution phase was crystallized from the base glass. Theoretically, on the basis of the petrochemical calculation of the chemical composition into normative mineral molecules [17] diopside ($CaMgSi_2O_6$) and Ca-Tschermak's

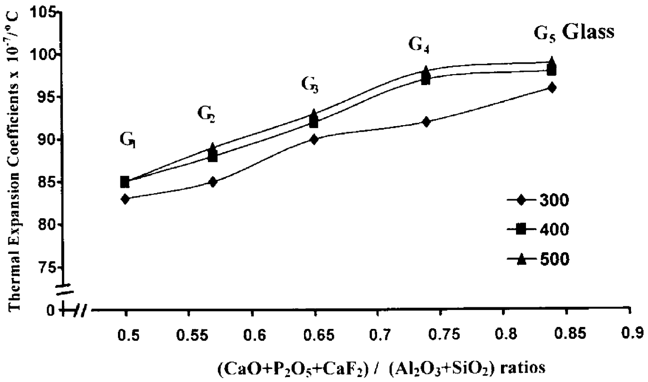

Fig. 5. Thermal expansion coefficients of glass samples with various ($CaO + P_2O_5 + CaF_2$)/($Al_2O_3 + SiO_2$) replacement ratios.

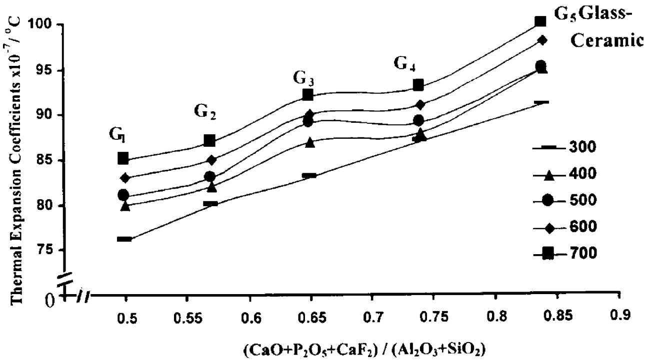

Fig. 6. Thermal expansion coefficients of glass-ceramic samples with various ($CaO + P_2O_5 + CaF_2$)/($Al_2O_3 + SiO_2$) replacement ratios.

($CaAl_2SiO_6$) phases could be formed from the base glass composition. It is assumed therefore that there is a preferential tendency for diopside to capture Ca-Tschermak in its structure and these finding results are in a good agreement with those reported by Sakata [18] who determined the limit of the isomorphous substitution of Tschermak's component $CaAl_2SiO_6$ in diopside—$CaMgSi_2O_6$ as 40 mol% which corresponds to 18.8 mol% of Al_2O_3. Omar et al. [19] showed that complex pyroxenes containing up to 48% of the $CaAl_2SiO_6$ component under non-equilibrium conditions of crystallization could be obtained. Ca-Tschermak is a pyroxene phase [20]. The present results revealed that diopsidic pyroxene contains 33.33% of Ca-Tschermak' components in its structure which corresponds to 6.63 mol% of Al_2O_3. The amount of aluminium sharing in the pyroxene structure is dependent upon the original composition of the glass and the crystallization parameters [19]. There is no crystalline aluminium containing phases that could be detected by the XRD. This supports the view that aluminium ions could be incorporated in the diopside solid solution structure. Theoretically, it is assumed [17] that the aluminous pyroxene solid solution phase formed in glass-ceramic of G_1 or G_1a has probably the following formula:

$$Ca(Mg_{0.75}, Al_{0.25})(Al_{0.13}, Si_{0.87})_2O_6$$

For sample G_2a the replacement of ($CaO + P_2O_5 + CaF_2$) by (Al_2O_3 + SiO_2) up to ratio 0.57, giving rise of the aluminous pyroxene solid solution phase, which has the probable formula:

$$Ca(Mg_{0.8}, Al_{0.2})(Al_{0.11}, Si_{0.89})_2O_6$$

On increasing the ($CaO + P_2O_5 + CaF_2$)/($Al_2O_3 + SiO_2$) replacement ratio up to 0.66, i.e., sample G_3a, the resulting aluminous pyroxene solid solution phase may exhibit the following formula:

$$Ca(Mg_{0.84}, Al_{0.16})(Al_{0.09}, Si_{0.91})_2O_6$$

On further increasing the ($CaO + P_2O_5 + CaF_2$)/(Al_2O_3 + SiO_2) replacement ratio up to 0.80, i.e., sample G_4a, the resulting aluminous pyroxene solid solution phase formed might have the following probable formula:

$$Ca(Mg_{0.89}, Al_{0.11})(Al_{0.06}, Si_{0.94})_2O_6$$

On the same basis, sample G_5a with increasing (CaO + $P_2O_5 + CaF_2$)/($Al_2O_3 + SiO_2$) replacement ratio up to 0.85, it seems also that the aluminous pyroxene solid solution phase has the probable formula:

$$Ca(Mg_{0.96}, Al_{0.04})(Al_{0.04}, Si_{0.96})_2O_6$$

XRD analysis revealed also that on increasing (CaO + P_2O_5 + CaF_2), i.e., glasses G_2a–G_5a, fluorapatite phase was developed as well. The fluorapatite phase content was increased by increasing its components in the glass, i.e., CaO, P_2O_5, CaF_2 as proved by the XRD of G_2a–G_5a. It has previously been postulated [13] that the important factors that determine whether a glass will bulk nucleate to fluorapatite can be arranged as follows:

1. The Ca:P ratio should be 5:3 which is the Ca:P ratio in the apatite phase.
2. There should be sufficient fluorine present from a chemical/compositional point of view for the fluorapatite phase to form, and this postulation is in agreement with the results reported in the present work.

The system $Ca_5(PO_4)_3F$–$CaMgSi_2O_6$ was previously investigated by Tulyaganov [10], who revealed that there is no evidence for the formation of solid solution phases or liquid immiscibility gap between diopside and fluorapatite phase. This can explain the formation of fluorapatite phase and increase its content together with the predominant pyroxene solid solution phase in the glasses.

4.1. Thermal expansion

The thermal expansion is a complex property connected with the magnitude and distribution of force acting in the system and reflects any change of the distribution of forces with increasing thermal vibration [21]. In addition, the volume of a material increases with temperature due to the increasing amplitude of vibration of the atoms associated with changing interatomic distance and bond angles [22]. In glass, this mechanism alone is responsible for the flat straight lines section of the expansion curve, which extends up to the lower annealing temperature and determines the end of the region of elastic behaviour.

The thermal expansion of glass is not only a function of temperature, but also depends among other factors such as composition, structure of the glass, e.g., degree of polymerization, type of structural units, the nature and contribution of the different cations, whether they occupy forming or modifying positions in the glass network. Accordingly, the thermal expansion data can yield valuable information regarding, for example the structural changes induced by modification of composition or heat treatment [23].

The addition of ($CaO + P_2O_5 + CaF_2$) instead of (Al_2O_3 + SiO_2) in glasses led to increase the expansion coefficients of the glasses, the role played by CaO, P_2O_5 and CaF_2 in the coherency of the glass structure must be taken into account. The Ca^{2+} ions in such silicate glasses may exhibit the octahedral coordination state with oxygen. These octahedral calcium groups possess lower single bond strengths (32 kcal mol^{-1}) compared with that of Mg^{2+} (37 kcal mol^{-1}) and Si^{4+} (106 kcal mol^{-1}) or Al^{3+} (101−79 kcal mol^{-1}) [21]. Therefore, the α-values of the glasses was then increased. Also, the presence of P_2O_5 and CaF_2 increased the expansion coefficients of the studied glasses, due to both P_2O_5 and CaF_2 causing a great disturbance in the arrangement of the glass-network. CaF_2 is more powerful in decreasing the coherency of the glass-network than P_2O_5 [2,13].

The addition of ($B_2O_3 + Na_2O + TiO_2$) as minor additives in glass compositions increased the expansion coefficient values and decreased both T_g and T_s of the studied glasses. This may be explained on the basis that these additives relieved the rigidity of the glass structure, which led to increase in the lattice vibration and caused an increase in the relative contribution of the anharmonicity term [24], i.e., an increase in the α-values and the decrease in both T_g and T_s values could be expected.

The thermal expansion of crystalline solids can be markedly different from those of the parent glasses. The crystallization process greatly altered the thermal expansion of the glasses. Therefore, the glass-ceramic materials may have high or low coefficients of expansion depending on the expansion coefficient and elastic properties of the crystal phases formed including the residual glass matrix [25]. In most cases, the expansion coefficient of the crystalline materials generally increases with glass phase content in the material.

An extremely wide range of thermal expansion coefficients are covered by the different crystal types and the development of these phases in appropriate proportions forms the basis of the production of glass-ceramics with controlled thermal expansion coefficients. It has been reported that pyroxenes had high positive values of their expansion coefficient. Diopside and Ca-Tschermak's, which are considered to be pyroxene members have α-values of 78 $\times 10^{-7}\,^{\circ}C^{-1}$ (25–1000 °C) [26] and 88 $\times 10^{-7}\,^{\circ}C^{-1}$ (25–1200 °C), respectively [20]. While fluorapatite has α-values of (74–119) $\times 10^{-7}\,^{\circ}C^{-1}$ (20–300 °C), [27]. Abe [28], revealed that the natural tooth enamel has thermal expansion coefficient of 114 $\times 10^{-7}\,^{\circ}C^{-1}$ (20–400 °C).

According to the previous consideration, it follows therefore that samples G_2a–G_5a have higher thermal expansion coefficients (α-values) than that of sample G_1a, may be attributed to the formation of highly expanding fluorapatite phase in these samples.

The higher α-values of the samples containing (B_2O_3 + Na_2O + TiO_2) than those free of these additives can be explained by assuming that most of the amounts of Na_2O and B_2O_3 were present in the glassy matrix, which contains enough non-bridging ions [29], giving rise to a less coherent network and subsequently a higher expansion coefficient.

5. Conclusions

The crystallization characteristics of the glasses based on CaO–MgO–Al_2O_3–P_2O_5–SiO_2–CaF_2 system were investigated. The crystallization tendency of glasses was improved by increasing ($CaO + P_2O_5 + CaF_2$) at the expense of (Al_2O_3 + SiO_2) and also improved by adding ($Na_2O + B_2O_3 + TiO_2$) as minor additives.

Various pyroxene solid solution of diopsidic type together with fluorapatite phases were developed during the heat treatment. The pyroxene solid solution was identified as diopside-Ca-Tschermak's solid solution, the limit of isomorphous substitution of Ca-Tschermak's component in diopside as 33.33%, which corresponds to 6.63 mol% Al_2O_3.

No evidence for the formation of solid solution between pyroxene solid solution and fluorapatite phase could be achieved from the results obtained. The present results are totally informative concerning the role of glass oxide constituents and the compatibility between the crystalline phases in determining the nature of the solid solution formed.

Fine microstructure of fibrous growths was developed by increasing the fluorapatite in the glass-ceramic materials obtained.

The α-values of the studied glasses ranged between 78 $\times$ 10^{-7} and 99 $\times 10^{-7}\,^{\circ}C^{-1}$ in the (25–500 °C) temperature range and those of crystalline products ranged from 66 $\times$ 10^{-7} to 100 $\times 10^{-7}\,^{\circ}C^{-1}$ in the (25–700 °C) temperature range.

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