Ceramics International 33 (2007) 233–238

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Role of TiO_2 and ZrO_2 on crystallizing phases and microstructure in Li, Ba aluminosilicate glass

G.A. Khater *, M.H. Idris

Saudi Geological Survey, P.O. Box 54141, Jeddah 21514, Saudi Arabia

Received 4 July 2005; received in revised form 26 July 2005; accepted 29 August 2005

Abstract

Different concentrations of TiO_2 and ZrO_2 were incorporated in Li, Ba aluminosilicate glass to establish their effects on the crystallization process. The kinetics of phase transformations, the final crystalline phase assemblages and the microstructures formed were found to be dependent on the types and concentration of the nucleant involved. The presence of ZrO_2 and TiO_2 were found to enhance the crystallizability of the glass. ZrO_2 is much better than TiO_2 in promoting homogeneous nucleation and growth of extremely fine-grained microstructure of β-eucryptite ss and hexacelsian. ZrO_2 retarded the formation of β-spodumene ss and monoclinic celsian. TiO_2 in low concentrations greatly facilitates the crystallization process and favors the transformation of β-eucryptite ss → β-spodumene ss and hexacelsian → monoclinic celsian.

Keywords: Crystallization; β-Eucryptite ss; β-Spodumene ss; Hexacelsian; Monoclinic celsian

1. Introduction

Glass-ceramics are crystalline materials formed through the controlled crystallization of glass during specific heat treatments. The bulk chemical composition, nucleant added, final phase assemblage and microstructure are the most important factors affecting their technical properties. Crystallization of glass from the surface or from a small number of sites in the interior usually results in low strength materials with coarse-grained microstructures; in contrast, efficient nucleation of crystals from numerous centers results in fine-grained microstructures and consequently high-strength materials. The role of nucleating agents in initiating glass crystallization from a multitude of centers was the major factor allowing the introduction of glass-ceramics into industrial applications [1–3].

The crystallization of some glasses, based on the spodumene ($LiAlSi_2O_6$) with successive additions of celsian $BaAl_2Si_2O_8$ [4–6] showed that, although the tendency towards bulk crystallization increased with increase in celsian content, relatively non-uniform coarse-grained textures were produced. The resulting crystalline phase assemblages depend largely upon bulk chemical composition, crystallization parameters and the extent of isomorphous substitution as well as rate of cooling.

Crystal nucleation is a fundamental process of phase transition in glass melts based on molecular level fluctuations under a regime of supersaturation. The time and temperature dependent kinetics of crystal nucleation are of crucial importance in determining the glass forming abilities of melts and play an important role in their wide ranging technological applications as glass ceramic materials. Whereas for most devitrifications the composition of glass and crystal differ, a limited number of glass compositions crystallize isochemically, i.e. without changes in composition [7]. Nucleation can occur in such glasses on pre-existing surfaces and in the absence of any initial surface [8]. The nucleation kinetics of the latter process (homogeneous volume nucleation) has been described using the results of the classical nucleation theory [9–12].

The main objective of the present study was to investigate the various effects of different additions of the nucleating agents TiO_2 and ZrO_2, on the crystallizability, phase assemblages, isomorphism and polymorphism of the crystallizing spodumene or celsians, respectively, and on the resultant microstructures.

---

* Corresponding author.
E-mail address: kater.ja@sgs.org.sa (G.A. Khater).

0272-8842/$32.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.08.016

2. Experimental procedure

2.1. Glass composition and preparation

A base glass was prepared for the experimental work with the composition shown in Table 1.

Local Saudi sand and kaolin and chemically pure $BaCO_3$, Li_2CO_3, TiO_2 and ZrO_2 were used as starting materials for batch preparation. The weighed batch materials, after thorough mixing were melted in Pt crucibles in an electrically heated globar furnace at temperatures ranging from 1300 to 1500 °C for 3–5 h depending upon the nucleant involved. The melts containing ZrO_2 were rather more viscous than those containing TiO_2 and therefore required higher temperatures and longer periods of melting. The homogeneity of the melt was achieved by swirling of the melt-containing crucible several times at about 20 min intervals. After melting and refining, the bubble-free melt was cast onto a hot steel marver into buttons and rods. The hot glass samples were then transferred to a preheated electric muffle furnace for annealing.

2.2. Differential thermal analysis (DTA)

Scans were carried out using a Perkin-Elmer (7 series) microdifferential thermoanalyser using 60 mg of powdered glass sample, of grain size less than 0.60 mm and greater than 0.2 mm, were used against Al_2O_3 powder as a reference material. A heating rate of 20 °C/min and sensitivity setting of 20 μV/in. were maintained for all the runs.

2.3. Heat-treatment

The glass samples were heated in a muffle furnace from room temperature to the required temperature and kept at the intended temperature for 1 h, after which the furnace was switched off and the samples were allowed to cool inside it to room temperature.

A double-stage heat-treatment schedule was used to study its effect on the microstructure. Glass samples were first soaked at 680 °C for 1 h and then at 900 °C and/or 1050 °C for 1 h.

2.4. X-ray diffraction analysis

Identification of crystals precipitating in the course of crystallization was conducted by the X-ray diffraction analysis of the powdered samples. The X-ray diffraction patterns were obtained using a Philips type (BW 1710) adopting Ni-filtered Cu Kα radiation. All instrument settings were maintained for all the analyses using a Si disk as an external standard, this was necessary to make the measurements based on the peak height more accurate.

Table 1
Base glass composition

Nominal phase composition (wt%)		Calculated oxides constituents (wt%)			
Celsian	Spodumene	BaO	Li_2O	Al_2O_3	SiO_2
30	70	12.25	5.62	27.33	54.81

2.5. Microscopy

The mineralogical constitution and microstructure of almost all the heat-treated specimens were examined optically in thin sections using a polarizing Carl Zeiss research microscope.

3. Results

3.1. Effect of titanium dioxide (TiO_2)

TiO_2 was incorporated in the glass G3 in amounts of 1.5, 3.0 and 4.5 g per 100 g of glass oxide. The addition of TiO_2 to the glass batch reduced the melting temperature and also the viscosity of the resultant melt, as compared with titanium-free batches. The effect of these TiO_2 additions on the mineralogical constitution and microstructures of the resultant crystalline materials can be outlined as follows.

The presence of TiO_2 was found to enhance the crystallizability of the glass. This is clear from the DTA curves (Fig. 1 curves b–d) where the exothermic crystallization peak was

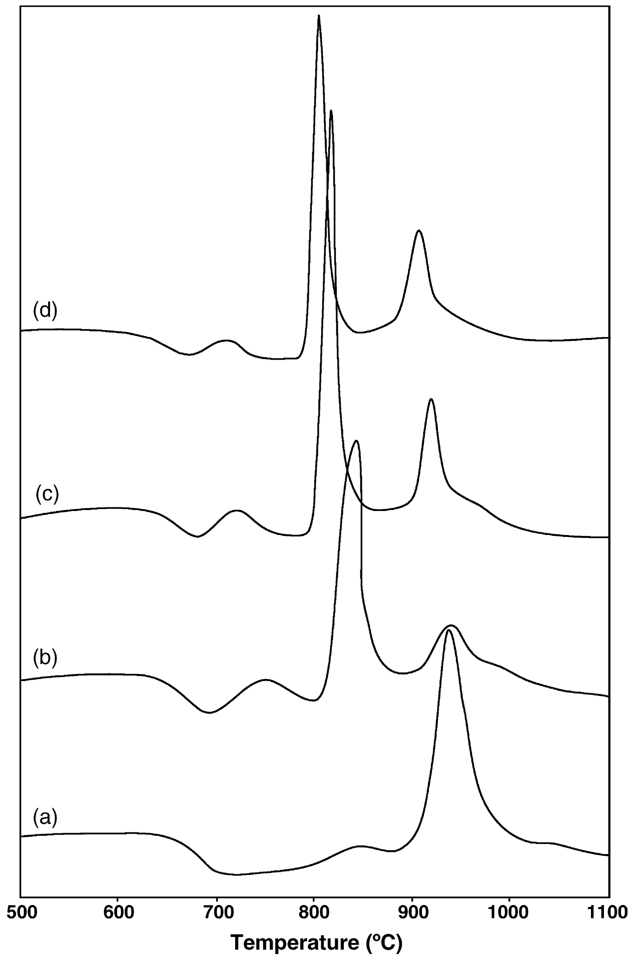

Fig. 1. DTA curves of G3 glasses: (a) without additives; (b) with 1.5% TiO; (c) with 3.0% TiO_r; (d) with 4.5% TiO.

Table 2
Summary of DTA results of glasses with and without additions of the nucleation catalysts TiO_2 and ZrO_2

Glass no.[a]	Nucleator used (g/100 g glass)	Endothermic peak temperature (°C)	Exothermic peak temperature (°C)
G3	–	702	860,945
G1.5 T	1.5 TiO_2	686	748,833,933
G3 T	3.0 TiO_2	676	720,814,918
G4.5 T	4.5 TiO_2	659	709,780,907
G1 Z	1.0 ZrO_2	726	844,1042
G1.5 Z	1.5 ZrO_2	730	841,1044

[a] Where T = TiO_2; Z = ZrO_2.

Table 3
X-ray identification of the crystalline phases developed in the glasses containing TiO_2 and ZrO_2 at selected heat-treatment temperatures

Glass no.[a]	Heat-treatment parameters (°C, h)	Phases identified by X-ray[a]
G3	680 °C 1 h, 800 °C 1 h	β-euc. ss + hexacel
	680 °C 1 h, 900 °C 1 h	β-euc. ss + hexacel
G1.5 T	680 °C 1 h, 800 °C 1 h	β-spod. ss + monocel.
	680 °C 1 h, 900 °C 1 h	β-spod. ss + monocel
G3.0 T	680 °C 1 h, 800 °C 1 h	β-spod. ss + monocel
	680 °C 1 h, 900 °C 1 h	β-spod. ss + monocel
G4.5 T	680 °C 1 h, 800 °C 1 h	β-spod. ss + monocel
	680 °C 1 h, 900 °C 1 h	β-spod. ss + monocel
G1.0 Z	680 °C 1 h, 1050 °C 1 h	β-euc. ss + hexacel
G1.5 Z	680 °C 1 h, 1050 °C 1 h	β-euc. ss + hexacel

[a] Where G3 = base glass; T = TiO_2; Z = ZrO_2; β-euc = β-eucryptite; β-spod. = β-spodumene; ss = solid solution; hexacel. = hexacelsian; monocel. = -monoclinic celsian.

increased in intensity and shifted at the same time, towards lower temperature (Table 2, Fig. 1). It is noteworthy that this effect of TiO_2 on the crystallizability is more pronounced in glass (G4.5 T).

XRD patterns of glasses (G1.5 T, G3.0 T and G4.5 T) treated at 680 °C for 1 h and then at 900 °C for 1 h, are shown in (Fig. 2).

The presence of TiO_2, even in small quantities, greatly affects on both the crystalline phase composition and the microstructure of the formed ceramic materials.

From the mineralogical point of view, the presence of TiO_2 in glass G3 favored monoclinic celsian and β-spodumene ss formation and inhibited β-eucryptite ss and hexacelsian crystallization. The X-ray diffraction analysis (Fig. 2 pattern a Table 3) indicated that the glass 3 (free of catalyst) yielded β-eucryptite ss and hexacelsian (at 680 °C for 1 h and then at 900 °C for 1 h). Meanwhile, for the TiO_2 containing samples (1.5 T, 3.0 T and 4.5 T), yielded β-spodumene ss and monoclinic celsian when it was treated at the same conditions (Table 3, Fig. 2 patterns b, c and d). The formation of monoclinic celsian together with β-spodumene ss was only achieved after treatment at 1050 °C for 40 h in base glass (free of catalyst) [4]. Therefore, this small percentage (1.5 g) of TiO_2 incorporated in the glass proved to be greatly effective in catalyzing monoclinic celsian and β-spodumene ss even at the earliest stages of crystallization, and in lowering their crystallization temperature. Its addition affects the transformations of the metastable hexacelsian → stable monoclinic celsian and metastable β-eucryptite ss → stable β-spodumene ss.

Microscopic examination of the double-stage heat-treatment glasses showed that the TiO_2 additions are mostly effective on the nucleation process. These are translated by the high crystallizability of the glasses and the relatively finer textures (Figs. 3–6).

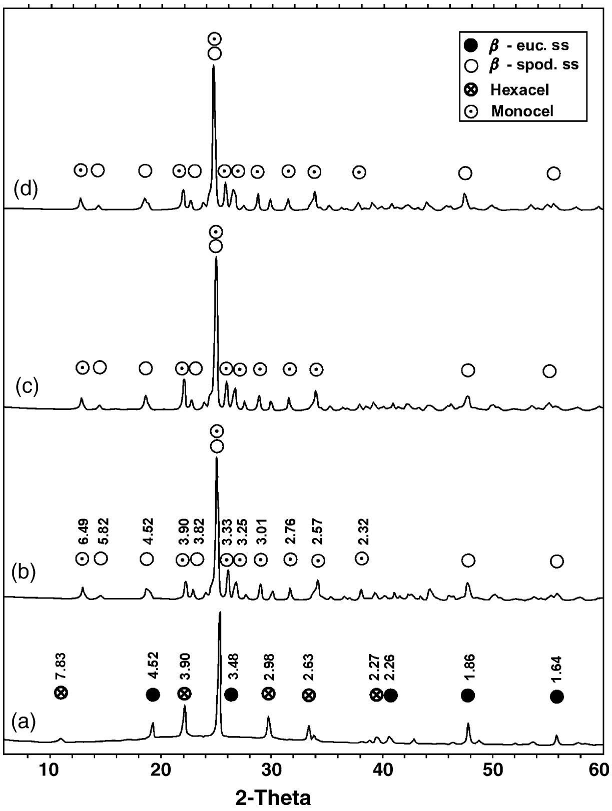

Fig. 2. X-ray diffraction patterns of G3 glasses heat-treated at 680 °C for 1 h and then at 900 °C for 1 h: (a) without additives; (b) with 1.5% TiO_2; (c) with 3.0% TiO_a; (d) with 4.5% TiO_2.

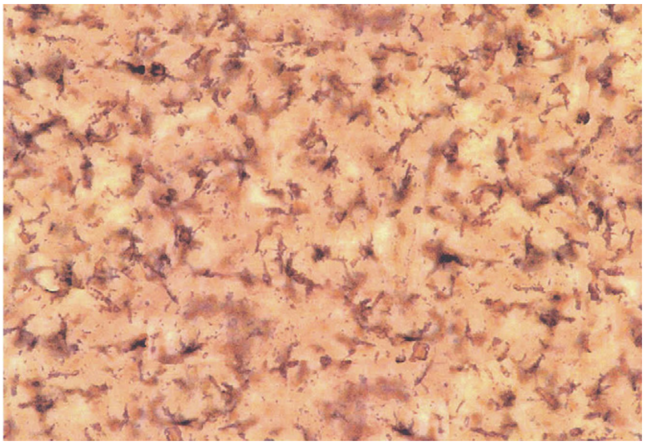

Fig. 3. G3 (680 °C, 1 h + 900 °C, 1 h). Shapeless of β-eucryptite ss with hexacelsian P.N., ×400.

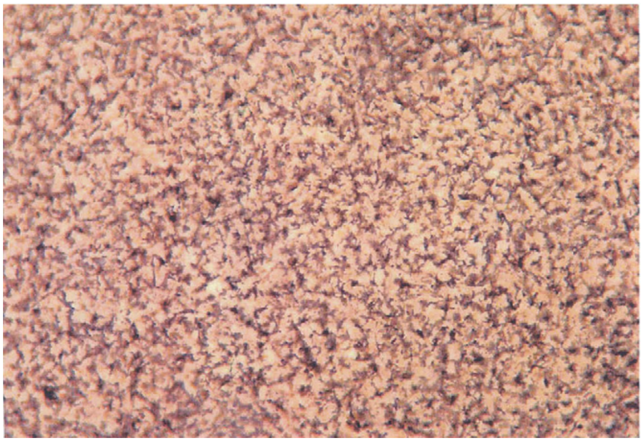

Fig. 4. Glass G1.5 T heat-treated at (680 °C, 1 h + 900 °C, 1 h). Very fine crystallization of β-spodumene ss and monotlinic celsian P.N., ×400.

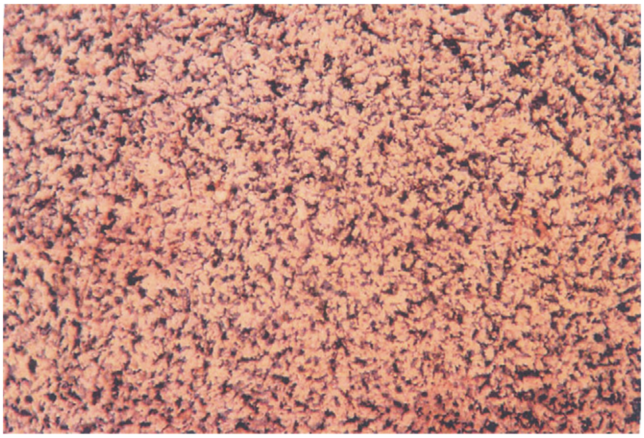

Fig. 5. Glass G3 T heat-treated at (680 °C, 1 h + 900 °C, 1 h). Similar to the above but of finer texture P.N., ×400.

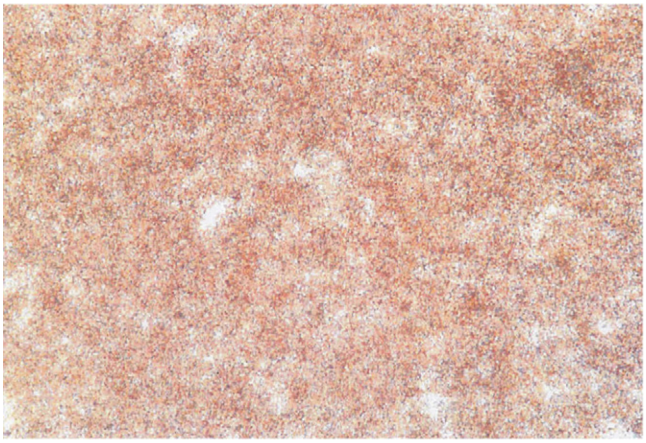

Fig. 6. Glass G4.5 T heat-treated at (680 °C, 1 h + 900 °C, 1 h). Dense holocrystalline mass to uniform very fine-grained texture of β-spodumene ss and monoclinic celsian P.N., ×400.

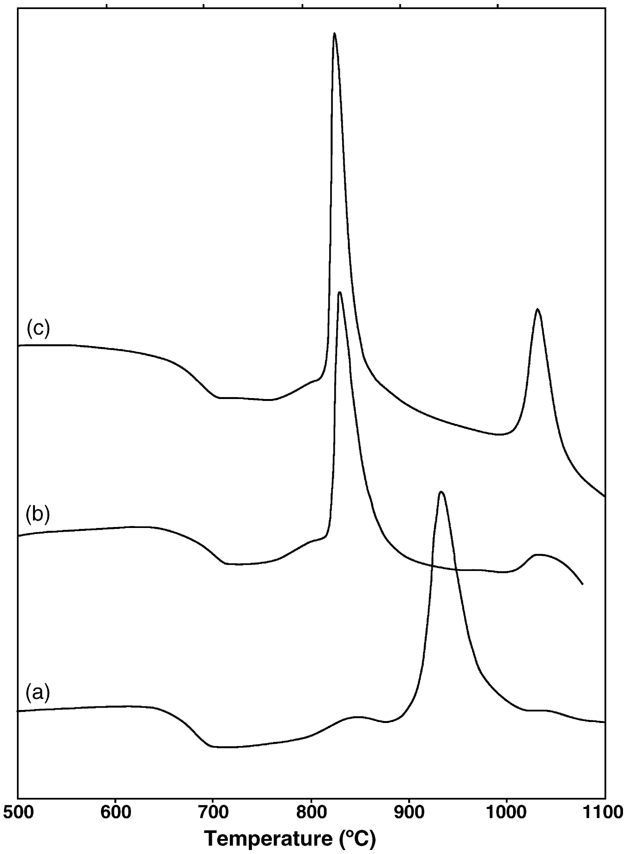

Fig. 7. DTA curves of G3 glasses: (a) without additives; (b) with 1.0% ZrO_2; (c) with 1.5% ZrO_2.

3.2. Effect of zirconium dioxide (ZrO_2)

The presence of ZrO_2 was found to enhance the crystallizability of the glass. This is clear from DTA curves (Fig. 7 curves b and c) where the exothermic crystallization peak was increased in intensity and shifted at the same time, towards lower temperature (Table 2 and Fig. 7).

XRD patterns of glasses (G1 Z and G1.5 Z) treated at 680 °C for 1 h then at 1050 °C for 1 h, are shown in (Fig. 8).

From the mineralogical point of view the presence of ZrO_2 in glass enhances the formation of both β-eucryptite ss and hexacelsian and stabilizes them. The X-ray diffraction analysis (Fig. 8 pattern a, Table 3) indicates that the glass G3 (free of catalyst) yields β-eucryptite ss and hexacelsian after being treated at 680 °C for 1 h and then at 900 °C for 1 h. For the ZrO_2-containing glasses [G1 Z and G1.5 Z (Fig. 8, Table 3)] yielded β-eucryptite ss and hexacelsian were developed after being treated at 680 °C for 1 h and then at 1050 °C for1 h. It can be noticed that there is no major effect of ZrO_2 on the transformation on both of β-eucryptite ss → β-spodumene ss and hexacelsian → monoclinic celsian.

From the textural point of view, the microscopic examination revealed that ZrO_2 induced a great number of crystallization centers leading to greatly fine-grained microstructures (Figs. 3, 9 and 10).

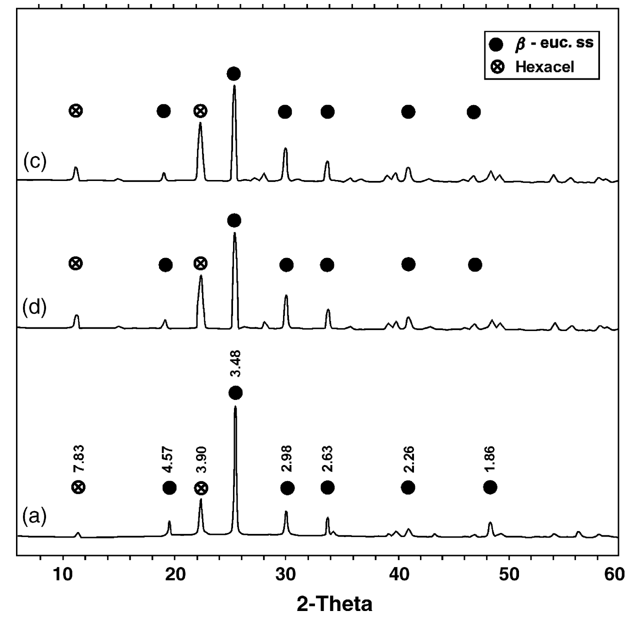

Fig. 8. X-ray diffraction patterns of G3 glasses heat-treated at 680 °C for 1 h and then at 1050 °C for 1 h: (a) without additives; (b) with 1.0% ZrO_2; (c) with 1.5% ZrO_2.

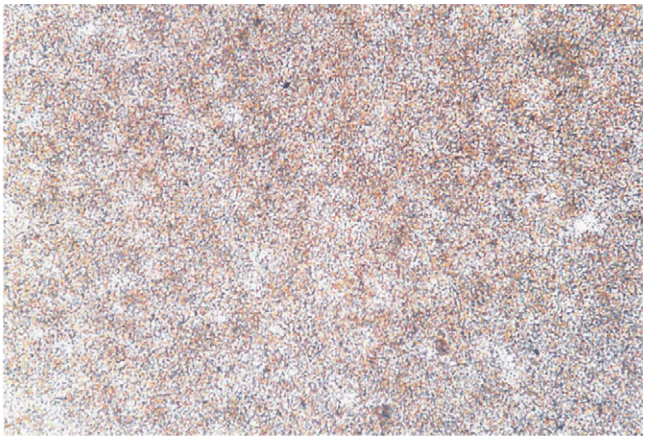

Fig. 9. Glass G1.0 Z heat-treated at (680 °C, 1 h + 1050 °C, 1 h). Very fine crystallization of β-eucryptite ss with hexacelsian P.N., ×400.

Fig. 10. Glass G1.5 Z heat-treated at (680 °C, 1 h + 1050 °C, 1 h). Almost similar to above but of finer texture P.N., ×400.

4. Discussion

4.1. Role of titanium dioxide (TiO_2)

According to the results obtained from TiO_2-containing glasses, it is quite evident that TiO_2 is greatly effective in the nucleation and crystallization processes.

In glasses containing TiO_2 as nucleation catalysts, it is generally agreed that TiO_2 leads to liquid unmixing, which may be referred to as phase separation [1]. On the other hand, several investigators [13–16] showed that in glasses containing appreciable amounts of TiO_2 the effective nuclei and small crystallites of titanium are compounds such as TiO_2 itself as titanates.

For any glass in which the ratio of oxygen ions/network forming cations is greater than 2, there must be non-bridging oxygen ions, a lowering of the free energy will follow, if chemical differentiation occurs to give domains in which the silica network is continuous and which are separated from each other by the non-bridging oxygens [17]. Such a microstructure will provide a larger number of potential nuclei for phases whose structural elements are related to the short-range order within the domains. It is postulated here that Ti^{4+} ions can create such domains by their tendency to occupy the non-bridging surface sites associated with non-bridging oxygen and Li ions. This tendency is consistent with the limited ability of Ti^{4+} ions to form stable tetrahedral network. Moreover, the rejection of the Ti^{4+} ions to the periphery is expected since the solubility of Ti^{4+} in the network silicate structure is very low. This criterion of considerations may be reflected on facilitating the melting process, decreasing the viscosity of the resultant melts and increasing the crystallizability of the corresponding glasses investigated.

From the mineralogical point of view, the TiO_2 effect can be summarized in the followings:

The presence of TiO_2 in the glass was found to catalyze the β-eucryptite ss → β-spodumene ss transformation.
The presence of TiO_2 in the glass was found to enhance the formation of monoclinic celsian.

These results are in good agreement with the literature concerning the nature of crystallization of lithium or barium aluminosilicates [18–20] where TiO_2 preferentially nucleated the keatite structure, i.e. enhanced the transformation of β-quartz ss to keatite ss and ZrO_2 preferentially nucleated or stabilized the high quartz structure in Li_2O–MgO–Al_2O_3–SiO_2 glasses nucleated either by TiO_2 and/or ZrO_2.

All the above mentioned effects of TiO_2 on the type of mineral phases formed may be related to changes in glass viscosity, since the additions of TiO_2 to glass is known to reduce the viscosity and consequently leads to more mobilization of the glass forming elements [21] to such an extent that the structure more complex silicate phases, β-spodumene ss and monoclinic celsian can crystallize out.

The presence of TiO_2 stimulates the formation of uniform fine-grained microstructures and favors the β-eucryptite ss → β-spodumene ss transformation in lithium manganese aluminosilicate glasses and also the presence of TiO_2 in spodumene lithium maganesium orthosilicate glasses lead to the formation of relatively fine-grained microstructure [22].

β-Eucryptite ss in titania-nucleated glass is, therefore, due to the downward displacement of its transformation temperature.

4.2. Role of zirconium dioxide (ZrO_2)

ZrO_2 has a marked shift of the temperature at which crystallization begins, to higher values, which is evidenced by the shift of the endothermic peak on the DTA curves to higher temperatures. This effect increased the amount of ZrO_2 was increased. ZrO_2 favors the formation of fine-grained textures especially when the glass was heat-treated at double-stage heat-treatment (Figs. 9 and 10). It favors also, the crystallization of β-eucryptite ss and hexacelsian and retarded the transformation of β-eucryptite ss to β-spodumene ss and hexacelsian to monoclinic celsian. The promotion of volume crystallization in zirconia-containing glasses after double-stage heat-treatments may be attributed to the enhancement of formation of Zr-bearing nucleation centers. The phases, which first appeared in the Li_2O–Al_2O_3–SiO_2 system nucleated by ZrO_2 and TiO_2, were presumed to be cubic ZrO_2 or $ZrTiO_4$ crystals. The cubic ZrO_2 particles precipitate and increase in size with increasing heat-treatment temperature [23].

The effect of ZrO_2 on retarding the β-eucryptite ss → β-spodumene transformation is consistent with most literature data [19,24]. This effect may be related to the initially formed Zr-bearing nucleant phase as well as to the increase in the viscosity of the glass which consequently leads to less mobility of the structural elements in the glass to such an extent that the transformation between such complex aluminosilicate structures is delayed.

The presence of ZrO_2 in the Li_2O–MgO–Al_2O_3–SiO_2 glasses retarded the β-eucryptite ss → β-spodumene ss transformation, enhanced sapphirine formation and inhibited the cordierite and spinel crystallization. And the transformation of the β-eucryptite ss → β-spodumene ss and hexacelsian to monoclinic celsian in the system LiO_2–BaO–Al_2O_3–SiO_2 [4–6].

The presence of ZrO_2 was not effective in hexcacelsian → monoclinic celsian transformation, and that hexacelsian phase increases with increasing zirconia content [25].

5. Conclusions

It is concluded that the characteristics of glass ceramics depend, to a great extent, on the type and amount of the nucleant used.

The presence of TiO_2 favors the formation of monoclinic celsian and β-spodumene ss and leads to the formation of uniform fine-grained microstructures. While ZrO_2, even in small concentrations induces the formation of very fine-grained microstructures and retarded the formation of β-spodumene ss and monoclinic celsian. There is no major effect on the transformation on both of β-eucryptite ss → β-spodumene ss and hexacelsian → monoclinic celsian.

Acknowledgement

The authors are greatly indebted to H.E. Dr. Mohammed A. Tawfiq, President of Saudi Geological Survey, for his valuable support, encouragement and the facilities provided.

References

[1] S.D. Stookey, Ind. Eng. Chem. 51 (1959) 805–808.
[2] P.W. McMillan, Glass-Ceramics, second ed., Academic Press, London, England, 1979.
[3] G.H. Beall, Am. Ceram. Soc., Special Pub. 5 (1972) 41.
[4] M.H. Idris, The Use of Saudi Sands for the Production of Glass Ceramic Materials, Ph.D. thesis, Cairo University, Egypt, 2002.
[5] M.H. Idris, G.A. Khater, Phys. Chem. Glasses 45 (2) (2004) 141.
[6] G.A. Khater, M.H. Idris, Ind. Ceram. 24 (1) (2004) 43.
[7] P.F. James, Ceram. Trans. 30 (1993) 3.
[8] R. Müller, E.D. Zanotto, V.M. Fokin, J. Non-Cryst. Solids 274 (2000) 208.
[9] E.G. Rawlands, P.F. James, Phys. Chem. Glasses 20 (1) (1979) 1–8.
[10] P.F. James, J. Non-Cryst. Solids 73 (1985) 517.
[11] E.D. Zanotto, P.F. James, J. Non-Cryst. Solids 74 (1985) 373.
[12] M.C. Weinberg, E.D. Zanotto, J. Non-Cryst. Solids 108 (1989) 99.
[13] R.D. Maurer, J. Appl. Phys. 33 (1962) 132.
[14] M. Toshiro, in: Proceedings of the 8th International Congress on Glass, 1968, p. 113.
[15] P.E. Doherty, D.W. Lee, R.S. Davis, J. Am. Ceram. Soc. 50 (2) (1967) 77.
[16] E.V. Poduskko, A.B. Kozlova, The Structure of Glass (3), Consultant Bureau, New York, 1964, p. 77.
[17] T.I. Barry, D. Clinton, L.A. Lay, R.A. Morrell, R.P. Miller, J. Mat. Sci. 5 (2) (1969) 117.
[18] W. Sack, H. Schneider, Glastech. Ber. 39 (1966) 126.
[19] D.R. Stewart, J. Am. Ceram. Soc. (1972) 38.
[20] A.W.A. El-Shennawi, A.A. Omar, A.M. Morsey, Thermochem. Acta 58 (1982) 125.
[21] P.S. Rogers, Min. Mag. (1970) 741.
[22] A.W.A. El-Shennawi, A.A. Omar, A.R. El-Ghannam, Ceram. Int. (1990) 47.
[23] Y. Moriya, D. Warraington, R. Douglass, Phys. Chem. Glasses (1967) 19.
[24] G.A. Khater, Preparation and Study of Glass-Ceramics Containing Celsian, Ph.D. thesis, Ain Shams University, Egypt, 1990.
[25] J.C. Debsikdar, O.S. Sowemimo, J. Non-Cryst. Solids 144 (1992) 269.