

CRYSTALLIZATION OF CALCIUM ZINC ALUMINOSILICATE GLASSES

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The crystallization behaviour of some glasses in the CaO–ZnO–Al₂O₃–SiO₂ system was investigated using different heat-treatment parameters. Cr₂O₃ and CaF₂ were used as nucleating agents. Differential thermal analysis, X-ray diffraction, dilatometry and scanning electron microscopy were used in this study. Melilite, α - and β -willemite, anorthite, wollastonite, pseudowollastonite and petedunnite phases developed in the investigated glasses. The formation of compatible and incompatible phase assemblages and the effect of Cr₂O₃ and CaF₂ are illustrated. Glass-ceramics with fine-grained microstructures and CTE values ranging from 36 to 73 $\times 10^{-7} K^{-1}$ in the 20–700°C range were obtained.

INTRODUCTION

Glass-ceramic science opens a wide range of possibilities for designing new materials. The properties of glass-ceramics are mainly determined by their constituent phases and microstructures, which depend on the composition of the parent glass, as well as on the thermal treatment and addition of nucleating agents. The more complex the composition of the glass is, the greater the diversity of the expected crystalline phases will be, and the higher the probability of a successful combination of properties in the resultant glass-ceramic [1].

In recent years, a great deal of interest has been focused on the fabrication and luminescence properties of a wide variety of oxide based phosphors in order to obtain efficient luminescent materials for flat panel display devices [2-6]. Willemite, Zn₂SiO₄, has been identified as a suitable host matrix for many rare earth and transition metal dopant ions for efficient luminescence [3-6]. Glass-ceramics containing willemite have been known, for many years, as materials for electronic applications [e.g.7]. Willemite is also characterized by a low thermal expansion coefficient and its brilliant crystals are desired for the fabrication of glazes [8].

The hardystonite phase, on the other hand, possesses improved bending strength and fracture toughness as compared to hydroxyapatite and may possess good biocompatibility [9].

This paper aims at studying the crystallization behavior of some glasses in the system CaO–ZnO–Al₂O₃–SiO₂ to obtain willemite and melilite (hardystonite)-containing glass-ceramics. The formation of compatible and incompatible phase assemblages and the effect of Cr₂O₃ and CaF₂ are also illustrated.

EXPERIMENTAL

Table 1 shows the composition of the investigated glasses. The glasses were prepared by melting the required amounts of reagent grade chemicals (CaCO₃, ZnO, Al₂O₃, SiO₂, CaF₂, Cr₂O₃) in platinum-2 % rhodium crucibles at 1450°C for two hours in an electrically heated furnace. CaF₂ and Cr₂O₃ were added as nucleating agents in amounts of 5g and 0.5g/100g glass oxides respectively.

The thermal behavior of the glass was determined using DTA technique. The DTA scans were carried out on glass powders with a particle size of 150–300 μ m, at 10 °C/min heating rate, using a computerized system (Model Shimadzu), in a dynamic pure nitrogen atmosphere, at a flow rate of 50 cm³/min. Heat-treatment of the glass was carried out according to the DTA results, i.e. at the endothermic and exothermic peak temperatures, as well as, according to single-stage regimes at different temperatures for different soaking

Table 1. Chemical composition of the investigated glasses (wt.%).

Series	Oxide Glass No.	SiO ₂	Al ₂ O ₃	CaO	ZnO	CaF ₂	Cr ₂ O ₃
1 st	W	42	10	18	30	–	–
	WF	42	10	18	30	5	–
	WC	42	10	18	30	–	0.5
2 nd	WE*	30	5	18	47	–	–
	WEF	30	5	18	47	5	–
	WEC	30	5	18	47	–	0.5

*Approximately corresponds to the willemite- hardystonite- gahnite eutectic

periods. The crystallized phases were identified by X-ray diffraction analysis using Ni-filtered $\text{CuK}\alpha$ radiation (Philips, PW1390 diffractometer).

The thermal expansion coefficient was measured for the obtained glass-ceramics using a Linseis (L74/1250) dilatometer at a heating rate of $5^\circ\text{C}/\text{min}$.

The microstructure of the glass-ceramics was analyzed via SEM (Jeol-840A Electron Probe Microanalyzer operating at 20 kV). Here freshly fractured surfaces of the samples were chemically etched using a 10 % HF solution for 15 sec. The etched samples were thoroughly washed with distilled water and thin gold layers were sputtered over the surfaces.

RESULTS AND DISCUSSION

Thermal Analysis

The DTA traces of all glass samples of the 1st series (Figure 1) showed similar behavior, exhibiting one endothermic effect in the $680\text{--}710^\circ\text{C}$ temperature range and a broad exothermic peak system in the $895\text{--}990^\circ\text{C}$ temperature range.

The temperature of glass transformation (T_g), caused by increase in heat capacity due to transformation of the glass structure, shifted to a lower temperature in the glass containing CaF_2 and slightly shifted to a higher temperature in glass containing Cr_2O_3 . The 1st exothermic peak shifted to lower temperatures by about 20 and 30°C relative to the base glass and became broader in glasses containing CaF_2 and Cr_2O_3 respectively. The 2nd exothermic effect shifted to lower temperatures by about 40°C in CaF_2 -containing glass and by 30°C in Cr_2O_3 -containing glass. In the base glass (W), the 2nd exothermic peak split into two peaks at 964°C and at 987°C .

DTA traces of glasses of the 2nd series (Figure 2) showed one endothermic effect in the temperature range $660\text{--}680^\circ\text{C}$ and three exothermic peaks in the range $800\text{--}960^\circ\text{C}$. The endothermic effect shifted to lower

temperatures by adding either Cr_2O_3 or CaF_2 . The first exothermic peak shifted to a lower temperature and became more intense and sharp with addition of CaF_2 , and shifted to a higher temperature when Cr_2O_3 was added. The 2nd exothermic effect is broad and has a wide span in the case of the base glass (WE). This span decreased when adding Cr_2O_3 or CaF_2 and the peak shifted to lower temperatures. The 3rd exothermic effect is small but pronounced in the base glass (WE). This peak greatly shifted to lower temperatures by adding either Cr_2O_3 or CaF_2 . Generally, it is noticed that the crystallization span is wider in the base glass ($\sim 250^\circ\text{C}$) than in glasses containing nucleation catalyts.

The decrease of the glass transition temperature (T_g), crystallization temperature (T_p) and increase of peak sharpness in glasses of the 2nd series compared to those of the 1st series can be attributed to the increase of ZnO content in the 2nd series glasses, which causes a decrease in the viscosity and increased tendency for bulk crystallization [10–11]. This is because increasing ZnO content leads to a decrease in the activation energy of crystallization [12].

The incorporation of CaF_2 in the batch, remarkably reduces the viscosity of the resulting melts and glasses and, consequently, the crystallization onset temperature. This may be due to substitution of fluorine for bridging oxygen atoms, owing to the similarity of F^- and O^{2-} radii, with consequent depolymerization of these melts by replacement of $=\text{Si-O-O}=\text{Si}=\text{O}$ bridges with pairs of the weaker $=\text{Si-F}$ bonds [13]. This results in weakening of the glass network structure.

Crystallization of the glass

Phase formations (Table 2) and microstructures, developed in the investigated glasses of the 1st series after heat-treatments at different temperatures and for different times, were studied. Crystallization started sluggishly by both surface and bulk modes in the base

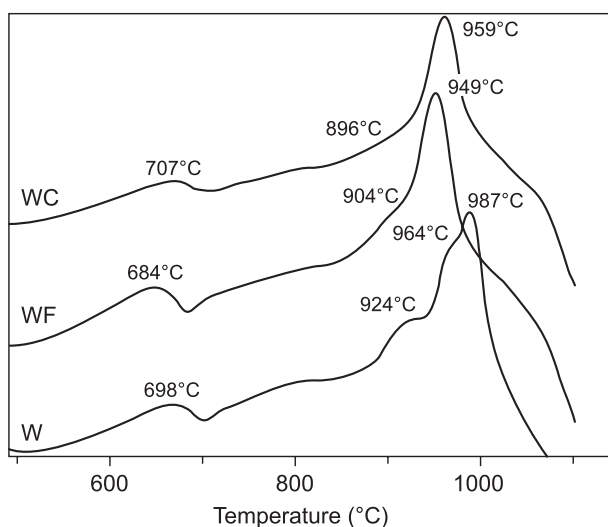


Figure 1. DTA traces of glasses of the first series.

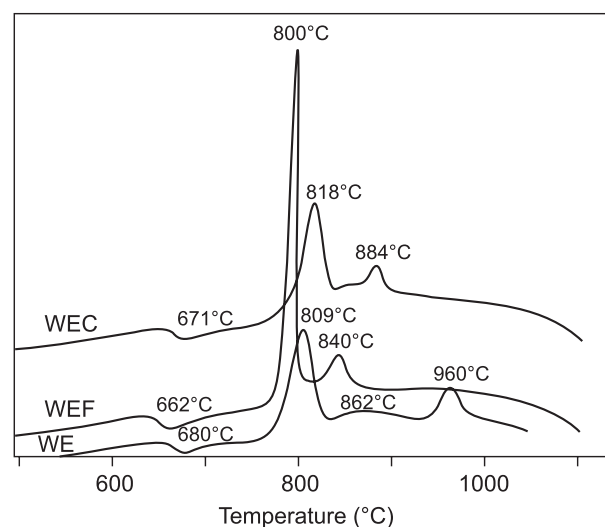


Figure 2. DTA traces of glasses of the second series.

glass (W), treated at 900°C for 2 h, by the formation of willemite (α -willemite) and minor amount of plagioclase (anorthite,) forming an inhomogeneous microstructure. By increasing the soaking time to 10 h at 900°C, these two phases increased in quantity and wollastonite and melilite phases started to appear (Figure 3a). The crystallization was dominated by bulk rather than by surface mode and the crystals became more developed and distinct when increasing the time of heat-treatment (Figure 4a). Double-stage heat-treatments of this W glass slightly enhanced melilite formation after a 2 h treatment at 900°C.

The incorporation of CaF₂ (5g/100g glass) in the batch (sample WF) enhanced bulk crystallization at earlier stages of heat-treatment compared to the base glass, however, with the development of less fine microstructures. Samples heat-treated at 900°C for 2 h exhibited mainly bulk crystallization with the development of willemite and minor melilite and traces of plagioclase (Figure 3b) as well as a small quantity of residual glass. By increasing the soaking time up to 10 h at the same temperature, the amount of melilite and plagioclase (anorthite) phases increased considerably beside the major willemite (Figure 3c) (note: wollastonite was not observed in the X-ray diffraction analysis).

Double-stage heat-treatment of the fluorine-containing glass at 750°C for 1 h + 900°C for 2-10 h, enhanced the crystallization process without affecting the type of developed phases. However, double-stage heat-treatments for longer durations (750°C for 1 h + 900°C for 10 h) greatly enhanced the crystallization of melilite. Crystallization took place by surface and bulk modes resulting in homogenous fine-grained microstructures composed of interlocked crystals (e.g. Figure 4b, note the Y shaped growth pattern characteristic of melilite).

The incorporation of Cr₂O₃ (0.5 gm/100gm glass) in the base glass (WC) shifted the onset of crystallization to higher temperatures. Crystallization took place mainly

by surface mode in contrast to the base and fluorine-containing glasses. Glass samples heat-treated at 900°C for 2 h showed weak surface crystallization with a large amount of residual glass. Increasing the soaking time up

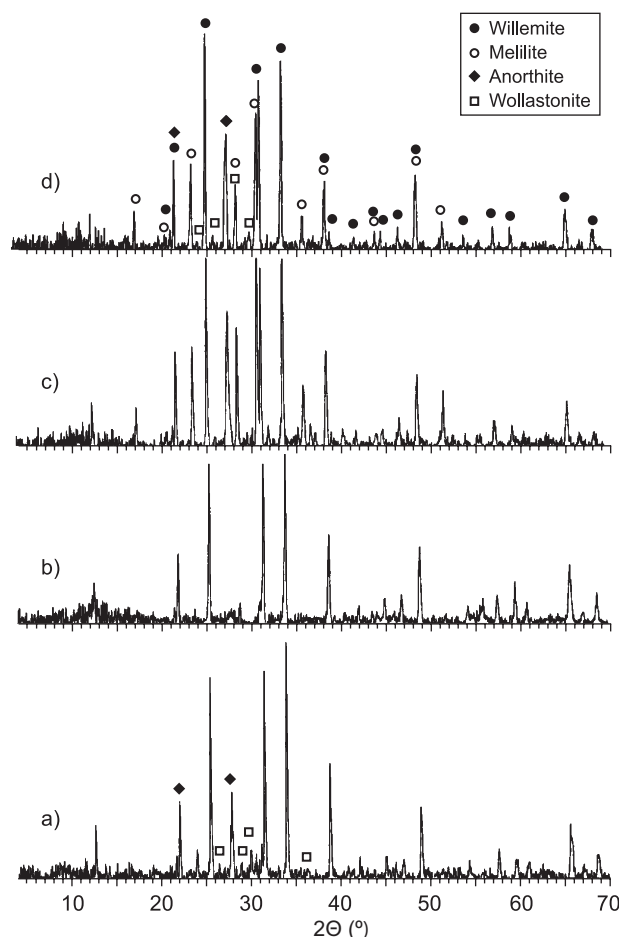


Figure 3. XRD patterns of: (a) sample W treated at 900°C for 10 h, (b) sample WF treated at 900°C for 2 h, (c) sample WF treated at 900°C for 10 h and (d) sample WC treated at 900°C for 10 h.

Table 2. Phases developed in the investigated glasses after different heat-treatments arranged according to their relative amounts.

Heat-treatment	W	WF	WC	WE	WEF	WEC
750°C for 2 h				Wi, β W		PWo,Pet,Wo
750°C for 6 h				Wi, β W	Wi,Me	PWo,Pet,Wo
800°C for 1 h				Wi, Me, β W		
900°C for 1 h				Wi, Me	Wi,Me	Me,Wi
900°C for 2 h	Wi,Pl	Wi,Me,Pl	Wi,Pl,Me, Wo		Wi,Me	
900°C for 10 h	Wi,Pl,Wo,Me	Wi,Me,Pl	Wi,Me,Pl,Wo			
1100°C for 1 h				Wi, Me, Pl		
1100°C for 10 h				Wi,Me, Pl		Me,Wi
750°C for 1 h + 800°C for 1 h				Wi,Me, β -W		
750°C for 1 h + 900°C for 2 h	Wi,Pl,Me	Wi,Me, Pl	Me,Wi,Pl,Wo	Wi,Me,Pl	Wi,Me	Wi,Me
750°C for 1 h + 900°C for 10 h	Wi,Pl,Wo,Me	Me,Wi,Pl	Wi,Pl,Me,Wo	Wi,Me,Pl	Me,Wi	Wi,Me

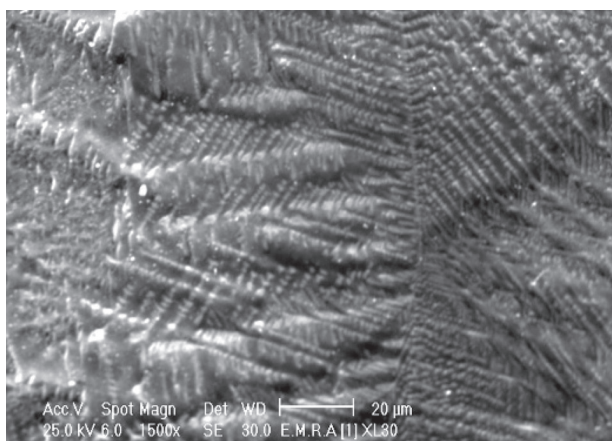
Wi = Willemite, Me = Melilite, Pl = Plagioclase, Wo = Wollastonite, PWo = Pseudowollastonite, β W = β Zn₂SiO₄, and Pet = Petedunnite

to 10 h at the same temperature greatly enhanced bulk crystallization of willemite, melilite, plagioclase and trace amounts of wollastonite, with a small amount of residual glass phase (Figure 3d) forming a fine-grained microstructure.

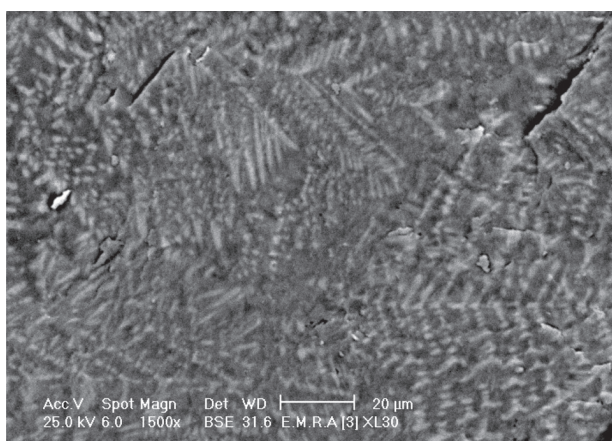
Double-stage heat-treatment, of the Cr_2O_3 -containing glass (WC), at 750°C for 1 h + 900°C for 2 h led to better crystallization than in case of single-stage

treatment and enhanced the crystallization of melilite, willemite and plagioclase. After heat-treatment at 750°C for 1 h + 900°C for 10 h, the amount of plagioclase considerably increased and that of melilite decreased. The microstructure of this sample is shown in Figure 4c.

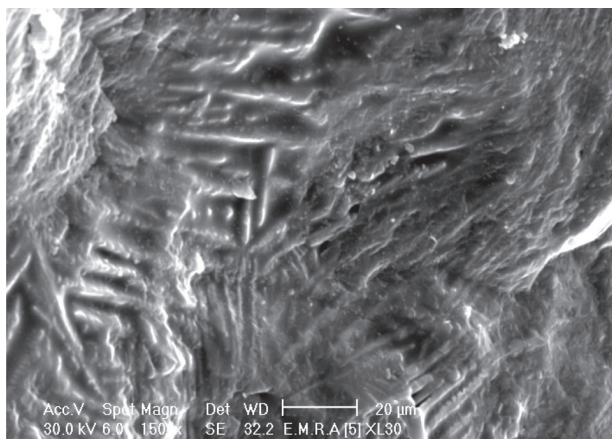
Glass sample WE of near-eutectic composition developed glass-in-glass phase separation with the crystallization of α - and β -willemite after heat-treatment at



a) glass W heat treated at 900°C for 10 h



b) glass WF heat treated at 750°C for 1 h + 900°C for 10 h (homogenous fine-grained texture of dendritic crystals)



c) glass WC heat treated at 750°C for 1 h + 900°C for 10 h

Figure 4. SEM micrographs of studied glasses.

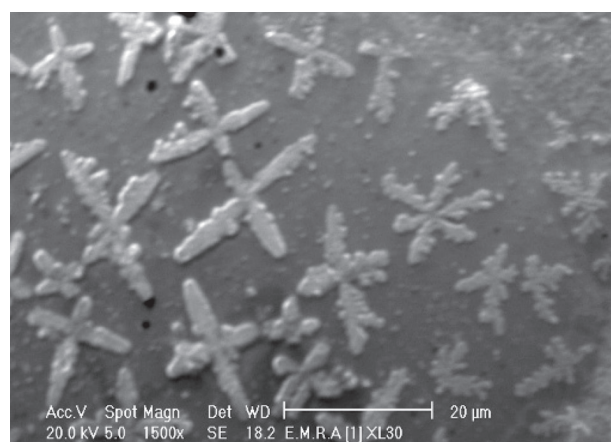
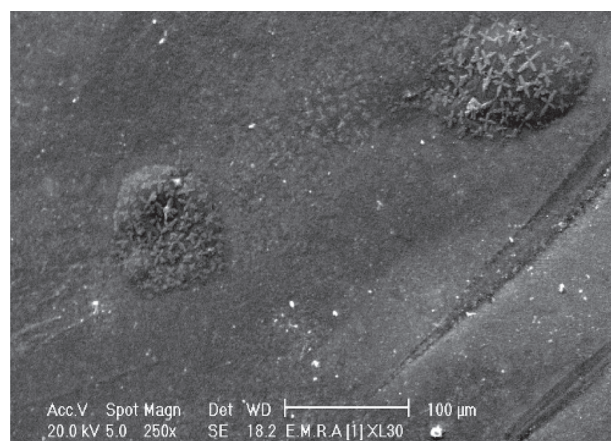
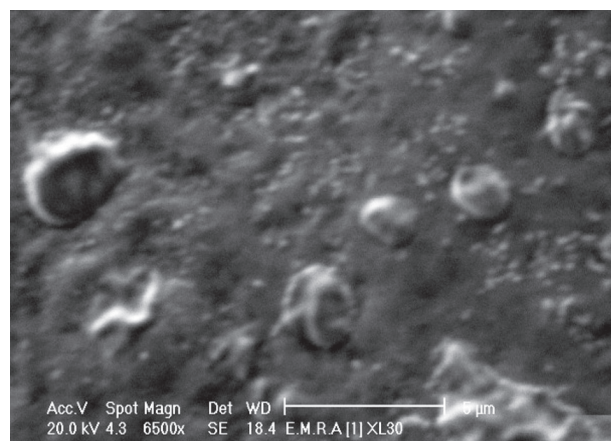


Figure 5. SEM images of glass WE heat treated at 750°C for 6h under different magnifications, showing globules of phase separation with α - and β -willemite crystals developed inside them.

750°C for up to 6h (Figure 5 and Figure 6a). At 800°C for 1 h a melilite phase of near hardystonite composition started to appear beside the above mentioned phases (Figure 6b). The sample exhibited bulk crystallization of interlocked dendritic cross-shaped crystals of α -willemite enclosing globules of anhedral β -willemite in a homogenous fine-grained groundmass (Figure 7). Double-stage heat-treatment at 750°C for 1 h followed by heat-treatment at the temperature of the 1st exothermic effect (800°C) for one hour resulted in the formation of the same phases as mentioned above.

Heat-treatment at 900°C for 1 h led to disappearance of β -Zn₂SiO₄ (β -willemite) and crystallization of α -willemite, as the sole zinc orthosilicate phase, with some melilite (Figure 6c). Increasing the temperature to 1100°C for 1-10 h resulted in better crystallinity and the appearance of plagioclase beside the above mentioned phases (Figure 6d).

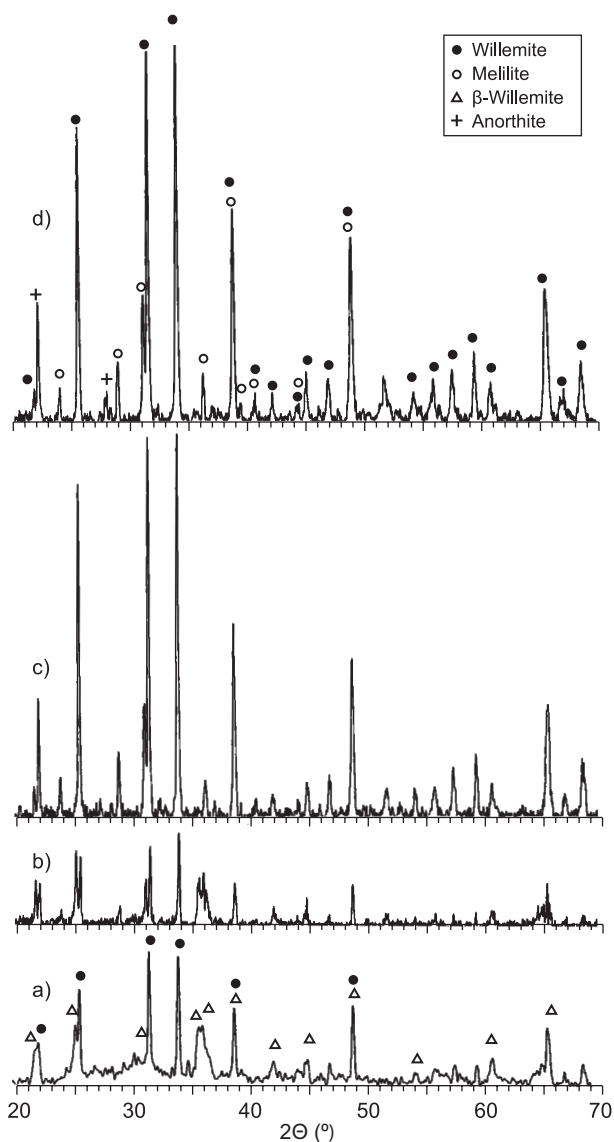


Figure 6. XRD patterns of glass WE heat treated at: a) 750°C for 6 h, b) 800°C for 1 h, c) 900°C for 1 h and d) 1100°C for 10 h.

Judging by the relative intensities of the XRD peaks of these two α - and β -zinc orthosilicate polymorphs, it can be concluded that β -Zn₂SiO₄ (β -willemite) crystallized first at the lower temperatures and then, gradually, converted to α -willemite as the heat-treatment temperature was increased.

Double-stage heat-treatment at 750°C for 1 h followed by 800°C for 1h did not affect the type of the crystallized phases (α , β willemite and melilite), nor their relative amounts. Double-stage heat-treatments at 750°C for 1 h + 900°C for 1-10 h resulted in materials similar to those after single-stage treatment at 900°C for 1h, however, with appearance of traces of plagioclase. Finer-grained microstructures developed through bulk crystallization.

Under experimental conditions above 800°C, only the α -Zn₂SiO₄ form (willemite) was found to be stable [14]. β -Zn₂SiO₄ is thermodynamically metastable under such conditions and can, therefore, be expected to convert into the equilibrium form. Williamson and Glasser [15] reported that β -Zn₂SiO₄ is thermodynamically metastable and converts to the stable α -willemite on prolonged heating; and that, at 1000°C, the rate of conversion of the β -phase is very rapid, whilst below 600°C it is very slow. Pinckney [16] reported the formation of β -Zn₂SiO₄, in the willemite-leucite system, in the 700-850°C range. Phase equilibrium studies confirm that the α -willemite form is the sole thermodynamically stable binary compound in the ZnO–SiO₂ system [17]. However, the metastable β -Zn₂SiO₄ is obtained quite readily as a devitrification product in glasses of suitable compositions. The crystal structures of both willemite forms (α - and β -Zn₂SiO₄) consist of frameworks of SiO₄ and ZnO₄ tetrahedra. The β -Zn₂SiO₄ phase has a crystal structure related to those of the silica polymorphs tridymite and cristobalite [18].

The incorporation of 5 % CaF₂ in the eutectic glass shifts the crystallization of willemite and melilite to lower temperatures. It promotes the crystallization

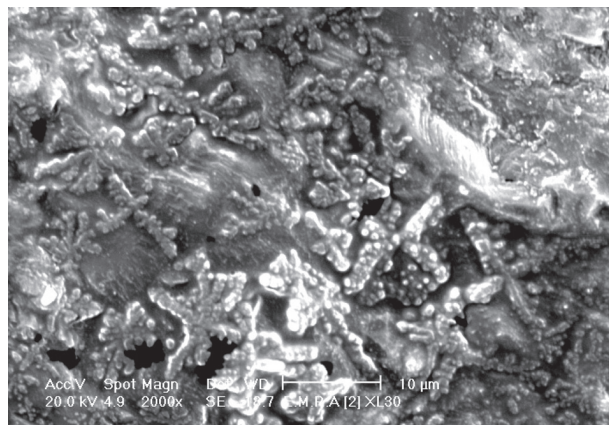


Figure 7. SEM micrograph of glass WE heat treated at 800°C for 1 h showing intimate intergrowth of anhedral β -willemite crystallization inside α -willemite dendritic crystals (cross shapes).

of hardystonite and facilitates the $\beta \rightarrow \alpha$ willemite transformation. These two phases, willemite and melilite (hardystonite), crystallized in samples heat-treated at as low as 750°C for 6 h. Heat treatment at 900°C for 1-2 h resulted in higher degrees of crystallinity, in general, with more development of melilite as the heat-treatment time at 900°C was increased (Figure 8a). Fine-grained microstructures were developed.

Double-stage heat-treatments at 750°C for 1 h + 900°C for 2-10 h caused more crystallization of melilite relative to that of willemite (Figure 8b,c). SEM analysis shows bulk crystallization forming a homogenous, very fine-grained microstructure (Figure 9).

Cr₂O₃-containing samples (WEC) heat-treated at 750°C for 2-6 h developed pseudowollastonite, wollastonite and petedunnite (CaZnSi₂O₆), in a large amount of residual glass (Figure 10).

The presence of Cr₂O₃ in the glass was generally found to enhance the crystallization of melilite and willemite at higher temperatures. Thus samples heat-treated at 900-1100°C for 1-10 h developed fine-grained bulk crystallization of melilite and willemite only, with higher degrees of crystallinity upon increasing temperature and/or time of heat-treatment within the above mentioned limits. Double-stage heat-treatment of this glass at 750°C for 1 h + 900°C for 2-10 h resulted in development of more willemite relative to that of the melilite phase, forming finer microstructures than those after single-stage treatments.

The obtained results reveal that crystallization of the 1st series glasses starts at 900°C for 2 h with the formation of willemite, and anorthite as a minor phase. By increasing the soaking time up to 10 h anorthite considerably increases in amount, wollastonite and melilite

phases begin to separate. Double-stage heat-treatments at 750°C for 1 h + 900°C for 2-10 h resulted in finer microstructures.

The incorporation of fluorine in the glass composition (sample WF) greatly enhances the process of crystallization of the separated phases. Fluorine greatly favoured melilite formation and assisted in the crystallization of anorthite. In this context, fluorine facilitated the willemite and wollastonite reaction to form melilite. This is because fluorine decreases the viscosity, thus helping the system to approach equilibrium. Double-stage heat-treatments affected only the microstructures of the samples leading to finer microstructures. In all cases, increasing the soaking time at 900°C greatly enhanced melilite formation. Cr₂O₃ addition, which has a reverse effect on viscosity, also enhances melilite formation, however through a different mechanism. There is a similarity in cell parameters between Cr₂O₃ ($a = 4.958 \text{ \AA}$) and melilite (hardystonite) ($c = 5.013 \text{ \AA}$). Consequently, Cr₂O₃ may be considered as a good nucleating agent for this phase.

In the near-eutectic composition (WE), β -willemite crystallizes first followed by willemite (α -Zn₂SiO₄) and melilite. The presence of fluorine ions in the glass structure (by addition of CaF₂) facilitates the mobility of ions and ionic complexes in the glass, thus enhancing the approach of the system towards equilibrium crystallization. The presence of Cr₂O₃ (sample WEC) enhances the crystallization of wollastonite, pseudowollastonite and the pyroxene petedunnite. Cr₂O₃ is known to be a favorite nucleating agent for pyroxene formation [19].

Opposite to the view of Hu, et al [12] that the increase of ZnO content causes microstructural coarsening leading to low bending strength and fracture toughness of the material, the fineness of the microstructures increased with increasing ZnO content in the present investigated glass-ceramics and, therefore, all the mechanical properties are expected to improve.

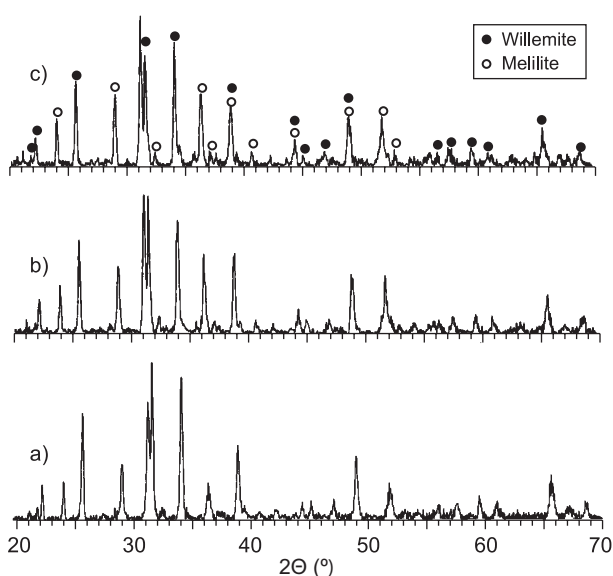


Figure 8. XRD patterns of glass WEF heat treated at: a) 900°C for 2 h, b) 750°C for 1 h + 900°C for 2 h and c) 750°C for 1 h + 900°C for 10 h.

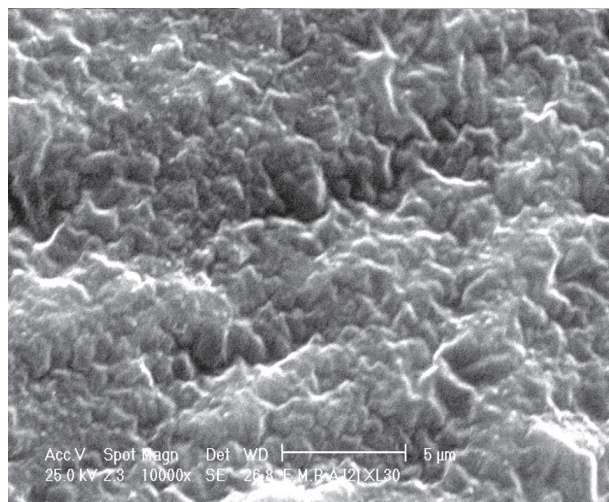


Figure 9. SEM micrograph of glass WEF heat treated at 750°C for 1 h + 900°C for 10 h, showing homogenous bulk crystallization forming a very fine-grained microstructure.

The formation of melilite phase took place in the investigated glasses containing sufficient amounts of CaO and ZnO and was accompanied by a decrease in the amounts of willemite and wollastonite. This fact indicates that CaO and ZnO are the essential oxides sharing in the building of this melilite phase (i.e., this melilite phase has a composition rich in hardystonite component). The composition of the melilite phase is greatly shifted towards that of hardystonite in compositions of the second series where the content of Al₂O₃ is low. On the other hand, melilite composition is shifted towards more gehlenite in solid solution in compositions of the first series, which contain more Al₂O₃, specially, at the early stages of crystallization before the separation of plagioclase (anorthite).

In the CaO–ZnO–Al₂O₃–SiO₂ phase diagram [20] wollastonite and willemite are not compatible and do not form together through equilibrium crystallization. Crystallization from the glass is, however, far from thermodynamic equilibrium and different phases, such as wollastonite, may form together with the willemite at the early stages of the crystallization process. The formation of such phase assemblage may be considered as the first step towards the formation of the chemically more complex melilite phase.

Gehlenite (Ca₂Al₂SiO₇), by itself is not compatible with silica as they react together, under favourable conditions, to yield anorthite (CaAl₂Si₂O₈) and wollastonite (CaSiO₃). However, the presence of zinc causes the formation of hardystonite (Ca₂ZnSi₂O₇), which forms solid solution with the gehlenite. Hardystonite, being compatible with silica, renders the resulting melilite phase increasingly stable towards reaction with silica. In other words, considerable sharing of zinc ions in the building of the crystallizing melilite phase stabilizes it towards the reaction with silica. In this context, the composition of the early formed melilite phase is gehlenite-rich to such an extent that it is incompatible with silica and as crystallization proceeds it becomes gradually impoverished in the gehlenite component and enriched in hardystonite, whereby a plagioclase phase

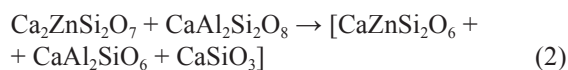
of anorthite composition forms. This is evidenced by the concomitant decrease of the quantity of melilite as anorthite separates, and also by the shift of the melilite diffraction lines towards lower 2θ values as crystallization proceeds indicating depletion of the melilite phase in gehlenite component and enrichment in hardystonite. Calculation of composition W to melilite (solid solution) and willemite reveals 46.5 % melilite, 34.1 % willemite and 19.4 % silica (wt.%). This melilite solid solution is rich in gehlenite and has calculated composition of 57.8 % gehlenite and 42.2 % hardystonite (wt.%). As crystallization proceeds towards thermodynamic equilibrium, part or all gehlenite in the melilite phase reacts with silica to form anorthite (CaAl₂Si₂O₈) so that the remaining melilite becomes gradually impoverished in the gehlenite component and more stable towards reaction with silica. Re-calculation of this composition to willemite- hardystonite -anorthite reveals 28.6 % willemite, 35% hardystonite, 27.3 % anorthite and 9.1 % residual silica (wt.%). The composition of the final melilite phase needs, however, further investigation.

Thus, willemite and wollastonite react together under favourable conditions of temperature and time to form melilite (hardystonite) according to the following equation:



The presence of fluoride ions weakens the glass structure, by replacing the strong Si–O bonds by weak Si–F bonds, which results in faster approach of the system to equilibrium conditions. Consequently, the metastable wollastonite phase does not form in such fluorine-containing glasses.

The formation of the pyroxene (petedunnite, CaZnSi₂O₆), in the near-eutectic glass composition WE, can be accounted for by the reaction of ionic complexes (ionic groupings) of hardystonite and anorthite compositions, thus preventing the separation of anorthite crystals:



Hardystonite + Anorthite → Pyroxene (petedunnite) solid solution

This pyroxene solid solution is, of course, metastable in the presence of silica with which it should react, under favourable conditions of temperature and/or time to form melilite (hardystonite) and anorthite phase assemblage in an approach towards thermodynamic equilibrium. The formation of the pyroxene phase is favoured by its lower activation energy of crystallization compared to that of anorthite [19].

In all cases, willemite is the first and easiest phase to form, whereas, the melilite phase appears later, and gradually increases in quantity as the heat-treatment parameters increase.

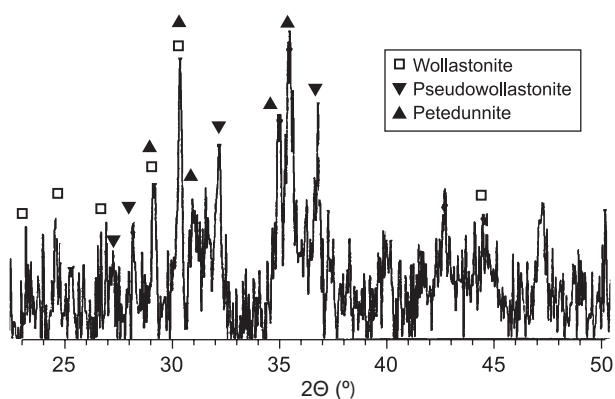


Figure 10. XRD pattern of glass WEC heat treated at 750°C for 6 h.

In all the investigated samples double-stage heat-treatments of the glass resulted in finer microstructures than single-stage treatments due to the development of phase separation and/or the formation of greater numbers of nuclei for the subsequent epitaxial crystal growth.

Thermal Expansion

The thermal expansion coefficients (α) of the obtained glass-ceramic samples heat-treated at 750°C for 1 h + 900°C for 10 h, generally show moderate values except sample WE, which gives low values (Table 3). It is known that, in glass-ceramics, the coefficient of thermal expansion is associated with the expansion characteristics of the constituent phases. The willemite phase is known to have very low α ($15 \times 10^{-7} \text{ K}^{-1}$); anorthite also has low α ($35 \times 10^{-7} \text{ K}^{-1}$). On the contrary wollastonite and melilite crystal phases have high α values (α wollastonite = $110 \times 10^{-7} \text{ K}^{-1}$, α 1 gehlenite = $72 \times 10^{-7} \text{ K}^{-1}$, α 3 gehlenite = $150 \times 10^{-7} \text{ K}^{-1}$ [21]).

Table 3. Thermal expansion coefficient (α) $\times 10^{-7} \text{ K}^{-1}$ of glass samples heat treated at 750°C for 1 h + 900°C for 10 h.

Sample	Temperature (°C)						
	100	200	300	400	500	600	700
W	53	51	54	56	57	58	–
WF	59	53	53	54	56	57	58
WE	16	20	26	31	33	35	36
WEF	70	67	70	71	72	73	73

The presence of F⁻ ions led to a slight increase in α values of glass-ceramics of the 1st series (sample WF), whereas, α largely increased in F⁻ - containing glass-ceramics of the 2nd series (sample WEF). This may be due to the retaining effect, which ZnO exerts on fluorine in such melts with higher content of this oxide [22], and increased melilite crystallization, a phase which has a larger thermal expansion coefficient than willemite. The presence of considerable amounts of plagioclase (anorthite), which has low α , in glass-ceramics of the 1st series counteracts the effect of melilite and wollastonite, which have higher α values.

CONCLUSIONS

The crystallization behaviour of some glasses in the CaO–ZnO–Al₂O₃–SiO₂ system was investigated using different heat-treatments. Cr₂O₃ and CaF₂ were used as nucleating agents. Differential thermal analysis, X-ray diffraction, dilatometry and scanning electron microscopy were used in this study.

In all cases, willemite is the first and easiest phase to form, whereas, melilite phase appears later and gradually increases in quantity as the heat-treatment parameters increase. The composition of the melilite phase is

greatly shifted towards that of hardystonite in low Al₂O₃ compositions, whereas it is shifted towards more gehlenite in solid solution in compositions which contain more Al₂O₃ specially, at the early stages of crystallization before the separation of plagioclase (anorthite).

Crystallization from the glass is far from thermodynamic equilibrium and therefore, different incompatible phases such as wollastonite and willemite may form together at the early stages of the crystallization process as a first step towards the formation of the chemically more complex melilite phase. Zinc oxide causes the formation of hardystonite (Ca₂ZnSi₂O₇), which forms solid solutions with gehlenite in compositions containing considerable amounts of Al₂O₃. Considerable sharing of zinc ions in the building of the crystallizing melilite phase stabilizes it towards reaction with silica. In this context, in glasses containing considerable amounts of Al₂O₃, the composition of the early formed melilite phase is rich in gehlenite to such an extent that it is incompatible with silica. As crystallization proceeds it becomes gradually impoverished in the gehlenite component and enriched in hardystonite, whereby a plagioclase phase of anorthite composition separates.

The incorporation of fluorine in the glass composition greatly enhances the process of crystallization, favours melilite formation (via willemite and wollastonite reaction) and assists in the crystallization of anorthite in compositions containing considerable amounts of Al₂O₃. Fluoride ions weaken the glass structure which results in faster approach of the system to equilibrium conditions. Consequently, the metastable wollastonite phase does not form in such fluorine-containing glasses.

In all cases, increasing the soaking time at 900 °C greatly enhances melilite formation. Cr₂O₃ addition also enhances melilite formation through the similarity in cell parameters between them.

In the near willemite-hardystonite-gahnite eutectic composition, β -willemite crystallizes first followed by willemite (α -Zn₂SiO₄) and melilite. The presence of fluorine ions in the glass structure also enhances the approach of the system to equilibrium crystallization. The presence of Cr₂O₃, in such composition enhances the crystallization of the pyroxene petedunnite (CaZnSi₂O₆). This pyroxene is actually a solid solution and is metastable in the presence of silica with which it reacts, under favourable conditions of temperature and/or time, to form melilite (hardystonite) and anorthite phase assemblage in an approach towards thermodynamic equilibrium. The formation of such pyroxene phase is favoured by its lower activation energy of crystallization compared to that of anorthite.

In all the investigated samples double-stage heat-treatments of the glass resulted in finer microstructures compared to single-stage treatments due to the development of phase separation and/or the formation of greater numbers of nuclei for the subsequent epitaxial crystal growth.

Glass-ceramics with fine-grained microstructures and thermal expansion values ranging from 36 to $73 \times 10^{-7} \text{ K}^{-1}$ in the $20\text{-}700^\circ\text{C}$ range were obtained.

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