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Crystallisation in the SrO-MgO-ZrO_2-SiO_2 (SMZS) system glasses

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The SrO-MgO-ZrO_2-SiO_2 quaternary system was first investigated in 1989. It was reported that the lowest liquidus temperature is as ∼1000°C and located near the SrO-SiO_2 edge of the composition tetrahedron. Since the system has a wide range of glass formation, it has been extensively examined with the present study. After melting, depending on viscosity, glass melts tend to crystallise on cooling if the cooling rate is too slow to prevent such phenomenon. It is this behaviour that initiated investigation into the crystallisation ability of this glass system. As SMZS glasses include zirconia, surface crystallisation is generally inhibited. Hereby, crystallisation mechanisms, identification of crystal phases and microstructure of glass ceramics produced are given.

1. Introduction

In glass technology, care is taken to avoid accidental crystallisation (devitrification). The compositions usually manufactured are selected so that risks of such phenomenon can be reduced. However, there is a class of materials called glass ceramics, which are obtained by controlled crystallisation of glass. The appropriate glasses are subjected to carefully programmed thermal treatments that result in the nucleation and growth of crystalline phases. The process is designed to convert the initial vitreous phase into a polycrystalline material. A certain portion of the initial glass generally remains at the end of the treatment. According to the nature of the starting glass and the thermal treatment, a large variety of materials can be obtained from this process.

In the system ZrO_2-SiO_2, the thermal stability and nature of the dissociation of zircon, $ZrSiO_4$, were extensively studied by Grain [1]. He also carried out detailed studies in the system ZrO_2-MgO. The MgO-SrO system has been investigated by Wartenburg and Prophet [2]. They reported a eutectic at 22.2 weight (wt.)% MgO level and at a temperature just above 1900°C but no compound formation.

Noguchi *et al.* [3], who constructed the ZrO_2-SrO phase diagram, established the liquidus boundaries and confirmed previously reported binary compounds $SrZrO_3$, $Sr_4Zr_3O_{10}$ and Sr_2ZrO_4, which melt congruently at 2646°C, 2674°C, 2325°C, respectively as well as the compound $Sr_3Zr_2O_7$ which dissociates in the solid state at about 1700°C to form $Sr_4Zr_3O_{10}$ and Sr_2ZrO_4.

The SiO_2-SrO system has been examined by several workers and a modified diagram was proposed by Fields *et al.* [4], which showed three compounds, Sr_3SiO_5, Sr_2SiO_4 and $SrSiO_3$ congruently melting at 2170°C, 2325°C and 1580°C, respectively.

A limited investigations of the system ZrO_2-SrO-SiO_2 was made by Dear [2] who determined the solid state compatible phases and reported the compound $Sr_6ZrSi_5O_{18}$ melting incongruently above 1600°C to form $SrZrO_3$ and liquid. The existence of this phase was later confirmed by Galkin and Chukhlantsev [5] who investigated the isoplethal section on the join SrO-$ZrSiO_4$ in the temperature range 1150–1350°C. No reported data have been found for the ternary system ZrO_2-MgO-SrO other than those for the limiting binary systems already mentioned. Ghanbari [6] examined the ZrO_2-SrO-SiO_2, ZrO_2-MgO-SrO and MgO-SrO-SiO_2 ternary systems in detail. He identified α-cristobalite, $ZrSiO_4$, $SrZrSi_2O_7$ that was reported to melt peritectically at 1470°C by himself [7], ZrO_2, Sr_3SiO_5, Sr_2SiO_4, $SrSiO_3$ and liquid phase in the ZrO_2-SrO-SiO_2 system, depending on the composition and firing temperatures. In the ZrO_2-MgO-SrO system, MgO, $Sr_4Zr_3O_{10}$, $Sr_3Zr_2O_7$, Sr_2ZrO_4, $SrZrO_3$, cubic-ZrO_2 and SrO have been identified. Additionally, in the MgO-SrO-SiO_2 ternary system, α-cristobalite, $MgSiO_3$, Mg_2SiO_4, $Sr_2MgSi_2O_7$, $SrSiO_3$, MgO, $Sr_3MgSi_2O_8$, Sr_2SiO_4 and liquid phases were determined.

It was shown that silica tends to combine with SrO rather that MgO, forming a glassy phase which is ejected from the bulk ceramic during sintering and hence small amounts of SrO may assist in the stabilisation of ZrO_2 by reducing the exsolution of MgO from Mg-partially stabilised zirconia (PSZ) (Drennan and Hannink [8], and Former *et al.* [9]). In the SMZS system the zirconia phase was found to be monoclinic in all quenched specimens and there appeared to be no stabilising effect of SrO in the presence of silica, a result similar to Ghanbari's study [7].

2. Experimental procedure

2.1. The coding of glasses

In order to find easily melting glass compositions in the SMZS system, at the beginning of the study 4 different

TABLE I The starting glass compositions in wt%

Composition	SiO_2	ZrO_2	SrO	MgO
1	50	4.6	37.7	7.7
2	50	6.5	38.0	5.5
3	50	8.3	35.2	6.5
4	50	8.3	32.7	9.0

glass compositions with 50% silica were chosen near eutectic points in the lights of Ghanbari's report [6], (Fig. 1). Glass compositions were coded in the form of $SiO_2/ZrO_2/SrO/MgO$ (in wt%) as 50/4.6/37.7/7.7, 50/6.5/38/5.5, 50/8.3/35.2/6.5 and 50/8.3/32.7/9 (Table I). When other oxides such as Al_2O_3 and TiO_2 were added, glass compositions were then named with the symbol of Al + Ti at the end of their codes, such as $SiO_2/ZrO_2/SrO/MgO/Al + Ti$.

As a second step the levels of MgO, SrO and ZrO_2 were kept constant at the relative proportions already used in the first 4 compositions as ZrO_2/SiO_2, SrO/SiO_2 and MgO/SiO_2 and the amount of silica in glasses was increased to see its effect on melting behaviour, some physical and thermal properties [10, 11] and finally chemical durability [12]. Consequently, 24 different glass compositions, with silica levels varying from 35 to 62%, were produced for this purpose.

2.2. Batch preparation

For preparing glass batches mainly Loch Aline sand (−53 μm) with high purity, $SrCO_3$, zirconium nitrate [$Zr(NO_3)_4$], TiO_2 and LiF (used for quantitative x-ray studies) from BDH Ltd. (UK), ZrO_2 from BDH Ltd. (UK) and Magnesium Electron Ltd. (UK), $Mg(OH)_2$ and $Al(OH)_3$ from Fisons Co. were used. Dried components of the batch were weighed ± 0.01 g to give a total batch weight of either 100 or 300 g glass. Then, the major components were first mixed together for 5 min manually, after that, minor components were sprinkled evenly over the surface of the batch. Finally, the whole batches are mixed for further 10 min. Occasionally, they were also mechanically rolled for 30 min to achieve thoroughly mixed batches.

2.3. Melting

For melting, depending on the temperature required, a gas furnace or an electrically heated furnace was employed. A preheated mullite and an alumina crucible were used for the glasses containing 60 to 50% silica. However, the glasses with 45 to 40% silica and higher amount of zirconia caused corrosive reactions between glass melt and mullite or alumina crucibles. Therefore, for these groups only a Pt crucible was used to prevent the deterioration of the crucible.

During batch loading, intervals of 15 min were applied. The furnace temperature was set to be in a range of 1400 and 1640°C throughout the study.

2.4. Crystallisation

For determining the crystallisation behaviour of glasses in SMZS system, type of crystalline phases, their size and shapes in final glass-ceramic products, the role of glass constituents on crystallisation, the effect of temperatures used in heat treatment cycle (HTC) on nucleation and crystallisation process, the combinations of differential thermal analysis (DTA), x-ray diffraction (XRD), optical microscopy, scanning

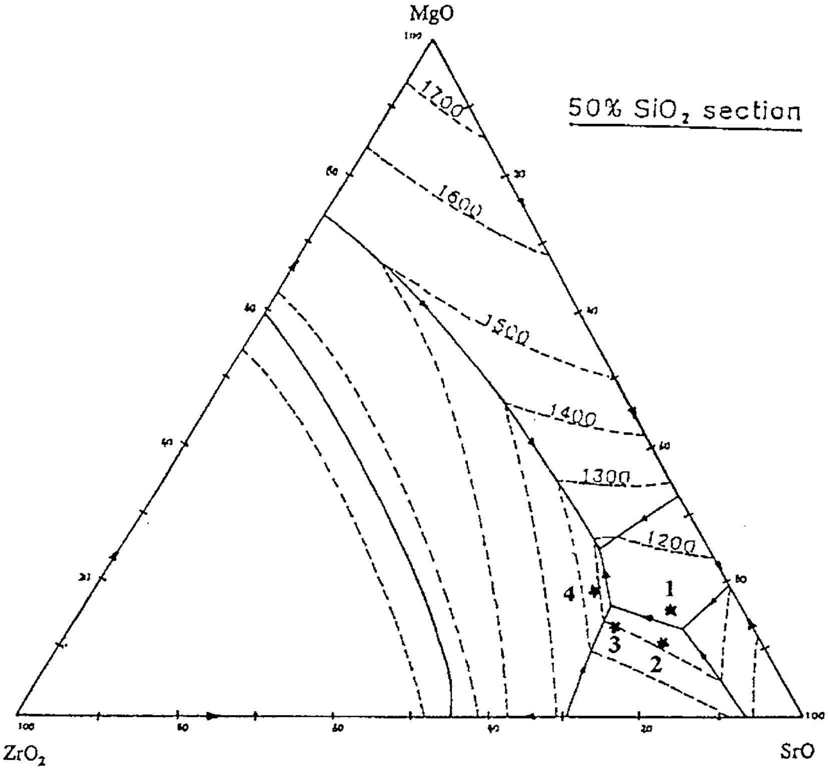


Figure 1 MgO-SrO-ZrO_2 phase diagram at 50 wt% silica section after Ghanbari [7]. It also shows the starting 4 compositions in the present study.

electron microscopy (SEM) and energy dispersive x-ray analysis (EDS) techniques were employed.

Quantitative x-ray analysis developed by Monshi and Messer [13] was also used for one chosen composition of glasses with 40% silica, 40/13.5/34/12.5, since the final stage of the current study concentrated on this group of glasses. First of all, major crystalline phases were determined for this glass heat treated by using a nucleation temperature of 790°C for 2 h and crystallisation temperature of 1130°C for a period of time changing from 11 to 48 h. The crystalline phases were identified as $Sr_2MgSi_2O_7$, $SrZrSi_2O_7$ and monoclinic (m)-ZrO_2; $SrSiO_3$ could not be detected by XRD studies for this particular glass. After identification, reference materials of these crystalline phases have been prepared [10]. Then, a mixture of these materials was made by using the composition of 25 wt% $SrZrSi_2O_7$, 35 wt% $Sr_2MgSi_2O_7$ and 20 wt% m-ZrO_2. XRD study of the mixture was conducted in order to identify the intensities of x-ray peaks of these crystalline phases. LiF was selected as the internal standard since some of x-ray peaks of CaF_2 have overlapped some of peaks of crystal phases. To find accuracy of slope ratio method, weight ratios of mixtures to LiF and reference material to LiF were chosen as 1 : 2 and 1 : 1. The peak areas were estimated from the chart by multiplying peak heights, after accounting for background, by the peak widths at half the peak heights. The intensity ratios were obtained by dividing the peak areas by the area of the LiF peak.

The selected peaks for m-ZrO_2, $SrZrSi_2O_7$, $Sr_2MgSi_2O_7$ and LiF were at 28.3, 29.3, 43.5 and 65.7° of 2θ values, respectively. Intensity ratios of each phase relative to the standard were plotted against the values of the weight ratios of the mixture to the standard. After determining the slopes of the analysis lines, the slopes of the reference lines were established. This was done in a similar way to that used for the analysis lines but the samples to be x-rayed were mixtures consisting of a pure phase and LiF at ratios of 0.5 and 1.

Mixture of three crystalline phases was made by using the composition of 35 wt% $Sr_2MgSi_2O_7$, 25 wt% $SrZrSi_2O_7$ and 20 wt% m-ZrO_2as mentioned above. The amount of these phases were found quantitatively as 35.74% $Sr_2MgSi_2O_7$, 25.70% $SrZrSi_2O_7$ and 20.64% m-ZrO_2 with a total error of 2.08% by means of slope method. After establishing both reference and analysis lines for m-ZrO_2, $SrZrSi_2O_7$, $Sr_2MgSi_2O_7$, samples of the 40/13.5/34/12.5 glass heat treated by using a serial of heat treatment, in which holding times at crystallisation temperature changed from 11 to 48 h, were crushed to fine powder and mixed with internal standard material LiF by the mixture to LiF ratio of 1 : 2 and 1 : 1. 20 min mixing in a mortar with acetone was made before x-ray sample of 100 mg powder was prepared. Intensity ratios versus weight ratio graphs have been determined for the prepared mixtures. It was noticed that when holding time at 1130°C increases the amount of residual glass in final glass ceramic product, which was hold at that temperature for 48 h, decreases down to 0.7%. The quantity of each crystalline phase was found by slope of mixture/slope of reference ratio.

2.5. Characterisation

Samples crystallised for different periods of time, were crushed and ground to a fine size. Then, they were mounted on a flat plate and scanned by a Philips PW 1050/25 goniometer with a graphite monochromator and PW 1010 generator operating at 50 kV and 30 mA current with Cu K_α monochromatic radiation (= 1.5418 Å) at a speed of 2°/min with a sensitivity of either 4×10^3 or 1×10^4. All materials were scanned over the range of 10 to 70°. The chart speed and the time constant was 20 mm/min and 14 sec, respectively.

For microstructural studies, glass ceramic samples were vacuum impregnated then, ground flat using diamond wheels with 120 and 220 grits. Polishing was carried out manually on silicon carbide papers with 240, 400, 600 and 1200 grits. Fine polishing was then continued on a rotating topping wheel. Diamond pastes of different grades (6, 3 and 1 μ) were applied to the relevant wheels and samples were polished on each wheel. Polished samples were investigated using a Polyvar (MET) optical microscope. For further microstructural studies of heat treated samples, a scanning electron microscopy (SEM-Cam Scan) operated at 20 kV was used. The polished samples were carbon coated. Working distance has changed from 24–22 mm. As well as surface investigation by SEM getting either a secondary electron or back scattered electron images, energy dispersive x-ray analysis (EDS) has also made in order to identify the composition of crystalline phases and make a comparison between the results achieved from this method and XRD.

3. Results and discussion

Crystalline phases were determined by XRD. According to these studies, the phases depending on glass composition and HTC's were identified as mainly α-cristobalite, zircon ($ZrSiO_4$), m-ZrO_2, $SrSiO_3$, $SrZrSi_2O_7$, $Sr_2MgSi_2O_7$. When silica content increased in a glass composition, the possibility of α-cristobalite formation was also increased. At higher level of silica, such as 61%, the main crystalline phases were α-cristobalite and zircon. After HTC 1 (Table II), the 61.5/8.5/25.4/4.6 glass was still largely glassy, but showed typical α-cristobalite peaks, which are labelled as c, as well as those of zircon, which are shown as zr and m-zirconia (z) in Fig. 2. After identifying x-ray peaks of these phases, crystallised samples were investigated using SEM. From Fig. 3, for the 61.5/8.5/23.5/6.5 glass $ZrSiO_4$ (white) needles and α-cristobalite dendrites (black coloured) can be seen in a glassy matrix. Crystallisation of both crystalline phases started from surface with crystal fronts growing inwards. EDS spectra for the 61.5/8.5/23.5/6.5 glass showed the existence of α-cristobalite and zircon, which is indicated in Figs 4 and 5, respectively.

Glasses with 55% silica have shown crystals of $Sr_2MgSi_2O_7$ as well as α-cristobalite, zircon and m-ZrO_2 after suitable heat treatments. Crystal peaks are shown in Fig. 6 for the 55/4.2/33.9/6.9 glass treated by HTC 2. The 55/5.8/34.2/5 glass was examined by

TABLE II Heat treatment parameters used for crystallisation of glasses in SMZS system[a]

	Heat treatment cycles (HTC)				
Glass	Nucleation temp. (°C)	Holding time (hour)	Crystal growth temp. (°C)	Holding time (hour)	HTC no
61.5/8.5/25.4/4.6 and 61.5/8.5/23.5/6.5	850	2	1150	16.5	1
55/4.2/33.9/6.9 and 55/5.8/34.2/5	770	3	1070	48	2
50/4.6/37.7/7.7	760	2	980	24	3
45/9.2/38.7/7.1	790	2	1200	16	4
40/10/39.3/10.7 and 40/10/42.2/7.8	750	3	950	48	5
40/10/39.3/10.7 and 40/10/42.2/7.8	800	2	1130	Over 48 h	6
40/8/40/12, 40/6/50/4, 40/15/35/10, 40/6/34.3/10.7/Al + Ti and 40/4/35/12/Al + Ti	800	2	1150	16	7
40/13.5/34/12.5	790	2	1130	12	8
40/13.5/34/12.5	790	2	1130	17	9
40/13.5/34/12.5	790	2	1130	19	10

[a] Heating rate from room temperature to nucleation temperature was 5°C/min, from nucleation to crystal growth temperature was 2°C/min and cooling rate was 1°C/min.

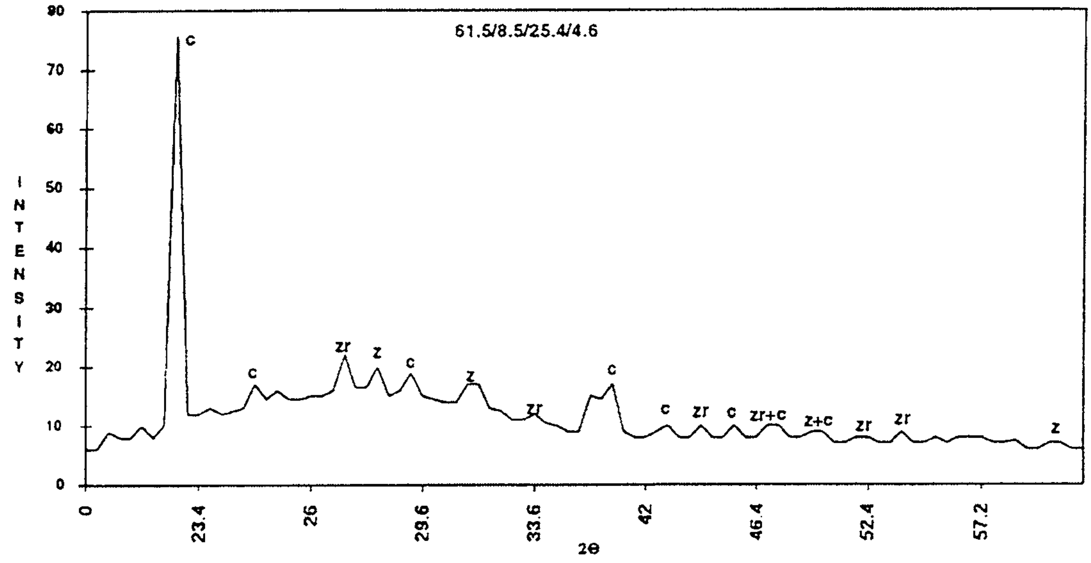
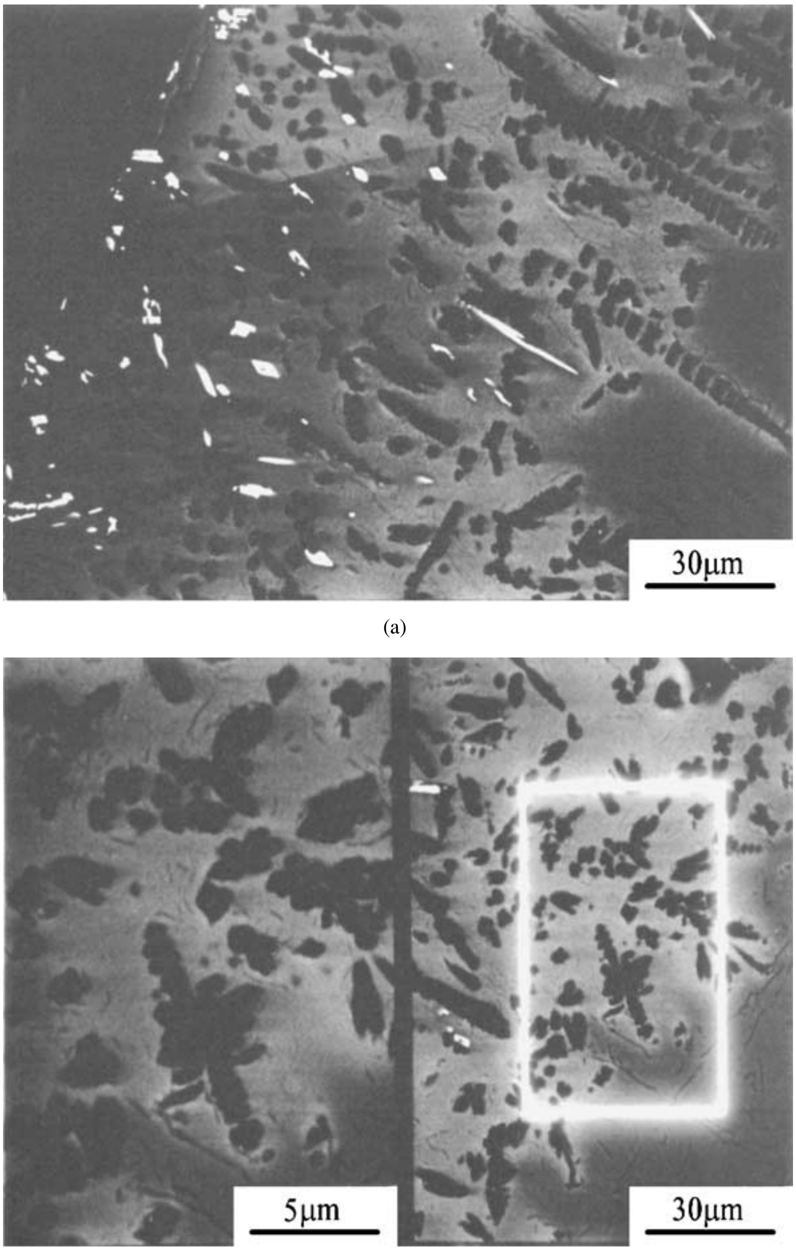


Figure 2 X-ray trace for the 61.5/8.5/25.4/4.6 glass heat-treated at 850°C for 2 h then at 1150°C for 16.5 h (HTC 1). c refers to α-cristobalite, zr, zircon and z, m-zirconia.

optical microscopy and it has been seen that crystallisation also started from the surface of the glass (Fig. 7). XRD peaks for α-cristobalite and zircon were not seen for glasses with 50% silica level. XRD results of the 50/4.6/37.7/7.7 glass treated by HTC 3 can be seen from Fig. 8. In this case only peaks of $Sr_2MgSi_2O_7$ and m-ZrO_2 were detected. High SrO and MgO contents in glass compositions seem to favour the $Sr_2MgSi_2O_7$ formation. For detailed phase determination of the glasses with 45 % silica treated by HTC 4, an SEM was employed (Fig. 9). As can be followed from Fig. 9, dark coloured dendrites were identified as $Sr_2MgSi_2O_7$ and dark grains as α-cristobalite in a glassy matrix.

For compositions with 45 and 40% silica, crystals of $SrSiO_3$, $Sr_2MgSi_2O_7$, $SrZrSi_2O_7$ and m-ZrO_2 were usually identified by XRD. Typical XRD peaks for the 40/10/39.3/10.7 and 40/10/42.2/7.8 glasses after HTC 6 (Table II) are given in Figs 10 and 11 where $SrSiO_3$ is shown as ss, $Sr_2MgSi_2O_7$ as s and m-ZrO_2 as z. Typical crystal existence starts from the surface for this group similar to the others. Fig. 12 also confirms surface crystallisation for the 40/10/42.2/7.8 and 40/10/39.3/10.7 glasses treated by HTC 5. By means of SEM and EDS m-ZrO_2 was found as white grains on $Sr_2MgSi_2O_7$ dendrites in a glassy matrix. These white m-ZrO_2 grains of the 40/8/40/12 glass could be secondary phase due to the change of glass composition around crystals (Fig. 13). EDS result for $Sr_2MgSi_2O_7$ is shown in Fig. 14. Fig. 15 indicates $Sr_2MgSi_2O_7$ rods (grey coloured) on which $SrSiO_3$ grains are present in the 40/10/39.3/10.7 glass treated by HTC 5. When the glass compositions of 40/8/40/12 and 40/15/35/10 are considered, it can be noticed that in the 40/15/35/10 glass zirconia content was increased up to 15% with the decrease in both SrO and MgO content at constant silica level. Although the same heat treatment (HTC 7) was used for both glasses, shape of crystal phases changed (Fig. 16), but



(a)

(b)

Figure 3 (a) SEM micrograph of the 61.5/8.5/23.5/6.5 glass treated by HTC 1, showing surface crystallisation (black dendrites are cristobalite and white needles zircon). (b) SEM micrograph of the same glass indicating the growth of dendritic cristobalite crystals inwards.

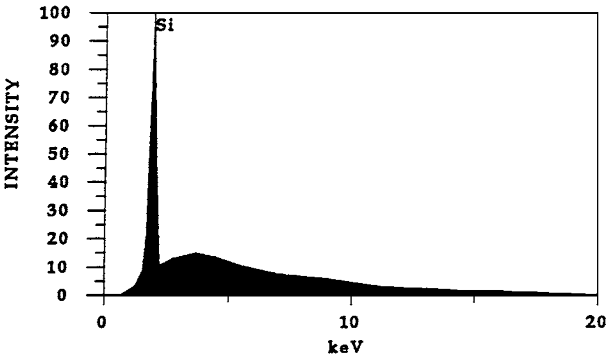


Figure 4 The EDS result for cristobalite in the 61.5/8.5/23.5/6.5 glass treated by HTC 1.

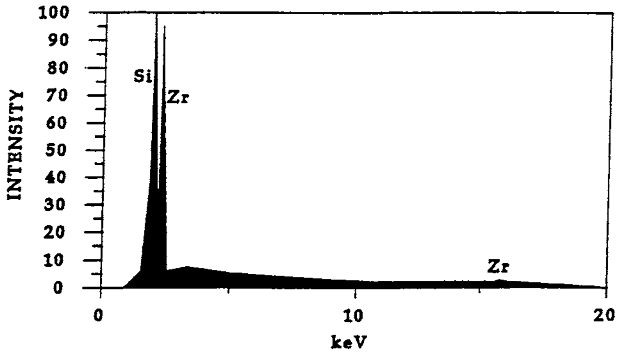


Figure 5 The EDS result for zircon in the 61.5/8.5/23.5/6.5 glass treated by HTC 1.

the crystallisation behaviour did not change. EDS analysis result for $SrZrSi_2O_7$ is given in Fig. 17. Although XRD patterns were taken from all heat treated glass samples, only a few examples are given in figures for glass compositions with silica content changing from 62 to 40% silica.

When Al_2O_3 was added into glass compositions labelled as 40/6/34.3/10.7/Al + Ti and 40/4/35/12/

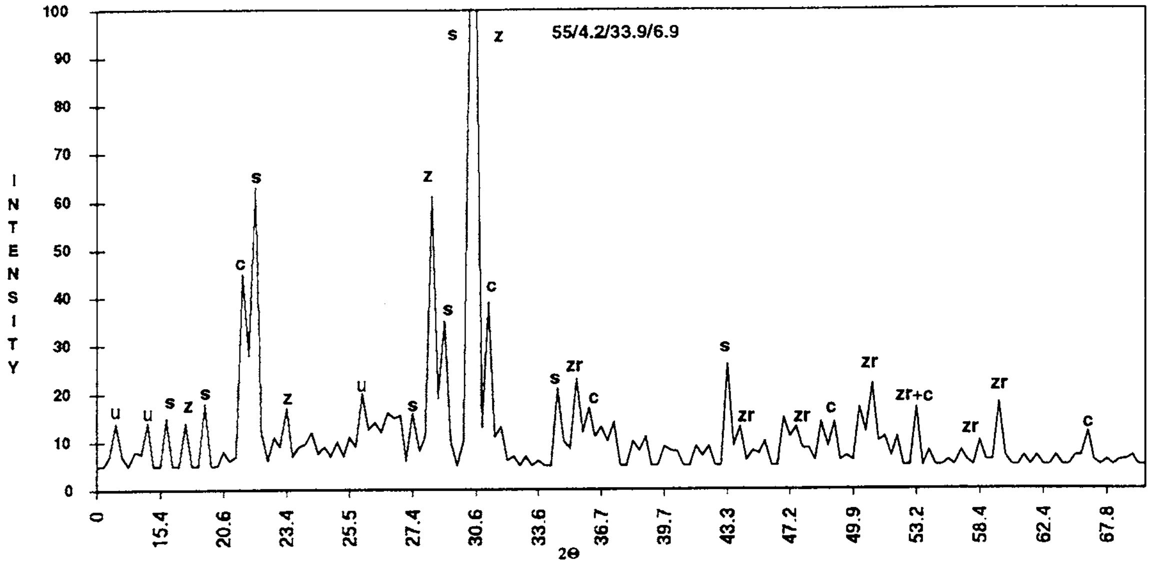
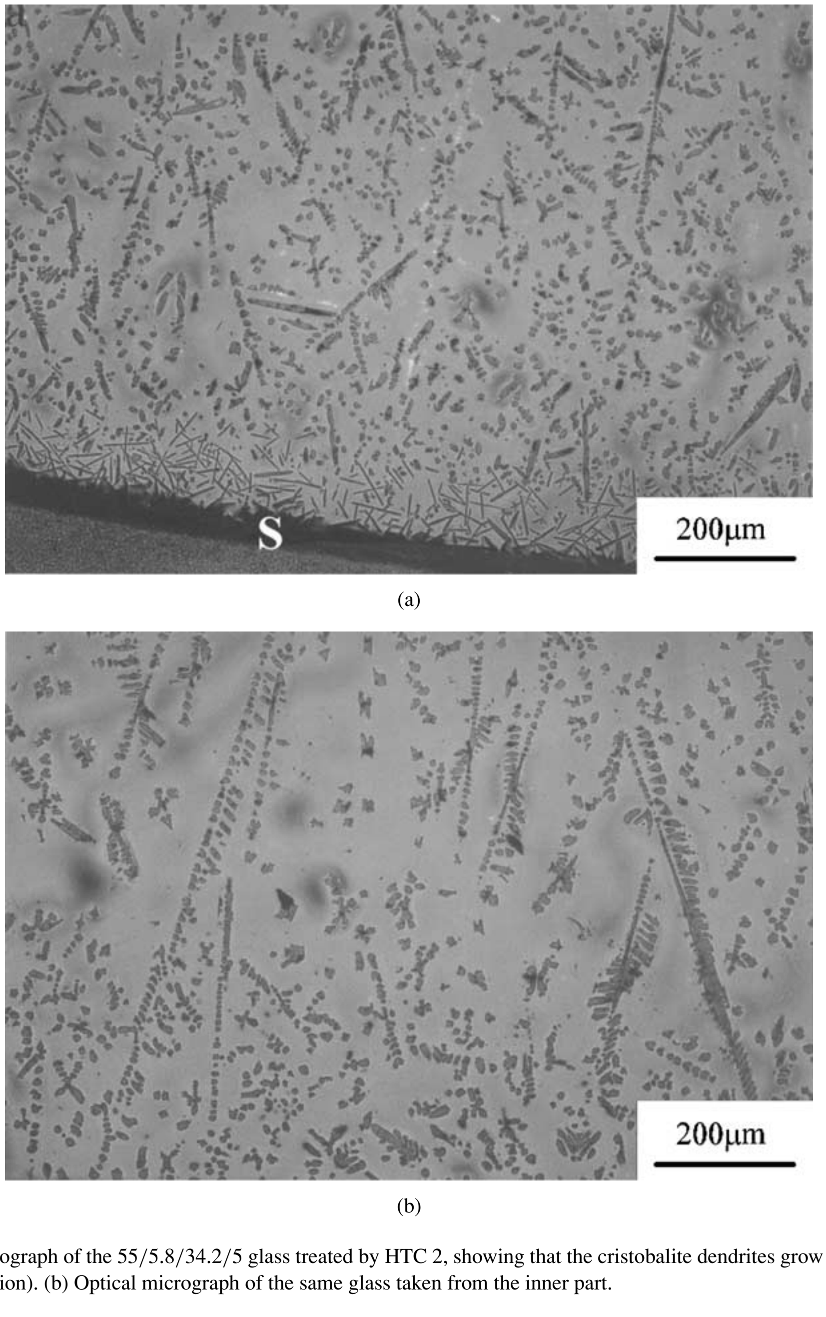


Figure 6 X-ray trace for the 55/4.2/33.9/6.9 glass heat-treated at 770°C for 3 h then at 1070°C for 48 h (HTC 2). c refers to α-cristobalite, zr, zircon, z, m-zirconia, s, $Sr_2MgSi_2O_7$ and u, unknown.



(a)

(b)

Figure 7 (a) Optical micrograph of the 55/5.8/34.2/5 glass treated by HTC 2, showing that the cristobalite dendrites grow inwards (S stands for the surface of glass cross section). (b) Optical micrograph of the same glass taken from the inner part.

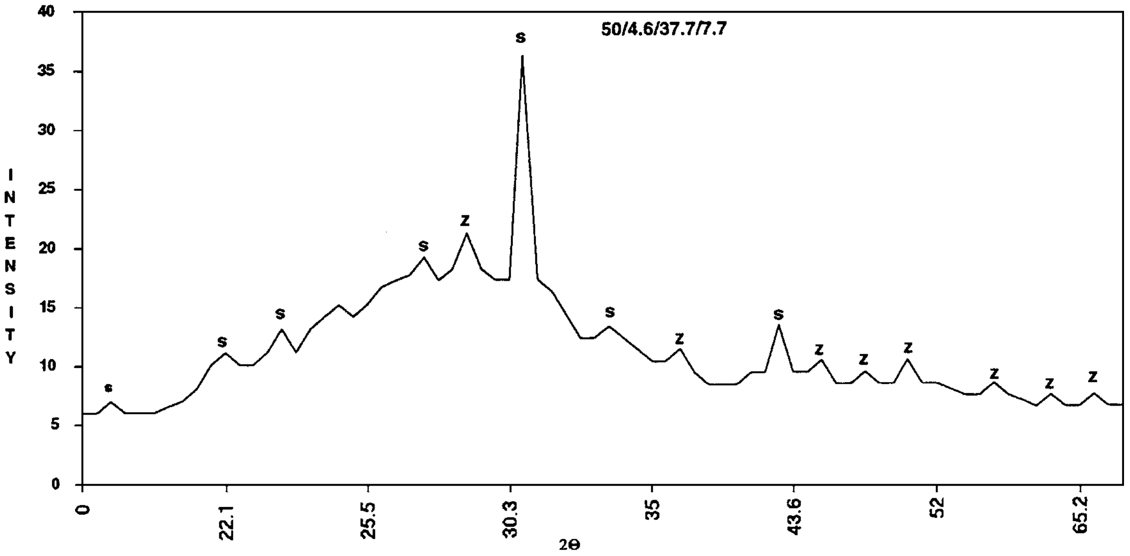


Figure 8 X-ray trace for the 50/4.6/37.7/7.7 glass heat-treated at 760°C for 2 h then 980°C for 24 h (HTC 3). s refers to $Sr_2MgSi_2O_7$ and z, m-zirconia.

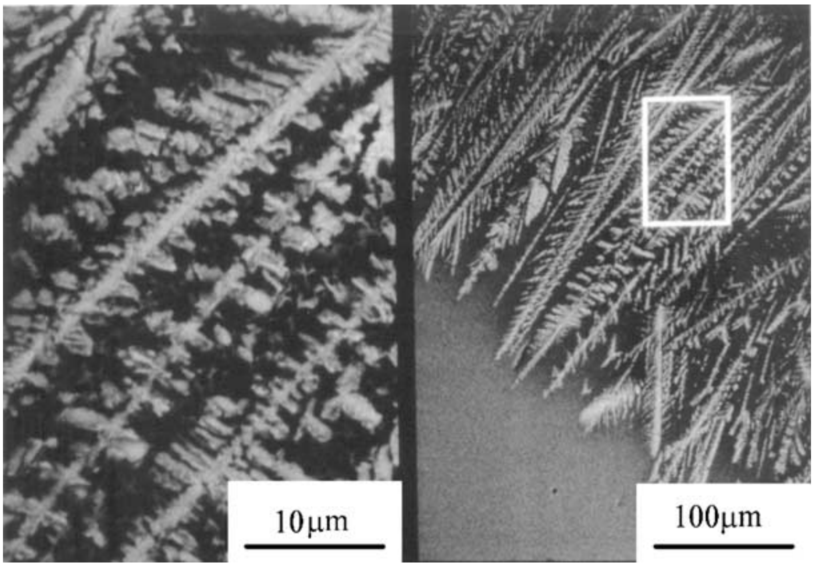


Figure 9 SEM micrographs of the 45/9.2/38.7/7.1 glass heat-treated at 790°C for 2 h then at 1200°C for 16 h (HTC 4). Dendrites were identified as $Sr_2MgSi_2O_7$.

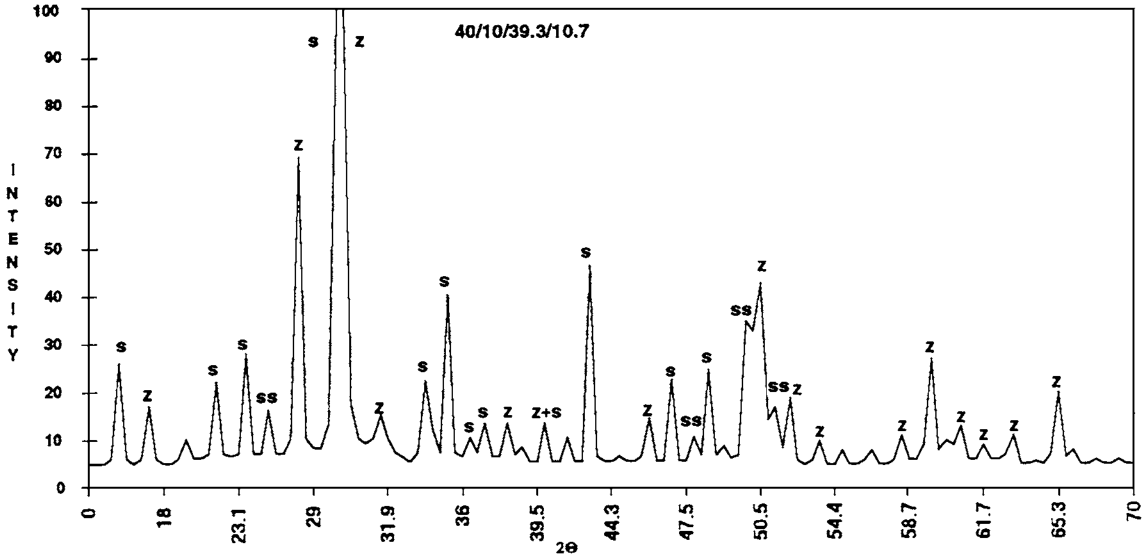


Figure 10 X-ray trace for the 40/10/39.3/10.7 glass heat-treated at 800°C for 2 h then at 1130°C for more than 48 h (HTC 6). s refers to $Sr_2MgSi_2O_7$, z, m-zirconia and ss, $SrSiO_3$.

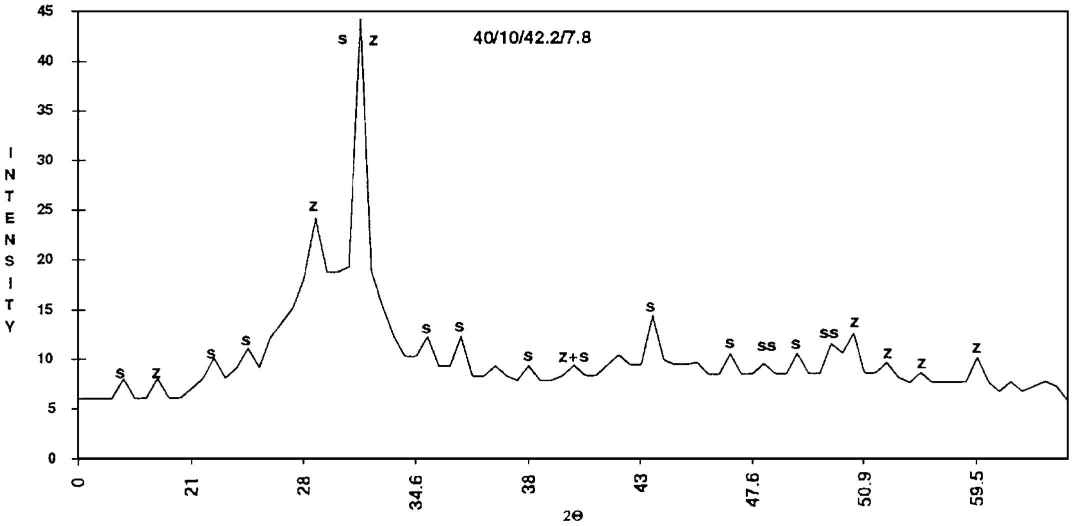
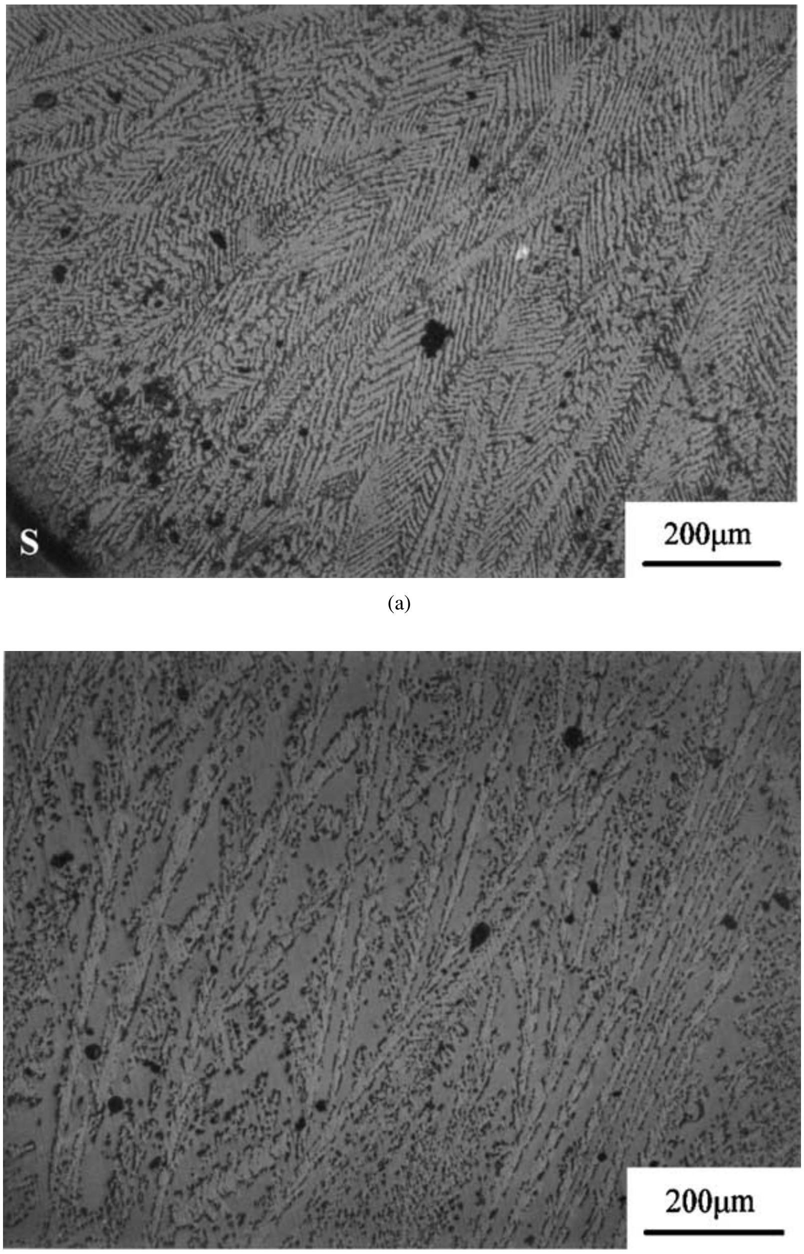


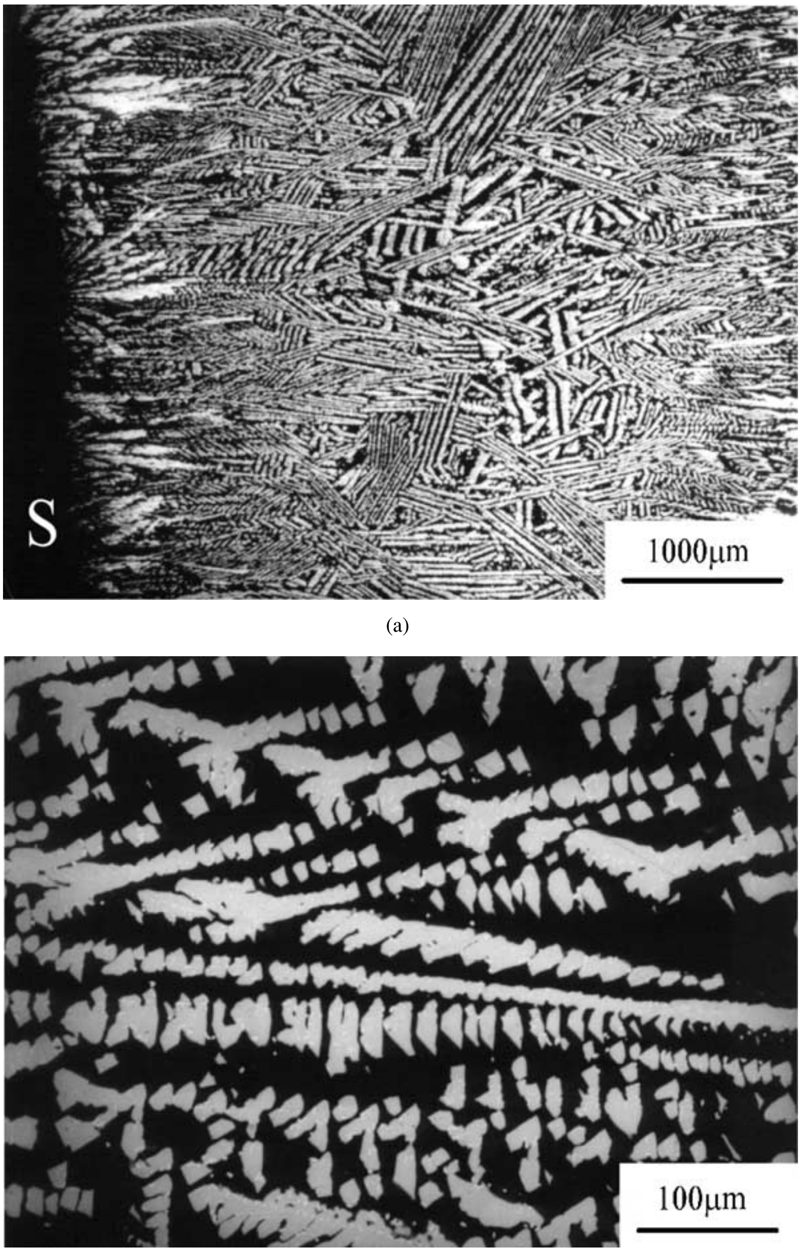
Figure 11 X-ray trace for the 40/10/42.2/7.8 glass treated by HTC 6. s refers to $Sr_2MgSi_2O_7$, z, m-zirconia and ss, $SrSiO_3$.



(a)

(b)

Figure 12 (a) The optical micrograph of the 40/10/42.2/7.8 glass heat-treated at 750°C for 3 h then at 950°C for 48 h (HTC 5) (S stands for the surface of glass cros section), (b) The optical micrograph of the 40//10/39.3/10.7 glass treated by HTC 5. Surface crystallisation of the glasses and the growth of dendrites can be seen.



(a)

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Figure 13 (a) SEM micrograph of the 40/10/39.3/10.7 glass treated by HTC 5 (S refers to the surface of glass cros section). (b) SEM micrograph of the 40/8/40/12 glass heat-treated at 800°C for 2 h then at 1150°C for 16 h (HTC 7) showing m-zirconia particles on the $Sr_2MgSi_2O_7$ dendrites.

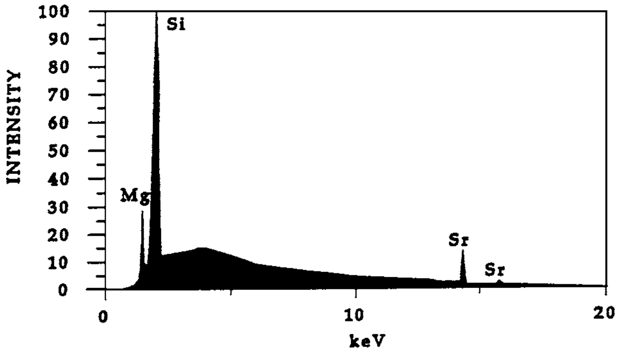
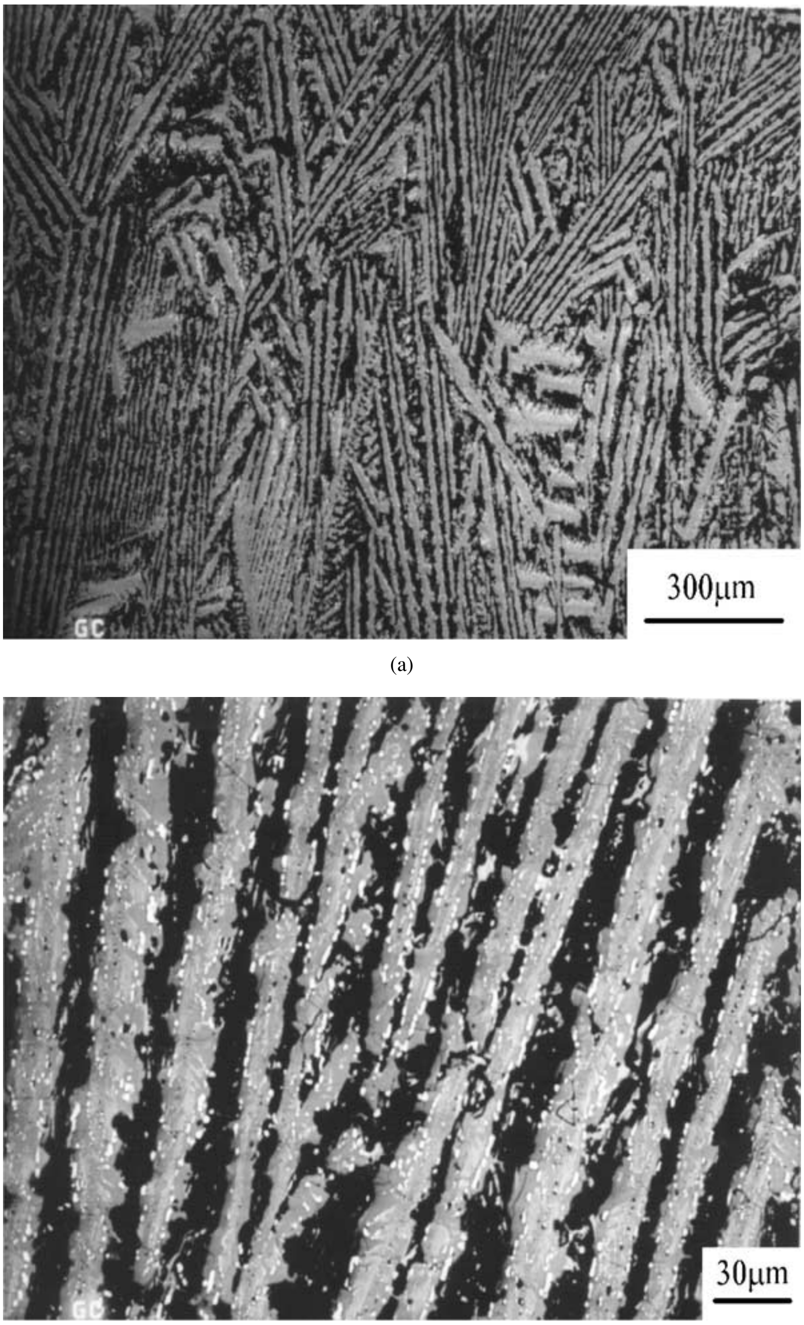


Figure 14 The EDS result for $Sr_2MgSi_2O_7$ in the 55/4.2/33.9/6.9 glass treated by HTC 2.

Al + Ti, x-ray traces showed that $SrAl_2Si_2O_8$ crystals also appeared as a minor phase.

The maximum temperature at which $Sr_2MgSi_2O_7$ coexists with liquid was reported as 1560 ± 15°C by Ghanbari [7]. The lowest temperature at which this compound coexists with liquid is 1150°C. When DTA was applied to glasses that give $Sr_2MgSi_2O_7$ crystal phase after a heat treatment, an exothermic peak was seen at about 1150°C on DTA graphs [10]. This peak was counted to belong to $Sr_2MgSi_2O_7$ for the 40/15/35/10, 45/2/45/8, 50/4/40/6, 50/10/25/15, 55/8/25/12, 40/6/34.3/10.7/ Al + Ti, 40/4/ 35/12/Al + Ti, 40/12.5/35/12.5 and 40/13.5/ 34/12.5 glasses. Ghanbari [7] also showed that parts of the system ZrO_2-SrO-SiO_2 exhibit low liquidus temperature down to about 1250°C and the existing field of $SrZrSi_2O_7$, which was previously unreported ternary compound before Ghanbari, is bounded by this lowest liquidus temperature. Where $SrZrSi_2O_7$ was detected by XRD pattern, DTA results also revealed an exothermic peak at about 1250°C for the 45/2/45/8, 40/15/35/10, 40/12.5/35/12.5 and 40/13.5/34/12.5 glasses. When a crystallised product of $SrSiO_3$ was



(a)

(b)

Figure 15 (a) and (b) SEM micrographs of the 40/10/39.3/10.7 glass treated by HTC 5. The grey colour rods were identified as $Sr_2MgSi_2O_7$ and white particles as $SrSiO_3$.

identified in XRD traces, the DTA graphs showed an exothermic peak at about 1050°C. This peak might be showing the formation of $SrSiO_3$ for the 50/10/25/15 glass. Although the glasses did not crystallise after melting, when they were re-heated from room temperature, some broader peaks were observed during DTA studies. However, the DTA records did not show clear, large peaks which may indicate easy and rapid crystallisation. The fact that the peaks are smaller and broader, this may indicate difficult nucleation and slow growth. The latter apparent peaks might be due to sintering, flow of glass, altering geometry of samples and degree of covering thermocouple tip. Nevertheless, according to XRD, SEM and EDS analysis of the glasses in the system, the formation of crystal phases of $SrSiO_3$, $Sr_2MgSi_2O_7$, $SrZrSi_2O_7$ is very clear and those smaller and broader peaks may be counted for being crystallisation peaks. On the other hand, to prove that peaks are due to crystallisation, one should examine samples quenched from just below and above each particular peak.

The exothermic peak of some glasses seen at temperatures above 1200°C in DTA could be explained as the peak which may belong to m-ZrO_2 since these glasses have not shown $SrZrSi_2O_7$ crystal phase after a heat treatment (Fig. 10 for the 40/10/39.3/10.7 glass and Fig. 11 for the 40/10/42.2/7.8 glass). Increasing ZrO_2 content in glass composition accelerates the formation of $SrZrSi_2O_7$ after a suitable heat treatment process. When ZrO_2 content was increased from 10% (the 40/10/39.3/10.7 and 40/10/42.2/7.8 glasses) to 13.5% (the 40/13.5/34/12.5 glass) x-ray peaks which

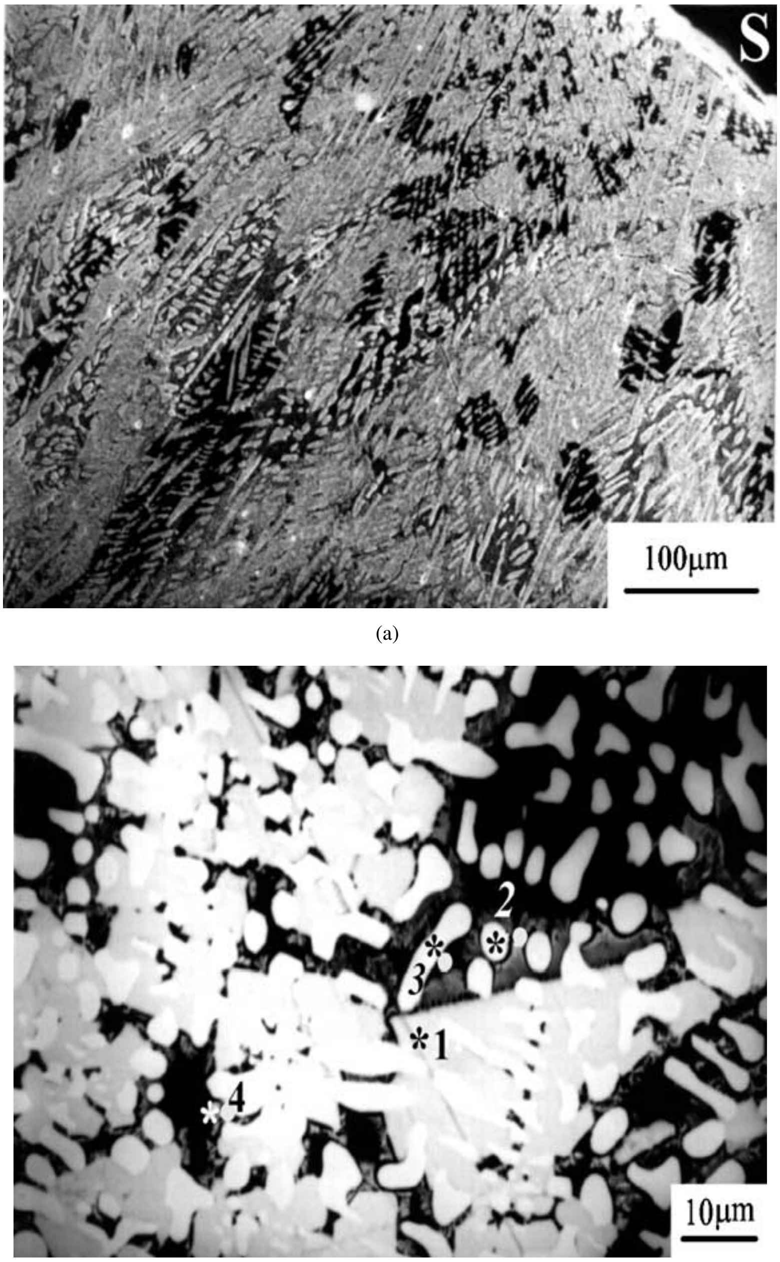


Figure 16 (a) and (b) SEM micrographs of the 40/15/35/10 glass treated by HTC 7 (S indicates the surface of glass cros section). 1 shows $Sr_2MgSi_2O_7$ crystal, 2, $SrZrSi_2O_7$ crystal, 3, $SrZrSi_2O_7$ crystal and 4, glassy phase.

belong to $SrZrSi_2O_7$ appeared and the formation of this crystalline phase has been detected with SEM and EDS studies. DTA results give two exothermic peaks at high temperatures of about 1239°C and 1285°C. These may belong to zircon and α-cristobalite respectively for the 55/8/25/12 glass.

Quantitative x-ray studies of the 40/13.5/34/12.5 glass showed that the major crystalline phase was $Sr_2MgSi_2O_7$ with the final amount of 60.96% after 48 h holding time at 1130°C. This glass has already reached up to 95.36% crystallisation after being held 11 h at 1130°C. During these heat treatment processes quantitative x-ray results have shown that the amount of $Sr_2MgSi_2O_7$, as major phase, was between 54 and 70%. As can be seen from the Fig. 18 almost complete elimination of glassy phase is possible. The other interesting result of this study is that there is a conversion of $Sr_2MgSi_2O_7$ to $SrZrSi_2O_7$ between 18 and 24 h then its reversal and this happens again at 41–48 h. These two crystals may have almost the same formation energy and even a little change in temperature might favour the formation of one of them. Such conversion could be happening with the reaction below:

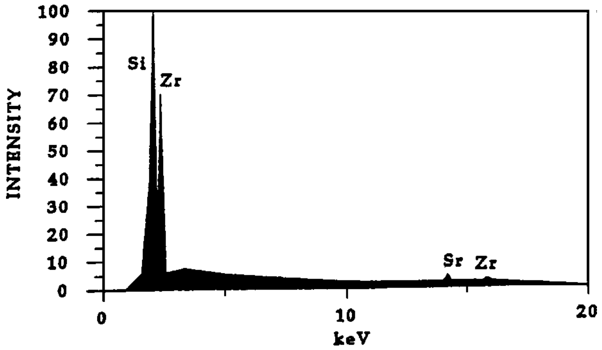


Figure 17 The EDS result for $SrZrSi_2O_7$ in the 40/15/35/10 glass treated by HTC 7.

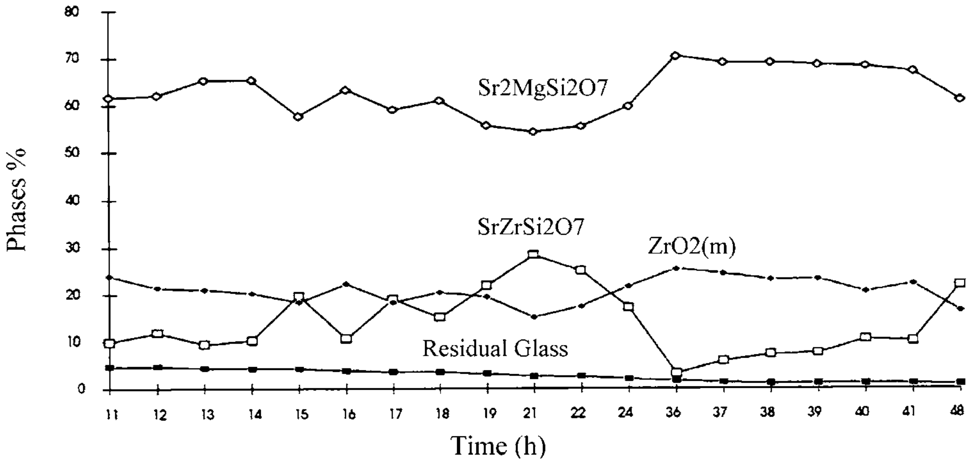


Figure 18 The amount of crystal phases of SrZrSi$_2$O$_7$, ZrO$_2$(m), Sr$_2$MgSi$_2$O$_7$ and residual glass according to the quantitative x-ray analysis of the 40/13.5/34/12.5 glass being nucleated at 790°C for 2 h then hold at 1130°C for 11–48 h.

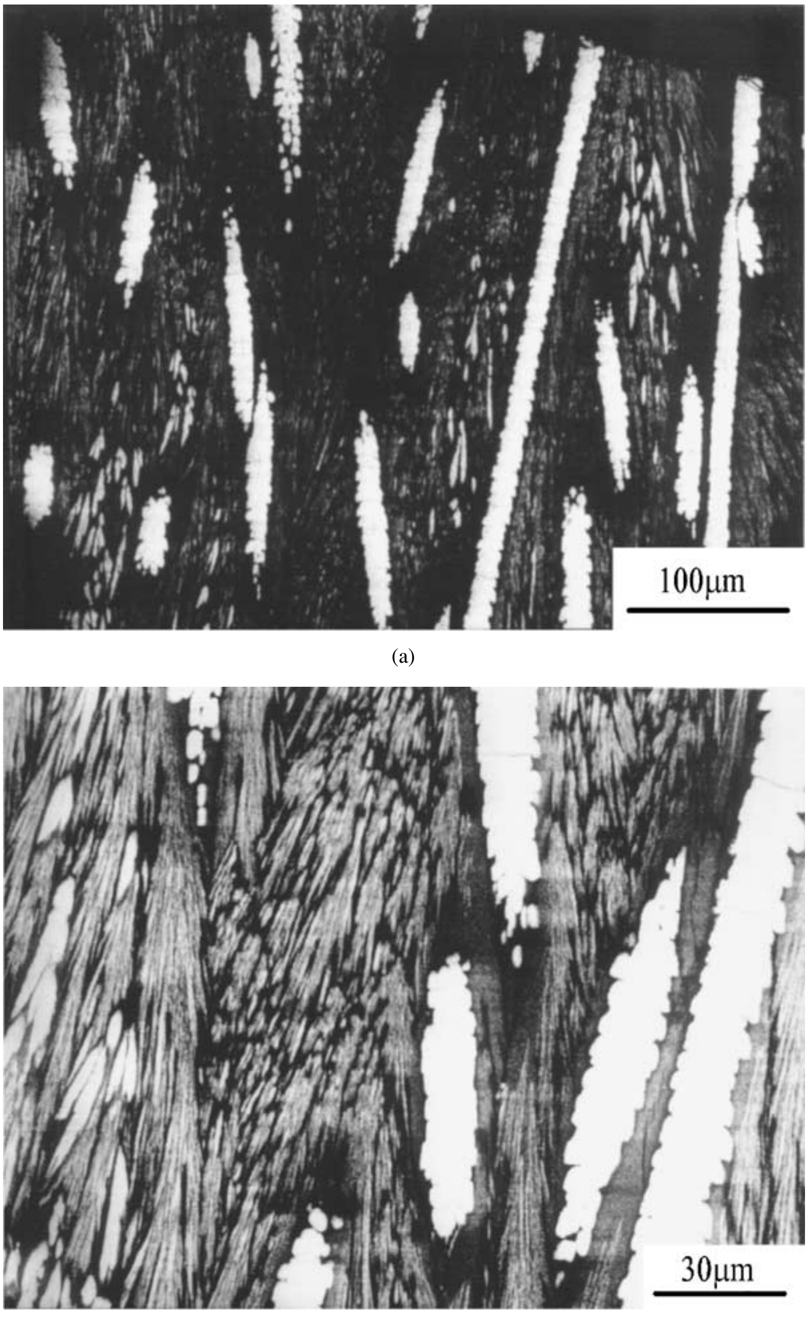
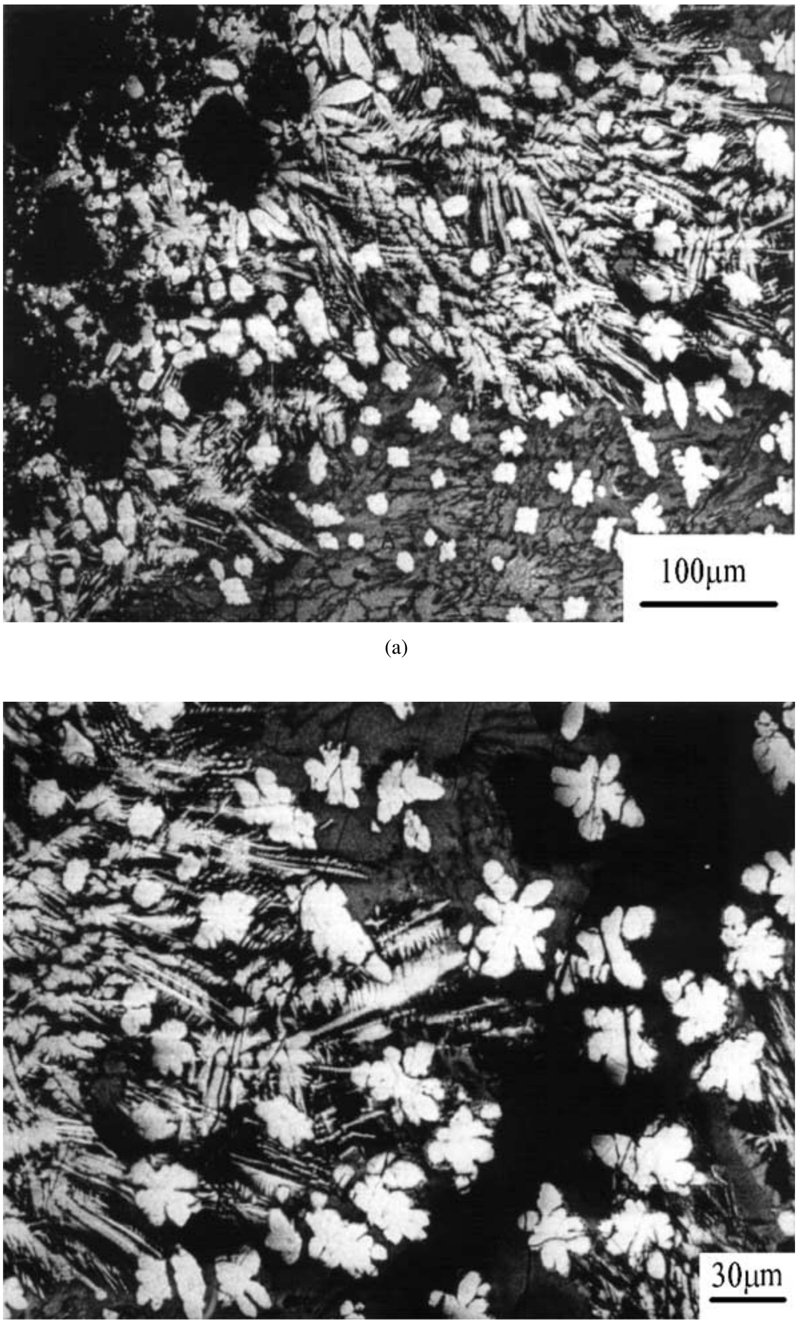


Figure 19 (a) and (b) SEM micrographs of the 40/13.5/34/12.5 glass heat-treated at 790°C for 2 h then at 1130°C for 12 h (HTC 8). In the images white colour rods were identified as Sr$_2$MgSi$_2$O$_7$.



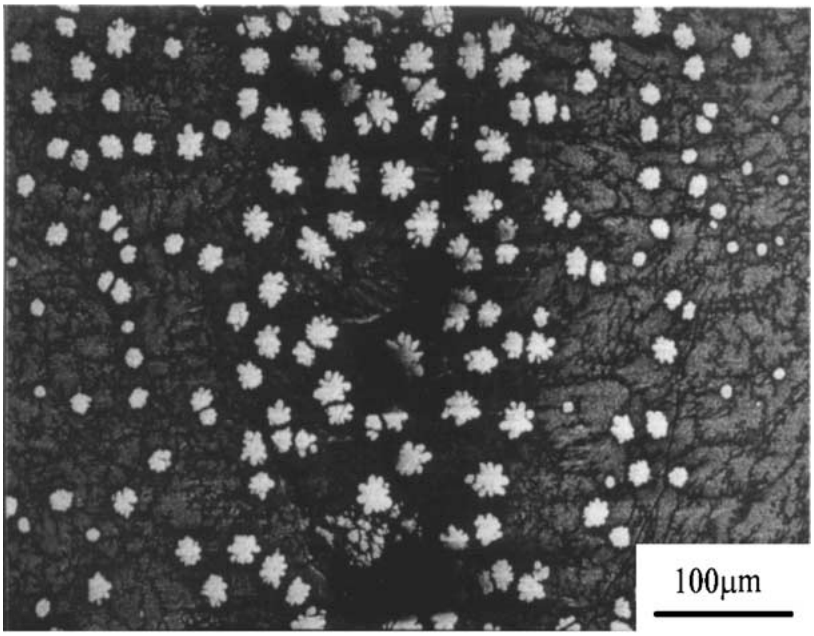
(a)

(b)

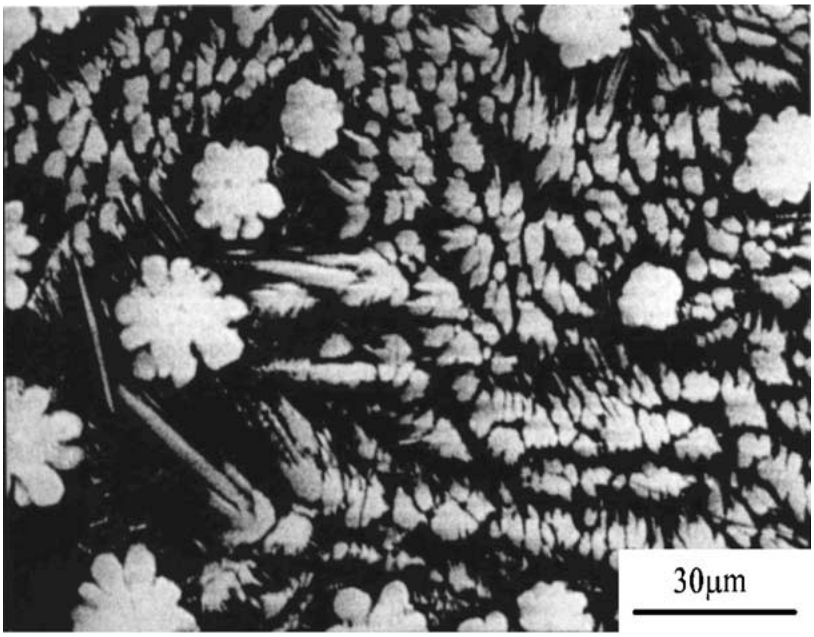
Figure 20 (a) and (b) SEM micrographs of the 40/13.5/34/12.5 glass heat-treated at 790°C for 2 h then at 1130°C for 17 h (HTC 9). Needles and leaf-like crystals were identified as $SrZrSi_2O_7$ and white colour flower-like crystals as $Sr_2MgSi_2O_7$ in both micrographs.

$$Sr_2MgSi_2O_7 + ZrO_2 \rightarrow SrZrSi_2O_7 + SrO + MgO$$

In order to find whether SrO and MgO go into glassy phase or act in a rather different way further microstructural studies are needed. An increase in the formation of $SrZrSi_2O_7$ was from 9.9 to 21.9% with a decrease in m-ZrO_2 content from 23.9 to 16.4%. The results suggest that m-ZrO_2 in glass may help the formation of $SrZrSi_2O_7$ with certain heat treatment time (Fig. 18). SEM pictures were taken from the 40/13.5/34/12.5 glass. Some of them can be seen from Figs 19–21. Different types of $Sr_2MgSi_2O_7$ crystals were detected. Fig. 19 has been taken from the surface of the 40/13.5/34/12.5 glass crystallised by being nucleated at 790°C for 2 h and hold at 1130°C for 12 h (HTC 8). White coloured rods have been identified as $Sr_2MgSi_2O_7$ crystals by EDS analysis. Surface crystallisation of the glass is quite obvious from Fig. 20. Fig. 21 was taken from a cross section. Crystals like leaves were identified as $SrZrSi_2O_7$ by means of EDS. Other three-step heat treatments have been used for the same glass in order to see time and temperature effect on crystallisation. Quantitative x-ray analysis have been made for 8 samples of the 40/13.5/34/12.5 glass (Table III). The temperature for nucleation was 790, and crystallisation temperatures were 1050 and 1150°C. Nucleation time was 1 and 2 h throughout this study. As can be seen from Table III, the lowest



(a)



(b)

Figure 21 (a) and (b) SEM micrographs of the 40/13.5/34/12.5 glass heat-treated at 790°C for 2 h then at 1130°C for 19 h (HTC 10) showing the forms of $Sr_2MgSi_2O_7$ crystals.

residual glass value was given by the glass sample after heat treatment in which 2 h nucleation was applied at 790°C (212). Holding time was 1 h at 1050°C and 2 h at 1150°C, respectively. Second lowest value of residual glass was reached after heat treatment in which nucleation time was 1 h at 790°C (122). Holding time for crystallisation was 2 h at 1050°C and 2 h at 1150°C. The former heat treatment gave the highest amount of $SrZrSi_2O_7$ with 22.58% and lowest amount of $Sr_2MgSi_2O_7$ with 58.56%. After 2 h nucleation at 790°C decreasing holding time at 1050°C from 2 to 1 h the heat-treated sample showed the highest content of residual glass, 4.77% (211). Temperature of 1050°C which is expected to be a temperature for $SrSiO_3$ formation may be having a positive effect on the $Sr_2MgSi_2O_7$ formation with higher holding time at this temperature. When looked at the quantitative x-ray analysis it can easily be realised that 2 h nucleation at 790°C results in a faster crystallisation. On the other hand, it was clear that with three-step heat treatment high amount of crystallisation can also be achieved within a short period of time. However, since the crystalline products are readily crystallised from surface, having coarse dendritic crystals, they are brittle materials. Adding a nucleation agent may improve crystallisation behaviour of the glasses in the system by providing bulk crystallisation and leading to a fine texture of glass ceramic products.

TABLE III Quantitative x-ray results for the samples of the 40/13.5/34/12.5 glass undergone a three-step heat treatment[a]

Symbol	$Sr_2MgSi_2O_7$ (%)	m-ZrO_2 (%)	$SrZrSi_2O_7$ (%)	Residual glass (%)
111	67.86	19.94	10.25	1.95
112	61.12	18.83	13.30	6.75
121	61.12	18.23	15.62	5.03
122	67.16	20.41	11.60	0.83
222	65.53	20.41	9.64	4.42
221	66.23	24.82	6.67	2.28
211	61.81	19.75	13.67	4.77
212	58.56	18.36	22.58	0.50

[a] Heat treatment at 790, 1050 and 1150°C for times which are shown as number, such as 211. First number indicates holding time at 790°C; second number holding time at 1050°C and third one holding time at 1150°C, respectively. Heating rate between these temperatures was 2°C/min.

4. Conclusions

1. The SMZS system glasses show surface crystallisation, resulting in brittle glass ceramics.

2. According to quantitative XRD analysis of the 40/13.5/34/12.5 glass with three-step heat treatment, 2 h nucleation at 790°C results in a faster crystallisation. On the other hand, with such a heat treatment high amount of crystallisation can also be achieved within a shorter period of time.

3. The formation of crystalline phases depend on the glass composition and heat treatment schedules and are found as mainly α-cristobalite, zircon, m-ZrO_2, $SrSiO_3$, $SrZrSi_2O_7$ and $Sr_2MgSi_2O_7$.

4. When silica content increases in a glass composition, the possibility of α-cristobalite formation also increases. At higher level of silica, such as 61%, the main crystalline phases are α-cristobalite and zircon.

5. Glasses with 55% silica posses crystals of $Sr_2MgSi_2O_7$ as well as α-cristobalite, zircon and m-ZrO_2 after a suitable heat treatment.

6. For compositions with 40 and 45% silica, crystals of $SrSiO_3$, $Sr_2MgSi_2O_7$, $SrZrSi_2O_7$ and m-ZrO_2 are usually identified.

7. When Al_2O_3 is introduced into glass compositions, after crystallisation of parent glass $SrAl_2Si_2O_8$ crystals also appear as a minor phase.

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