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Synthesis, crystallization behavior and microstructure of oxynitride glass–ceramics with different modifier elements

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Abstract

M–Si–Al–O–N (M = Y, Ca, Mg) oxynitride glasses were prepared by melting batches at 1600 °C for 2 h under N_2 atmosphere in a Si–Mo-heated resistance furnace. The appropriate heat treatment temperatures were selected according to the information provided by the differential scanning calorimeter (DSC) measurement. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to study the crystallization behavior of the glass–ceramics with different modifier elements. The results indicate that for this glass system, heat treatment has an effect on volume fraction of the crystalline phases and the microstructure of the glass–ceramics, whereas the effect on the types of the crystalline phases precipitated is small.

Keywords: Oxynitride glass–ceramics; Microstructure; Crystallization

1. Introduction

Oxynitride glasses have been studied intensively because of their excellent structure and properties. In the past few years, particular interest has been focused on the M–Si–Al–O–N system, where M is magnesium [1,2], calcium [3,4] and yttrium [5–7] acting as a modifying cation. Incorporation of nitrogen into the silicate network enhances glass formation and causes an increase in properties such as density, elastic moduli, microhardness and glass transition temperature. Observed property changes for oxynitride glasses with increasing nitrogen content is consistent with a structural model in which nitrogen substitutes for oxygen and, due to the incorporation of tri-coordinated nitrogen, creates a more cross-linked glass network and structure.

As with other silicates, oxynitride glasses may be heat treated at the appropriate temperatures to crystallize as glass-ceramics and do not require the addition of nucleating agents to promote the crystallization process [6,8,9]. Many studies on crystallization of oxynitride glasses, particularly in the Y–Si–Al–O–N system [8–11], have been carried out which have been identified suitable two step heat treatments for nucleation and growth of new phases to obtain oxynitride glass–ceramics with significant increase in mechanical properties like strength and elastic modulus. The specific crystalline phases formed upon heat treatment, and the extent of their formation determined the properties of the oxynitride glass–ceramics materials [12–14].

Previous work has investigated Y–Si–Al–O–N glass–ceramics. Sainz et al. [8] have found that $YAlO_3$ was the major crystalline phase after heat treatment and Luo et al. [15] have found that $Y_2Si_2O_7$ was the major phase of Y–Si–Al–O–N glass–ceramics. The purpose of this study is to characterize the crystallization mechanism and microstructure with different modifier elements in the M–Si–Al–O–N (M = Y, Ca, Mg) glass–ceramics system.

2. Experimental procedure

2.1. Glass synthesis

A base M–Si–Al–O–N oxynitride glass was prepared with a cation composition (in eq.%) of 24M:61Si:15Al:82O:18N, where M is Y, Ca and Mg. Y_2O_3 (99.9%, A&C Rare Earth Materials Center, China), α-Si_3N_4 (99.7%, averaged particle size 0.2 um; Sinopharm Chemical Reagent Co. Ltd., China),

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Table 1
Composition (in eq.%), thermal properties, density and Vickers hardness of the oxynitride glasses.

Sample no.	Composition (eq.%)	T_g (± 5 °C)	T_{c1} (± 5 °C)	T_{c2} (± 5 °C)	ρ (± 0.01 g cm^{-3})	H_v (± 0.10 GPa)
24Y18N	$Y_{24}Al_{15}Si_{61}O_{82}N_{18}$	917	1158	–	3.38	9.97
24Ca18N	$Ca_{24}Al_{15}Si_{61}O_{82}N_{18}$	861	1075	–	2.79	7.79
24Mg18N	$Mg_{24}Al_{15}Si_{61}O_{82}N_{18}$	855	1142	1216	2.83	10.43

Al_2O_3 (99.9%, Xilong Chemical Co. Ltd., China), $CaCO_3$ (99.9%, Xilong Chemical Co. Ltd., China), SiO_2 (99.9%, Xilong Chemical Co. Ltd., China), MgO (99.9%, Xilong Chemical Co. Ltd., China) were used as raw materials. Dried powders were weighed and prepared by mechanical agitation (using an attritor mill), milled in isopropyl alcohol for 24 h, and then dried again. The mixture was melted inside a silica crucible lined with BN powder at 1600 °C for 2 h under N_2 atmosphere (0.1 MPa), using a heating rate of 5 °C/min. Subsequently, the samples were first cooled with a cooling rate of 25 °C/min until a temperature of 900 °C annealing for 1 h to remove internal stresses and afterwards the samples were cooled down with furnace cooling to room temperature. Table 1 lists the nominal compositions in eq.% (equivalent percent) of these samples.

2.2. Characterization techniques

2.2.1. Density and Vickers hardness

The density (ρ) was measured by the Archimedes method, using distilled water. Vickers hardness (H_v) tests were carried out on polished glass samples using a Matsuzawa micro-hardness tester Model MXT-a 1 with a pyramid shaped diamond indenter, applying loads 9.8 N for 15 s. At least 10 measurements were taken for each sample. Indentation diagonals were measured to calculate hardness values in GPa.

2.2.2. Differential scanning calorimeter (DSC)

The differential scanning calorimeter (DSC, Netzsch 404PC, Germany) was used to determine the glass transition temperature (T_g) and crystallization temperature (T_c). About a 10 mg powder sample was placed in an alumina crucible and subjected to a heating rate of 10 °C/min from ambient temperature to 1400 °C in a flowing high purity argon environment. The experimental error on measured value was ±5 °C.

2.2.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) was carried out in order to analyze the crystalline phase of the samples by an X-ray diffractometer (D/max 2500 model, Rigaku, Japan) with Cu-Kα radiation ($\lambda = 1.54178$ Å) operated at 40 kV and 50 mA. Data were collected from $2\theta = 10$–$80°$ at a scanning rate of 8 deg/min.

2.2.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was carried out on cut samples of glass-ceramics mounted in epoxy resin and polished to 1 μm with diamond slurries. The mirror surfaces of samples were sputtered with a gold coating and a FEI Quanta 200 scanning electron microscope was employed for observing the crystal morphology.

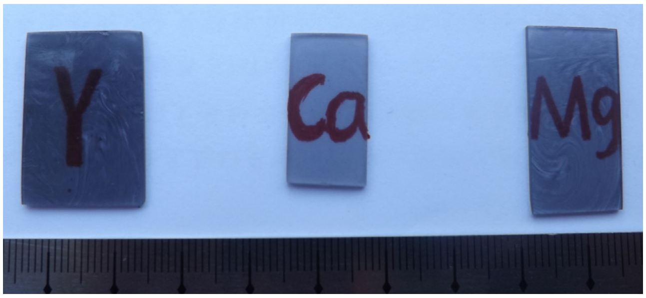

Fig. 1. Photograph of the oxynitride glass samples 24Y18N, 24Ca18N and 24Mg18N laid over the writing letters to show their transparency.

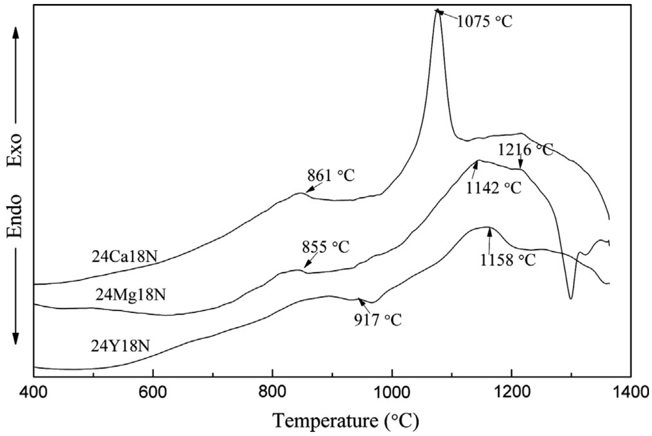

Fig. 2. DSC curves of oxynitride glass samples 24Y18N, 24Ca18N and 24Mg18N at heating rate 10 °C/min.

3. Results and discussion

3.1. Glass appearance

The appearance of the parent glasses obtained was primarily inspected by the naked eye. All the glass samples were highly homogeneous, transparent, bubble free and gray in color. The amorphous nature of these glasses was confirmed by the corresponding X-ray diffraction patterns, which did not show any crystalline phase. Fig. 1 shows fabricated glasses which are placed on a piece of written paper where the underlying letter is visible through all of them. Compared to oxide glasses, oxynitride glasses are of limited transparency, having colors varying between pale gray and almost black.

The density and Vickers hardness of base oxynitride glasses are given in Table 1. As can be seen in Table 1, the density of three basic oxynitride glasses is found to have values ranging from 2.79 to 3.38 g/cm^3 and increases with the increasing atomic mass of modifier elements (Mg, Ca, Y). The Vickers hardness varies from 7.79 to 10.43 Gpa. It is clear that the glass 24Ca18N which containing 24 eq.% calcium has a lower hardness value than other samples. It is mainly because the weaker cation field strength (CFS) of Ca^{2+} compared to Mg^{2+} and Y^{3+} which is consistent with our previous study [16].

3.2. DSC curves and the heat-treatment schedules

The DSC curves of the three glass samples 24Y18N, 24Ca18N, and 24Mg18N performed at a heating rate of 10 °C/min are shown in Fig. 2. The glass transition temperature (T_g) and crystallization temperature (T_c) of all the glasses studied are presented in Table 1. The glass sample 24Y18N has a glass transition temperature (T_g) of 917 °C and a crystallization temperature (T_c) of 1158 °C, while the T_g of glass samples 24Ca18N and 24Mg18N are 861 °C and 855 °C respectively. As can be seen in Fig. 2, glass sample

Table 2
Heat treatment conditions (°C, h) of the oxynitride glasses and the crystalline phases obtained after heat treatment.

Glass	Heat treatment conditions	Crystalline phase
24Y18N	900 °C, 2 h+1150 °C, 2 h	–
	900 °C, 2 h+1150 °C, 4 h	–
	900 °C, 2 h+1150 °C, 6 h	mullite ($Al_6Si_2O_{13}$)*
24Ca18N	900 °C, 2 h+1150 °C, 2 h	gehlenite ($Ca_2Al_2SiO_7$)*, anorthite ($CaAl_2Si_2O_8$)
	900 °C, 2 h+1150 °C, 4 h	gehlenite ($Ca_2Al_2SiO_7$) *, anorthite ($CaAl_2Si_2O_8$)
	900 °C, 2 h+1150 °C, 6 h	gehlenite ($Ca_2Al_2SiO_7$) *, anorthite ($CaAl_2Si_2O_8$)
24Mg18N	900 °C, 2 h+1150 °C, 2 h	$MgAl_2O_4$*, $Mg_2(SiO_4)$ and (Mg,Al)SiO_3
	900 °C, 2 h+1150 °C, 4 h	(Mg,Al)SiO_3*, $Mg_2(SiO_4)$ and $MgAl_2O_4$
	900 °C, 2 h+1150 °C, 6 h	(Mg,Al)SiO_3*, $Mg_2(SiO_4)$ and $MgAl_2O_4$

–: no phase participated.
*The main crystalline phase.

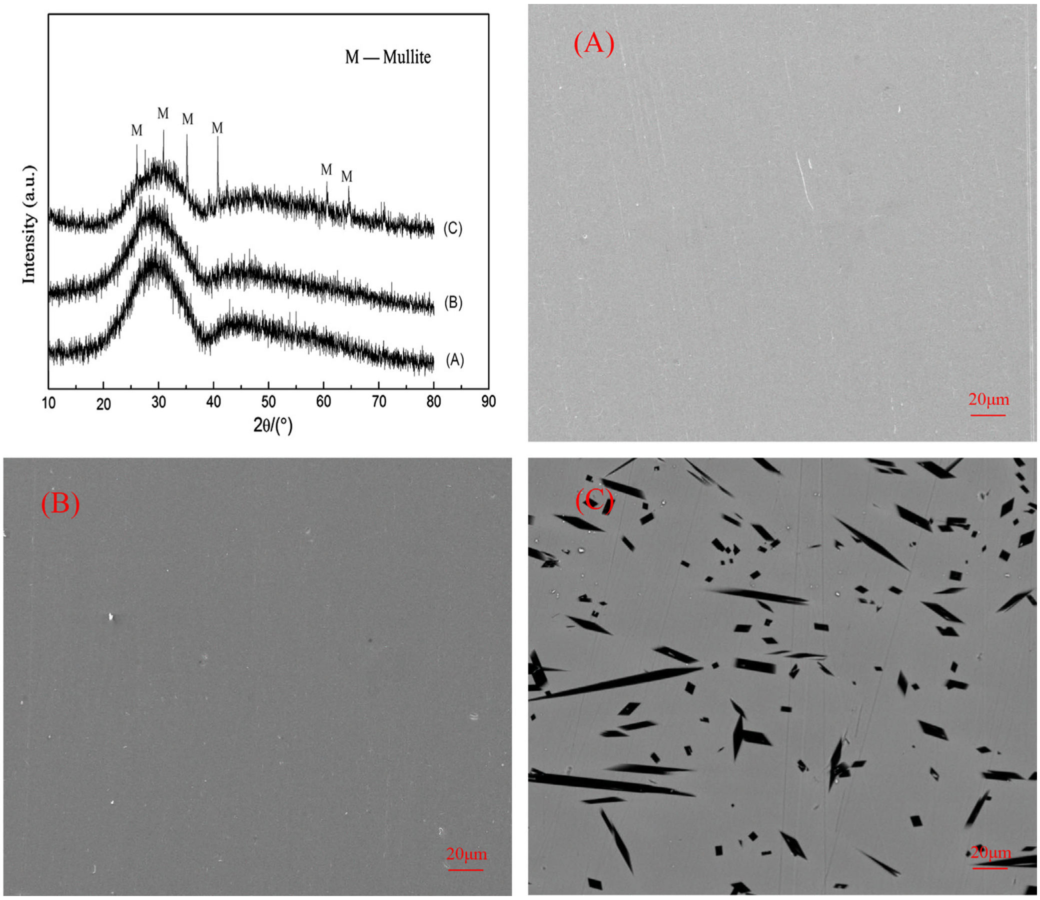

Fig. 3. XRD patterns and SEM micrographs of glass–ceramic sample 24Y18N obtained after different heat-treatment conditions: (A) 900 °C/2 h+1150 °C/2 h, (B) 900 °C/2 h+1150 °C/4 h, and (C) 900 °C/2 h+1150 °C/6 h.

24Mg18N exhibits a second crystallization peak temperature (T_{c2}) which is 1216 °C while the first crystallization peak temperature (T_{c1}) is 1142 °C. And it is easy to see that the exothermic peak of glass sample 24Y18N is weaker than that of glass samples 24Ca18N and 24Mg18N. The weak exothermic peak of 24Y18N can be attributed to the higher activation energy for the crystallization which was found to be 834 kJ/mol [17,18].

According to the DSC results, the annealed glasses were heat treated, and the treatment schedules are listed in Table 2. In the two step treatment, the glass specimens were heated to the nucleation temperature and held for 2 h, then heated to the crystallization temperature and held for 2 h, 4 h and 6 h, respectively. Following heat-treatment of the glasses, the glass–ceramics produced were analyzed by XRD and SEM.

3.3. Phase formation and microstructure of the glass–ceramics

For the glass sample 24Y18N heat-treated in the two previous conditions ((A) 900 °C/2 h + 1150 °C/2 h, (B) 900 °C/2 h + 1150 °C/4 h), no crystalline phase was detected by XRD. However, a small amount of crystalline phase began to precipitate when the crystallization time was extented to 6 h. XRD patterns and SEM micrographs of the glass–ceramic sample 24Y18N obtained at different heat-treatment conditions ((A) 900 °C/2 h + 1150 °C/2 h, (B) 900 °C/2 h + 1150 °C/4 h, (C) 900 °C/2 h + 1150 °C/6 h) are shown in Fig. 3. As can be seen in Fig. 3, heat-treatment at 900 °C for 2 h (nucleating) and 1150 °C for 6 h (crystallization) shows that the only observed crystallized phase was mullite ($Al_6Si_2O_{13}$, PDF# 15–0776) with plenty of residual glassy phase. It is clearly that the observations of XRD and SEM agree with the DSC results which show that it is more difficult to precipitate crystalline phase from glass sample 24Y18N than glass samples 24Ca18N and 24Mg18N because of the higher activation energy.

Fig. 4 shows the XRD patterns and SEM micrographs of the glass–ceramic sample 24Ca18N obtained at different heat treatment conditions. In these three glass–ceramic samples, gehlenite ($Ca_2Al_2SiO_7$, PDF# 79-2421) was identified as the main crystalline phase whilst anorthite ($CaAl_2Si_2O_8$, PDF# 89-1472) acted as the secondary crystalline phase. As can be seen in Fig. 4(A) and (B), there is a broad size distribution ranging from the large elongated grains down to smaller equiaxed grains. With the increasing crystallization time, the fine grains are growing up and together with each other. And the size of the crystals is very large, of the order of about 10 μm or greater in Fig. 4(C). The presence of gehlenite as the major crystalline phase was also confirmed by other crystallization studies of Ca–Si–Al–O–N glass systems [14,19]. The study of Hampshire et. al [20] not only showed that

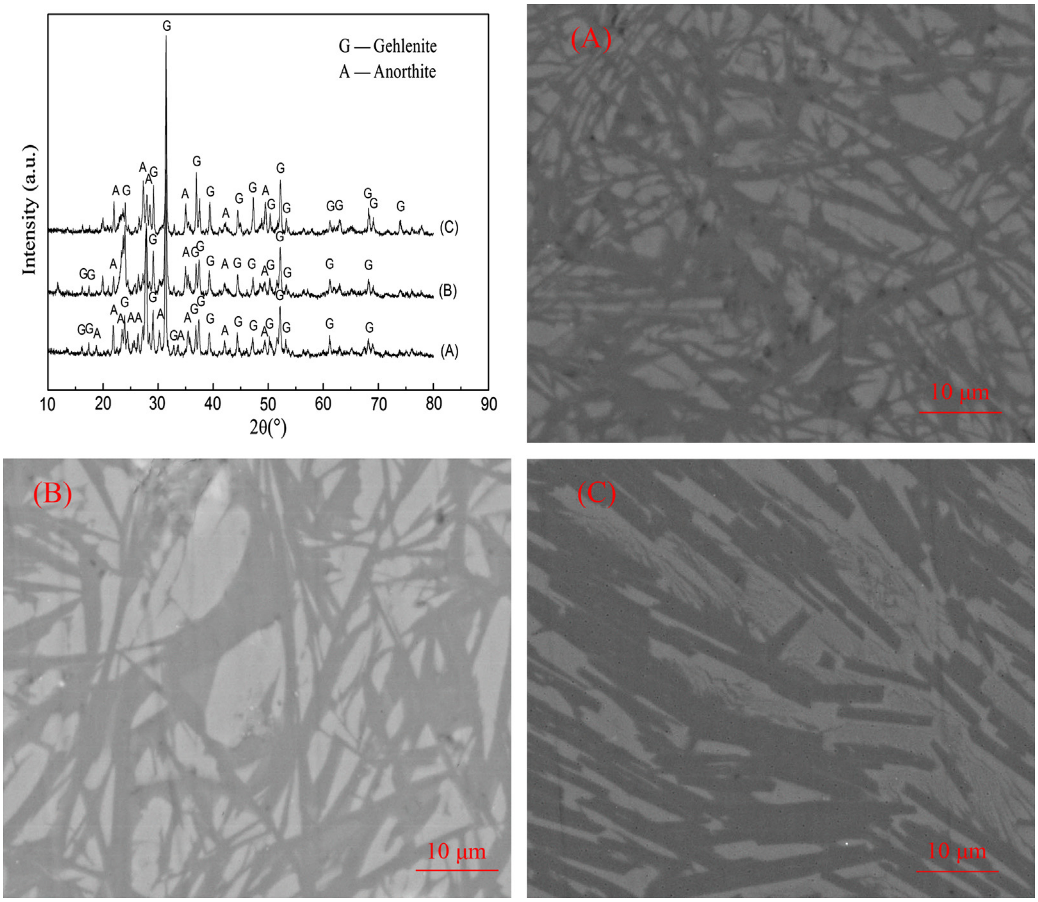

Fig. 4. XRD patterns and SEM micrographs of glass–ceramic sample 24Ca18N obtained after different heat-treatment conditions: (A) 900 °C/2 h + 1150 °C/2 h, (B) 900 °C/2 h + 1150 °C/4 h, and (C) 900 °C/2 h + 1150 °C/6 h.

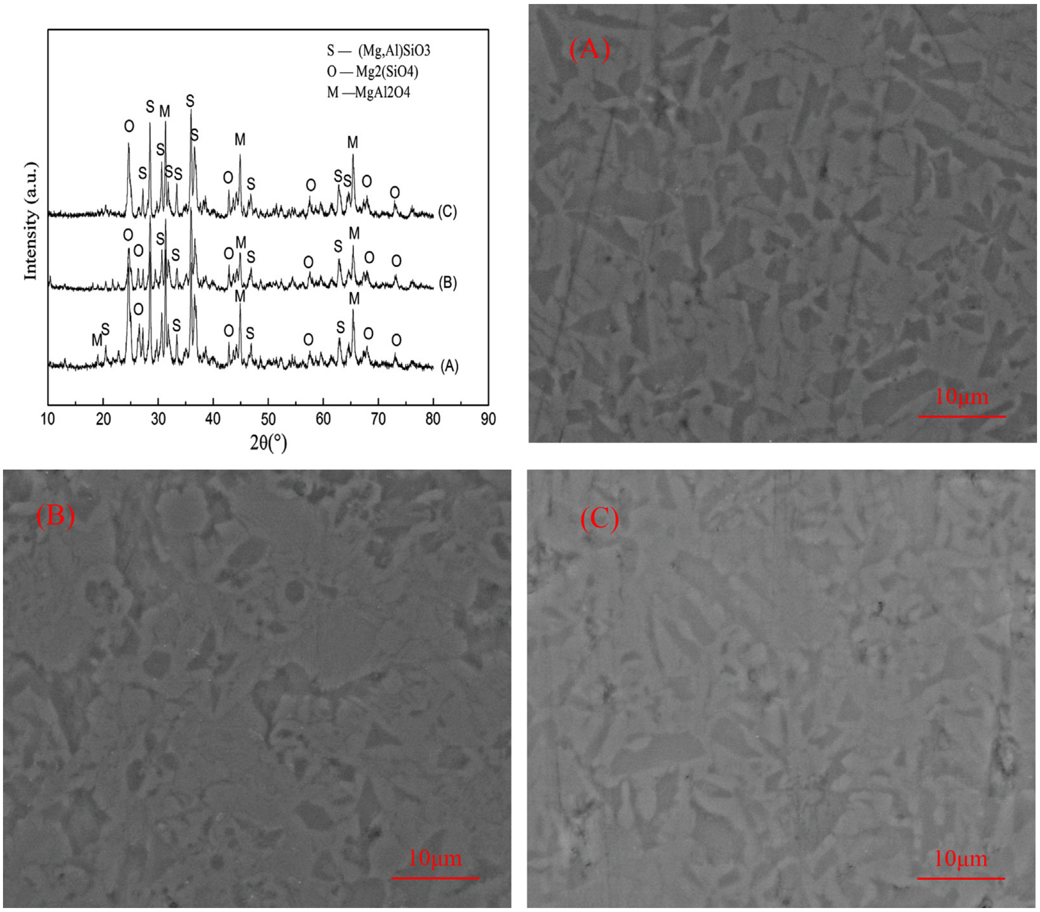

Fig. 5. XRD patterns and SEM micrographs of glass–ceramic sample 24Mg18N obtained after different heat-treatment conditions: (A) 900 °C/2 h + 1150 °C/2 h, (B) 900 °C/2 h + 1150 °C/4 h, and (C) 900 °C/2 h + 1150 °C/6 h.

gehlenite is the dominant crystalline phase following heat treatment of Ca–Si–Al–O–N glasses but also suggested that nitrogen may be accommodated in the gehlenite crystal structure.

The XRD patterns of glass–ceramic sample 24Mg18N in Fig. 5 show that the crystallization time has no effect on the types of the crystalline phase precipitated. However, with the increasing crystallization time, the main crystalline phase is different from previously identified phases. As can be seen in Fig. 5, crystalline phases identified for glass–ceramic sample 24Mg18N heat-treated in different conditions are (Mg,Al)SiO$_3$ (PDF# 35-0310), Mg$_2$(SiO$_4$) (PDF# 87-2042) and MgAl$_2$O$_4$ (PDF# 73-1959). MgAl$_2$O$_4$ was the main crystalline phase when the crystallization time was 2 h and (Mg,Al)SiO$_3$ was the main crystalline phase when the crystallization time was extented to 4 h and 6 h. SEM micrographs of Fig. 5(A), (B) and (C), shows the extensive crystallizations in glass–ceramic sample 24Mg18N at different heat treatment conditions and the degree of crystallization increases with the increase of crystallization time. In Fig. 5(A), irregular block-shaped crystals of MgAl$_2$O$_4$ can be seen as the major crystalline phase. The size of the crystals is very small, ca. 3–8 μm. With increasing crystallization time, the volume fraction of crystalline phases (Mg,Al)SiO$_3$ and Mg$_2$(SiO$_4$) began to increase and gather together, see Fig. 5(B) and (C). Previous work by Lederer et al. [21] has shown that on the crystallization of Zr-doped Mg–Ca–Si–Al–O–N glasses, a nitrogen-containing phase (Mg-petalite, 2Si$_2$N$_2$O · MgO · Al$_2$O$_3$) was precipitated in the glass–ceramics obtained. However, in the present study, no nitrogen-containing phase was found in all the glass–ceramics which indicating that nitrogen was presented in the residual glass phase.

4. Conclusions

The crystallization behavior and microstructure of M–Si–Al–O–N glasses with different modifier elements have been studied. For the glass sample 24Y18N, no crystalline phase was detected in the two previous conditions ((A) 900 °C/2 h + 1150 °C/2 h, and (B) 900 °C/2 h + 1150 °C/4 h). When the crystallization time was extented to 6 h, only a crystalline phase of mullite (Al$_6$Si$_2$O$_{13}$) was observed. In the glass–ceramic samples of 24Ca18N, gehlenite (Ca$_2$Al$_2$SiO$_7$) was identified as the main crystalline phase and anorthite (CaAl$_2$Si$_2$O$_8$) acted as the secondary crystalline phase. The crystalline phases identified for glass–ceramic sample 24Mg18N heat-treated in present conditions were (Mg,Al)SiO3, Mg2(SiO4) and MgAl$_2$O4. It has been found that is more difficult to precipitate crystalline phase from glass sample 24Y18N than glass samples 24Ca18N and 24Mg18N. In the present study, no nitrogen containing phases were obtained in all the glass–ceramic samples and the nitrogen content of the residual glass increases significantly.

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