# Crystallization and microstructures of Y–Si–Al–O–N glass–ceramics containing main crystal phase $Y_3Al_5O_{12}$

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**Abstract.** A glass with the nominal composition of 28Y48Si24Al83O17N (in equal percentage) was chosen as parent glass in this paper to prepare $Y_3Al_5O_{12}$-based glass–ceramics. Differential scanning calorimetry (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to assess the crystallization process of the parent glass. YAG as the only crystalline phase appears in all glass–ceramics produced under 1250°C. A small amount of O′-Sialon secondary phase starts to precipitate from parent glass samples as heat treatment temperature increases to 1250°C. Grain size of the dendrite crystal which corresponds to YAG phase increases and the dendrite branches get thickened as heat treatment temperature increases. Moreover, grain size of YAG phase resulting from two-stage heat treatment is much smaller than that of YAG phase obtained by one-stage heat treatment. The results are relevant to developing improved crystallization treatments for glasses with potential for crystallization to YAG-based glass–ceramics and for heat treatments of YAG/$\beta$-SiAlON materials.

**Keywords.** Y–Si–Al–O–N; glass–ceramics; heat treatment; crystalline phase; microstructure.

## 1. Introduction

$\beta$-SiAlONs ($Si_{6-z}Al_zO_zN_{8-z}$) are of interest as a kind of important engineering material for their excellent high-temperature properties (Jack 1976). Oxynitride glasses in Y–Si–Al–O–N system usually appear in yttria-densified $\beta$-sialon ceramics as intergranular glassy phases, which degrades the high-temperature properties of these ceramics. However, high-temperature properties of yttria-densified $\beta$-sialon ceramics can be greatly improved after a post-sintering heat treatment because partial or all Y–Si–Al–O–N glasses are converted into a mixture of crystalline phases which are more refractory (Lewis *et al* 1980; Bentsen *et al* 1984; Falk and Dunlop 1987). Among these crystalline phases, $Y_3Al_5O_{12}$ (yttrium alumina garnet, YAG) is the most satisfactory contender for improving high-temperature properties of $\beta$-SiAlON materials (Lewis *et al* 1980; Vomacka 1997). Therefore, the study on the crystallization of YAG from Y–Si–Al–O–N glasses to prepare YAG-based glass–ceramics is of interest.

Heat treatment of Y–Si–Al–O–N oxynitride glasses has shown the crystallization behaviour to be, in general, quite complex and in most cases the heat-treated products are multiphase (Leng-ward and Lewis 1985; Dinger *et al* 1988; Besson *et al* 1993; Hampshire *et al* 1994; Besson *et al* 1997; Liddell *et al* 1997; Ramesh *et al* 1998). A number of investigations (Lewis *et al* 1980; Leng-ward and Lewis 1985; Bonnell *et al* 1987; Ding *et al* 1989; Besson *et al* 1993; Vomacka and Babushkin 1996; Lemercier *et al* 1997; Vomacka 1997; Ramesh *et al* 1998) indicate that YAG as one of the crystalline phases usually appear in many Y–Si–Al–O–N glass–ceramics. These investigations also suggest that the crystallization of YAG from Y–Si–Al–O–N oxynitride glasses depends not only on matrix glass composition but also on heat treatment time and temperature. For the glass composition, the content of $SiO_2$ must be less than 25wt% (Ding *et al* 1989). For the heat treatment temperature, YAG can be precipitated at temperatures far below 1200°C, but its content is usually small (Besson *et al* 1993; Liddell and Thompson 1997; Vomacka 1997). YAG as the dominant phase usually crystallizes above 1200°C (Bonnell *et al* 1987; Ding *et al* 1989; Hampshire *et al* 1994). Note that some other crystal species like apatite ($Y_5Si_3O_{12}N$), different forms of $Y_2Si_2O_7$, intermediate phase and O′-sialon usually crystallize from Y–Si–Al–O–N glasses together with YAG. $Y_2Si_2O_7$ which has five polymorphic forms sometimes can even be the dominant phase (Vomacka 1997). Phase transformations of $Y_2Si_2O_7$ or intermediate phase in certain case can cause problems such as the thermal and the volume effects. Therefore, the crystallization of $Y_2Si_2O_7$ and the intermediate phase from the Y–Si–Al–O–N glass had better to be avoided in order to obtain YAG/$\beta$-SiAlON or YAG-based glass–ceramics materials with excellent properties.

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As per our knowledge, the crystallization of YAG from Y–Si–Al–O–N glasses as the only crystalline phase under 1200°C has never been reported. Moreover, the relationship between the morphology of YAG and the heat treatment temperature has never been investigated systematically. If YAG always exists in Y–Si–Al–O–N glass ceramics as dominant phase at a wide temperature range, many excellent properties of YAG/$\beta$-SiAlON materials will be prospective. The motivation of this research is to prepare glass–ceramics with YAG as the dominant crystalline phase, ideally, as the only crystalline phase at a wide temperature range. With such a goal, 28Y48Si24Al83O17N glass with relatively low $SiO_2$ content having potential for crystallization to YAG-based glass–ceramics was chosen as parent glass in this paper. Different heat treatments were performed on this glass. The crystalline products were identified and the microstructures of the glass–ceramics were observed.

## 2. Experimental

### 2.1 *Preparation*

The parent glass with the nominal composition of 28Y48Si24Al83O17N (expressed in wt% is 49·6 wt% $Y_2O_3$, 19·2 wt% $Al_2O_3$, 21·9 wt% $SiO_2$, 9·3 wt% $Si_3N_4$) was prepared in this paper. The starting materials were high-purity powders: $Y_2O_3$, $Al_2O_3$, $SiO_2$ and $Si_3N_4$. Dried powders were weighed, mixed in isopropyl alcohol for 24 h, and then dried again. A batch of approximately 80 g was then compacted into a graphite crucible lined with BN powder to avoid any sealing between the glass and the crucible. Then the batch was melted in a graphite element furnace in a nitrogen atmosphere (pressure of 0·2 MPa) at 1700°C for 2 h. After that, the melt was cooled by shutting off the power of the furnace. The cooling rate was approximately 20°C/min from 1700°C to 1000°C. Heat treatments of the parent glass samples to prepare glass–ceramics were carried out in a silicon carbide horizontal furnace in a nitrogen atmosphere.

### 2.2 *Characterization*

A differential scanning calorimeter (short for DSC, NETZSCH 449PC, Germany) was used to obtain DSC curve of the parent glass. About 10 mg powder glass sample was placed in an alumina crucible and heated at a rate of 10°C/min from ambient temperature to 1300°C in a flowing high purity argon environment. Crystalline phases in the prepared glass–ceramics were identified by an X-ray diffractometer (D/max 2500 model, Japan) with CuK$\alpha$ radiation. Microstructures of the polished glass–ceramics were observed by scanning electron microscopy (SEM, Sirion 200). Before the SEM observations,

glass–ceramics were etched in 10% HF for 6 min. Chemical compositions of the crystals distributed in glass–ceramics were further identified by energy dispersion spectrometer (short for EDS, EDX-GENESIS60S model, America).

## 3. Results and discussion

### 3.1 *Determination of the heat treatment schedules*

DSC curve of the parent glass is shown in figure 1. As shown in figure 1, the maximum exothermic peak temperature is 1160°C and no visible endothermic peaks are observed. DSC curve of 25·9Y41·3Si32·8Al89·1O10·9N glass has shown $T_g$ = 943°C, $T_{C1}$ = 1075°C, $T_{C2}$ = 1145°C (Vomacka and Babushkin 1996). $T_{C1}$ corresponds to the crystallization of an intermediate phase accompanied by the crystallization of $Y_2Si_2O_7$ and $T_{C2}$ corresponds to the crystallization of YAG phase. Obviously, 28Y48Si24 Al83O17N glass has a higher crystallization temperature (1160°C) than that (1145°C) of 25·9Y41·3Si32·8 Al89·1O10·9N glass. Nitrogen and silicon contents of 28Y48Si24Al83O17N glass are both higher than those of 25·9Y41·3Si32·8Al89·1O10·9N glass. As a result, 28Y48Si24Al83O17N glass has a more rigid glass network and the ions such as $Y^{3+}$, $Al^{3+}$ and $O^{2-}$ in this glass are more difficult to migrate, rotate, rearrange and adjust into lattice structure. Thus, a higher crystallization treatment temperature is required in order to promote the crystallization of the 28Y48Si24Al83O17N glass. Small amount of crystalline phases could be precipitated from the 25·9Y41·3Si32·8Al89·1O10·9N glass when it was treated at 970°C for nucleation and then subjected to 1150°C for crystal growth. Based on the above result and for comparison, 1000°C and 1050°C were chosen as the nucleation temperature of the 28Y48Si24Al83O17N glass. The crystallization temperatures of the glass were deter-
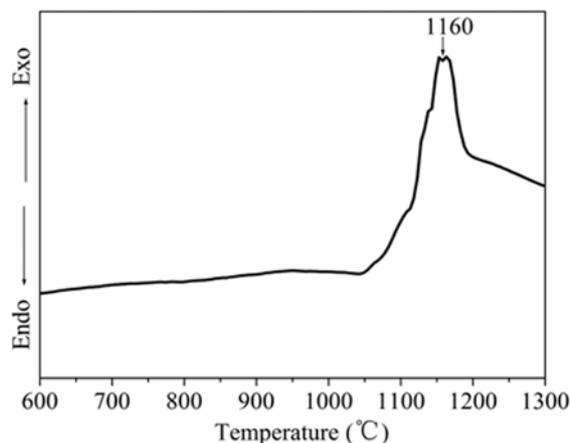


**Figure 1.** DSC curve of $Y_{28}Si_{48}Al_{24}O_{83}N_{17}$ glass powder at a heating rate of 10°C/min.

**Table 1.** Crystalline products and their volume fraction in the glass–ceramics obtained from the 28Y48Si24Al83O17N glass samples after twelve different heat treatment conditions.

| Sample | Thermal treatment condition (°, h) | Crystalline phases | Volume fraction of crystalline phases (%) ± 5% |
|--------|-----------------------------------|--------------------|-----------------------------------------------|
| #1 | 1000°C, 10h + 1100°C, 4 h | $Y_3Al_5O_{12}$ | 55·5 |
| #2 | 1000°C, 10 h + 1150°C, 4 h | $Y_3Al_5O_{12}$ | 62·1 |
| #3 | 1000°C, 10 h + 1200°C, 4 h | $Y_3Al_5O_{12}$ | 69·4 |
| #4 | 1000°C, 10 h + 1250°C, 4 h | $Y_3Al_5O_{12}$, O′-sialon (samll amount) | 75·6 |
| #5 | 1000°C, 10 h + 1300°C, 4 h | $Y_3Al_5O_{12}$ O′-sialon (samll amount) | 83·3 |
| #6 | 1050°C, 10 h + 1150°C, 4 h | $Y_3Al_5O_{12}$ | 73·1 |
| #7 | 1050°C, 10 h + 1200°C, 4 h | $Y_3Al_5O_{12}$ (33–0040) | 78·2 |
| #8 | 1050°C, 10 h + 1250°C, 4 h | $Y_3Al_5O_{12}$, O′-sialon (small amount) | 82·4 |
| #9 | 1050°C, 10h + 1300°C, 4 h | $Y_3Al_5O_{12}$, O′-sialon (small amount) | 90·7 |
| #10 | 1200°C, 10 h | $Y_3Al_5O_{12}$ | 57·4 |
| #11 | 1300°C, 10 h | $Y_3Al_5O_{12}$, O′-sialon (samll amount) | 79·8 |
| #12 | 1020°C, 10 h + 1200°C, 4 h | $Y_3Al_5O_{12}$ | 70·6 |

mined as shown in figure 1. Twelve different heat treatment conditions were adopted to investigate the crystallization behaviour of the parent glass in this paper. Twelve glass–ceramics ordered from #1 to #12 were obtained after the glass at different heat treatments. #1 to #5 glass–ceramics were prepared after the glass samples nucleated at 1000°C for 10 h and subsequently heated for 4 h at 1100°C, 1150°C, 1200°C, 1250°C, 1300°C, respectively. #6, #7, #8 and #9 glass–ceramics were obtained by increasing nucleation temperature from 1000°C to 1050°C in comparison with #2, #3, #4 and #5 glass–ceramics, respectively. #10 and #11 glass–ceramics were obtained after one-stage heat treatments at 1200°C for 8 h and 1300°C for 10 h, respectively. #12 glass–ceramic was nucleated at 1020°C for 10 h and subsequently treated at 1200°C for 4 h.

### 3.2 *Crystalline product identification*

XRD patterns of #1–11 glass–ceramics are shown in figure 2. For each glass–ceramic, the crystalline products and volume fraction of these crystalline phases were summarized in table 1. Volume fraction of the crystalline phases in each glass–ceramic was determined by JADE software based on its XRD pattern. It can be obtained simply by the ratio of the partial area of the crystallization peaks to the total area of the peaks (including the peaks of the crystalline phases and the residual glassy phase) at a fixed temperature. YAG as the only crystalline phase appears in #1–3, #6–7 and #10 glass–ceramics (see figures 2(a), (c) and (e)). Crystalline phases in #4–5, #8–9 and #11 glass–ceramics consist mainly of YAG and of a small amount of O′-sialon (see figure 2(b), (d) and (e)). Thus, YAG as major crystalline phase appears in all glass–ceramics prepared in this paper. The result agrees well with the earlier report (Vomacka 1997) that in glass compositions with high nitrogen content (for example 10·9 eq.%) the crystallization of YAG dominates from the onset of crystallization around 1100°C, whereas in

glass compositions with low nitrogen content (for example 5·6 eq.%) it begins to dominate only above 1250°C. Since nitrogen content of 28Y48Si24Al83O17N glass (17 eq.%) is much higher than those (5·6 eq.% or 10·9 eq.%) of the two glasses prepared in the earlier report (Vomacka 1997), YAG crystallizes out at around 1100°C in this study and dominates in the temperature range of 1100–1300°C. It can be concluded that glass–ceramics with YAG as single crystalline phase have been prepared in this paper by treating 28Y48Si24Al83O17N glass samples under 1250°C because crystallization temperatures of #1–3, #6–7 and #10 glass–ceramics are all lower than 1250°C. This result is quite different from the result of the earlier study (Vomacka 1997). In that study, the precipitation of YAG phase was accompanied by some amount of $\delta$- and $y$-$Y_2Si_2O_7$ and intermediate phase. The elevation of nucleation temperature from 1000°C to 1050°C does not change the crystalline products as shown in figure 3, but increases the volume fraction of the crystalline phases as shown in figure 4. When the glass was treated at constant nucleation temperature and nucleation time the volume fraction of crystalline phases is greatly improved by increasing the second-stage crystallization heat treatment temperature as shown in figure 4. The progressive crystallization of YAG results in the increase of the silicon and nitrogen contents in the residual glass.

O′-sialon as secondary phase starts to precipitate from parent glass specimens treated at 1250°C. Precipitation of O′-sialon phase from Y–Si–Al–O–N glasses treated above 1250°C has been reported in some earlier investigations (Leng-ward and Lewis 1985; Dinger *et al* 1988). These investigations indicated that nucleation of O′-sialon phase generally occurred after the composition of the residual glass had been enriched in nitrogen following the crystallization of oxide phase such as YAG or $Y_2Si_2O_7$. As shown in figures 2(b) and (d), intensities of the characteristic diffraction peaks attributed to O′-sialon phase increase as the second-stage crystallization
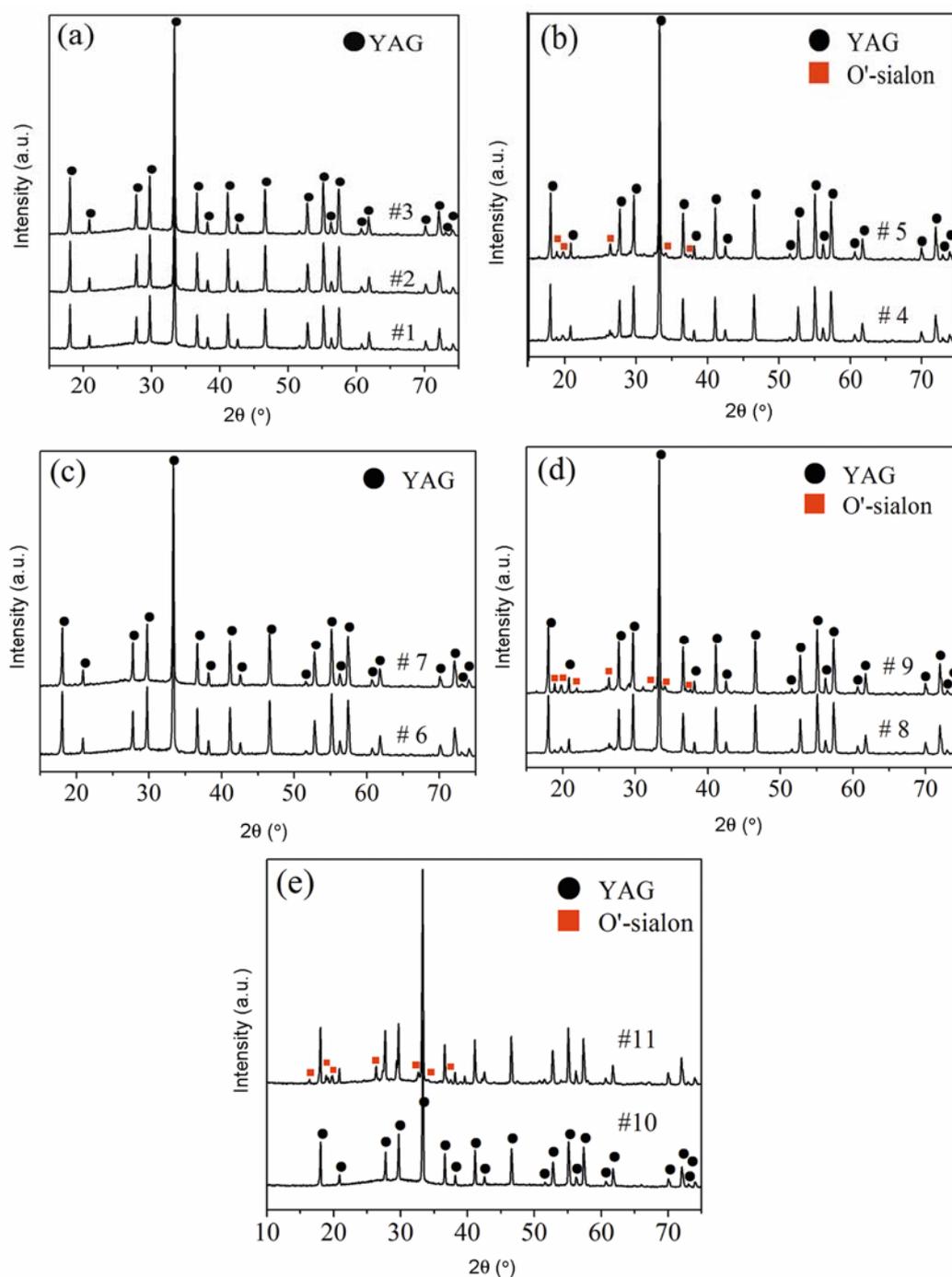
**Figure 2.** XRD patterns of the #1–11 glass–ceramics obtained after different heat treatment conditions: (**a**) 1000°C, 10 h + 1100°C, 4 h (#1); 1000°C, 10 h + 1150°C, 4 h (#2); 1000°, 10 h + 1200°C, 4 h (#3); (**b**) 1000°, 10 h + 1250°C, 4 h (#4); 1000°C, 10 h + 1300°C, 4 h (#5); (**c**) 1050°C, 10 h + 1150°C, 4 h (#6); 1050°C, 10 h + 1200°C, 4 h (#7); (**d**) 1050°C, 10 h + 1250°C, 4 h (#8); 1050°C, 10 h + 1300°C, 4 h (#9); (**e**) 1200°C, 8 h (#10); 1300°C, 10 h (# 11).

temperature increases from 1250°C to 1300°C. The fact indicates that the content of O'-sialon phase increases with increasing crystallization temperature. This result is quite different from the result observed in the earlier study (Ding *et al* 1989). In that study the content of the

minor phase whose chemical compostion was not identified by Ding *et al* (1989) decreases with increasing heat treatment temperature. This difference may be caused by the difference in glass compositions. Although there is a content increase in O'-sialon phase as crystallization tempe-

rature increases from 1250°C to 1300°C, only a small amount of O′-sialon are precipitated since only a few weak X-ray diffraction lines attributed to O'-sialon phase are present in the XRD patterns. In the XRD pattern of #9 glass–ceramic, the intensity (240 a.u) of the peak at $2\theta = 26\cdot4°$ corresponding to the strongest diffraction peak of O′-sialon phase is less than 10% of the intensity (3266 a.u.) of the peak at $2\theta = 33\cdot3°$ corresponding to the strongest diffraction peak of YAG phase. Since the total volume fraction of crystalline products (including YAG and O'-sialon) in #9 glass–ceramic is 90·7%, the volume fraction of YAG phase in #9 glass–ceramic is around
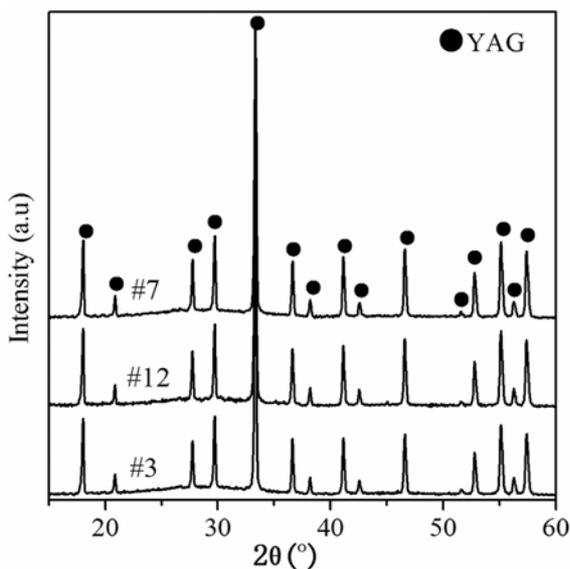


**Figure 3.** XRD patterns of the glass specimens nucleated for 10 h at 1000°C (#3), 1020°C (#12), 1050°C (#7), respectively, and subsequently heated at 1200°C for 4 h.
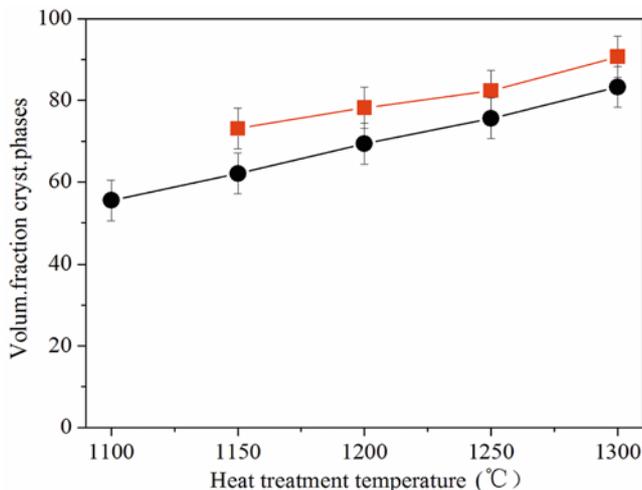


**Figure 4.** Volume fraction crystalline phases as a function of the second-stage heat treatment temperature (■, glass samples nucleated at 1050°C, ●, glass samples nucleated at 1000°C).

80%. As shown in table 1, the highest volume fraction of YAG phase in glass–ceramics obtained after heat treatments under 1250°C is 78·2% which is close to that (around 80%) of #9 glass–ceramic. Therefore, for the parent glass the elevation of crystallization temperature from 1200°C to 1300°C is not advantageous for the increase of the volume fraction of YAG phase but is advantageous for the increases of the content of O'-sialon phase. For the parent glass, the best way for the improvement of volume fraction of YAG phase is to treat the glass under 1250°C for longer nucleation or crystallization time. No O'-sialon crystals appear in #7 glass–ceramic although #7 glass–ceramic contains a large amount of YAG which leads to nitrogen content in the residual glass very high. It seems that the crystallization of O'-sialon phase from this parent glass is more dependent on the heat treatment temperature than on the nitrogen content in the residual glass.

The variation in dominant crystalline phase, especially the phase transformations of $Y_2Si_2O_7$ can cause thermal and volume effects in the final glass–ceramics, which will limit the application of these glass–ceramics. Apatite ($Y_5Si_3O_{12}N$), different forms of $Y_2Si_2O_7$ and intermediate phase were not detected in the glass–ceramics prepared in this paper. Thus, no variations in dominant crystalline phase were observed in this work and phase transformations caused by $Y_2Si_2O_7$ or intermediate phase were avoided. It seems that 28Y48Si24Al83O17N glass is a satisfactory matrix for prepring YAG-based glass–ceramics or YAG/$\beta$-sialon materials.

### 3.3 *Microstructure*

Microstructures of HF-etched glass–ceramics were observed in this paper. Glass–ceramics prepared in this study were etched in 10% HF for 6 min because residual glassy phase in these glass–ceramics has relative high stability in HF for the enrichment in nitrogen after the precipitation of YAG. SEM section micrographs of #3–4, #6–9, #11 glass–ceramics are shown in figure 5. As shown in figure 5, all micrographs consist of dendrite crystals. YAG with a dendritic morphology precipitated from Y–Al–Si–O–N glasses has been reported (Vomacka 1997). However, Vomacks did not report the relationship between the morphology of YAG and the heat treatment temperature systematically. The length of a large amount of dendrite crystals in #6–9 glass–ceramics is less than 20 μ and that of the dendrite crystals in #3–4 glass–ceramics is less than 10 μ. From the micrographs of #6 and #7 glass–ceramics as shown in figure 5, the dendrite crystals can be seen much more clearly and the grain size increases with the increase of the crystallization temperature from 1150°C to 1200°C. With further increase of the crystallization temperature from 1250°C to 1300°C, the dendrite branches get thickened (see micrographs
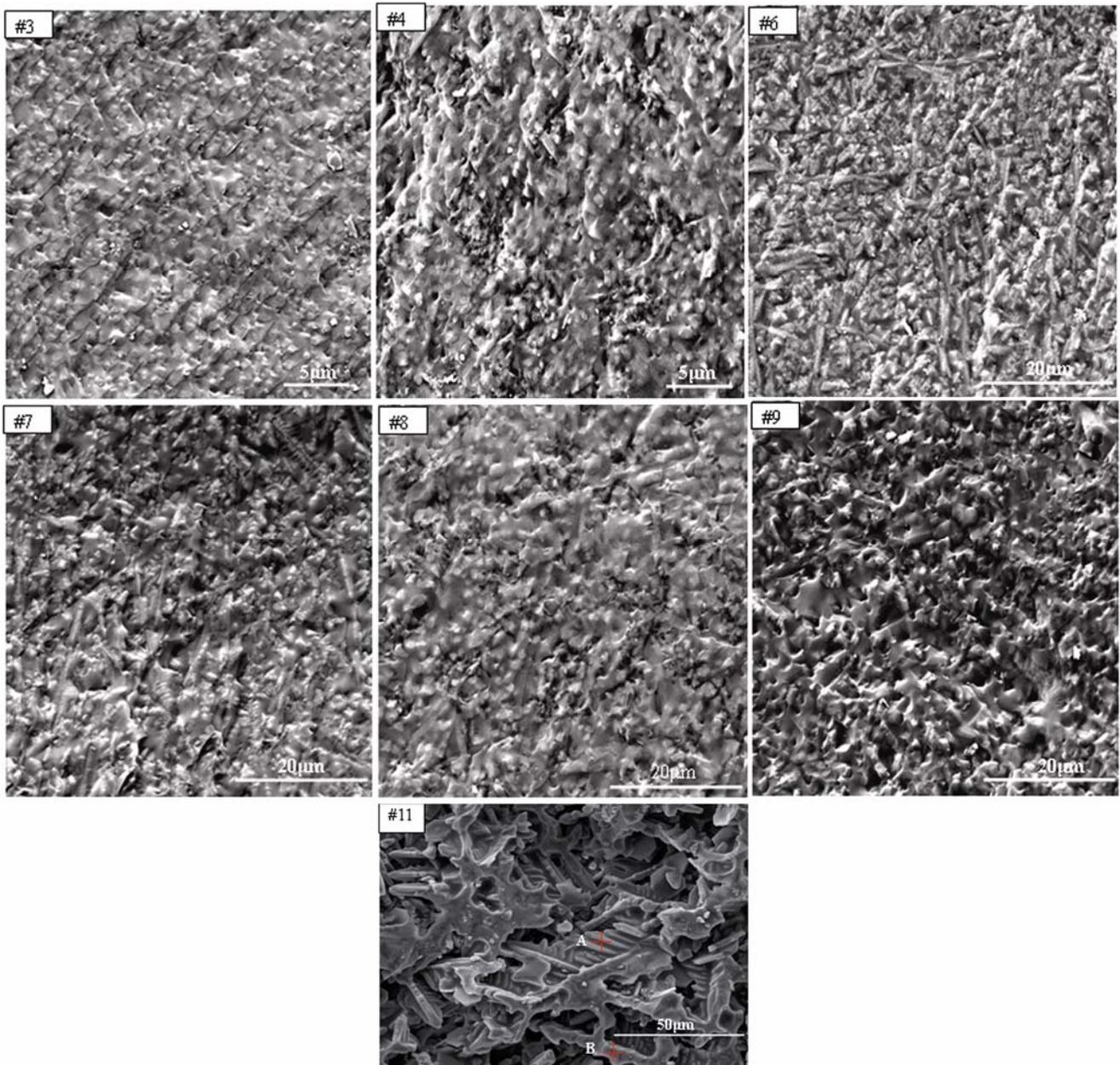
**Figure 5.** SEM section micrographs of the glass–ceramics obtained after different heat treatment conditions: 1000°C, 10 h + 1200°C, 4 h (#3); 1000°C, 10 h + 1250°C, 4 h (#4); 1050°C, 10 h + 1150°C, 4 h (#6); 1050°C, 10 h + 1200°C, 4 h (#7); 1050°C, 10 h + 1250°C, 4 h (#8); 1050°C, 10 h + 1150°C, 4 h (#9); 1300°C, 10 h (# 11).

of #8 and #9 glass–ceramics in figure 5). Comparing the micrographs of #3 and #4 glass–ceramics with those of #7 and #8 glass–ceramics respectively, it is clear that particle size of the dendrite crystals increases significantly when the crystallization temperature keeps constant but the nucleation temperature increases from 1000°C to 1050°C. As shown in figure 6, the micrograph of #11 glass–ceramic obtained by one-stage heat treatment at 1300°C for 10 h consists of dendrite crystals with much larger grain size in comparison with that of #9 glass–ceramic. The length of some dendrite crystals of #11 glass–ceramic even exceeds 50 µ.

High volume fraction of crystalline phases can also be observed. It can be seen from these SEM micrographs as shown in figure 5 that a large amount of crystals distribute on the micrographs and only small amount of pores caused by the erosion of residual glassy phase in HF acid are left. Volume fraction of crystalline phases in #11 glass–ceramic (79·8%) calculated from its XRD pattern is a little lower than that (90·7%) of #9 glass–ceramic, which can also be observed from their micrographs. The amount of pores left in the micrograph of #11 glass–ceramic is more than that of pores left in the micrograph of #9 glass–ceramic. For #9 glass–ceramic obtained by
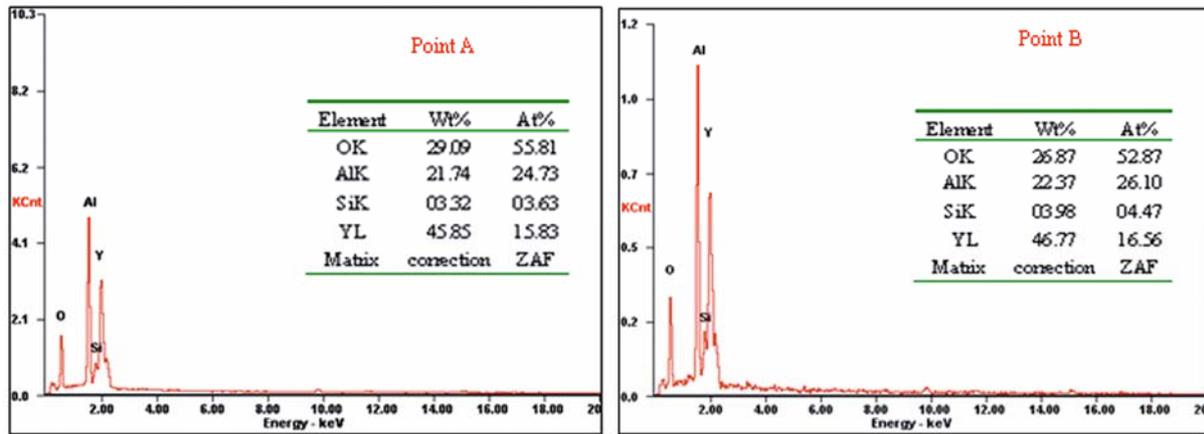
**Figure 6.**   SEM micrograph of #11 glass–ceramic and EDS spectra of points A and B marked in the micrograph.

two-stage heat treatment, a large amount of nuclei have been formed in the pretreatment stage and the following growth of these nuclei at the crystallization temperature for a relative short time makes the grain size relative small and the volume fraction of crystalline phase very high. However, for #11 glass–ceramic obtained by single stage heat treatment, there are two different factors to affect the volume fraction of crystalline phase. On the one hand, the glass is not treated at nucleation temperature, which makes the formation of crystal nuclei inadequate and results in a relative low volume fraction of the crystalline phase because of less crystal grain number. On the other hand, the parent glass is treated at a higher temperature for a long time, which results in forming the crystalline phases with higher volume fraction because of forming larger grain size. Obviously, two-stage heat treatment route for preparing the glass–ceramics has advantages in controlling grain size and in increasing volume fraction of YAG phases.

EDS analysis was preformed on points A and B which were marked in the micrograph of #11 glass–ceramic in figure 6. Since the grain size of the crystals distributed in micrograph of #11 glass–ceramic is large enough, the EDS analysis is meaningful. The result shows that the ratio of Y : Al in point A is $15 \cdot 83 : 24 \cdot 73$ (about 3 : 5) and that of Y : Al in point B is $16 \cdot 56 : 26 \cdot 1$ (about 3 : 5). The ratios of Y : Al in point A and point B close to that (3 : 5) of Y : Al in $Y_3Al_5O_{12}$. In this paper, YAG as the dominant crystalline phase is further proved by EDS.

## 4.   Conclusions

The glass-ceramics with single crystalline phase YAG and residual glass phase have been prepared by treating 28Y48Si24Al83O17N glass under 1250°C. With increasing crystallization treatment temperature, YAG always exists in the glass ceramics as major crystalline phase.

The second phase O'-sialon starts to precipitate from the residual glass enriched in nitrogen at 1250°C. All the prepared glass ceramics consist mainly of dendrite YAG crystals. As heat treatment temperature increases, the grain size increases and the dendrite branches get thickened. Two-stage heat treatment route has advantages for preparing the glass ceramics with fine crystal grain and high volume fraction of YAG phases. 28Y48Si24Al83O17N glass is proper to prepare YAG-based glass–ceramics and YAG/$\beta$-sialon composite materials because of high volume fraction of YAG phases.

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