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$CaO–SiO_2–Al_2O_3–Y_2O_3$ glasses as model grain boundary phases for Si_3N_4 ceramics

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Abstract

The glasses with compositions derived from the eutectic composition [37.78 $(Y_3Al_5O_{12})\cdot 62.22\,(SiO_2)$] of the quasi-binary glass system $(Y_3Al_5O_{12})$-(SiO_2) with addition of up to 20 mol.% CaO were investigated as model grain boundary phases for Si_3N_4 ceramics. The influence of CaO as model impurity on the physical properties of the glass (density, thermal expansion) and on the crystallisation behaviour was studied. Although the initial composition of the basic glass was that of yttrium-aluminium garnet ($Y_3Al_5O_{12}$–YAG), no crystalline YAG was detected. Apart from yttrium disilicate ($Y_2Si_2O_7$), anorthite ($CaAl_2Si_2O_8$), tricalcium aluminate ($Ca_3Al_2O_6$), and calcium yttrium oxide silicate ($Ca_4Y_6O(SiO_4)_6$), a new phase was detected, not found in the powder diffraction file (PDF) database. Cavities were formed within the devitrified glass due to the volume contraction after crystallisation. Possible implications for the mechanical properties of Si_3N_4 ceramics sintered with addition of Y_2O_3–Al_2O_3 are discussed in terms of the observed compositional dependences of the physical properties of $CaO–Y_2O_3–Al_2O_3–SiO_2$ glasses.

Keywords: Glass; Thermal properties; Grain boundaries; Si_3N_4; Crystallisation

1. Introduction

Silicon nitride ceramics are usually densified with the aid of various sintering additives (such as Al_2O_3, Y_2O_3, Yb_2O_3, etc.) in the temperature interval between 1750 and 2000 °C. These additives in combination with silicon dioxide, which is virtually always present at the surface of silicon nitride powder particles, and with nitrogen, which originates from the furnace atmosphere, or from dissolution of silicon nitride particles in the melt, form at the sintering temperature a liquid, which after cooling to room temperature transforms to amorphous glassy phase.[1–3] This phase is concentrated at grain boundaries, and in three and four-grain boundary junctions, commonly abbreviated as triple pockets.[1–3] Although silicon nitride usually exhibits excellent mechanical properties at room temperature, the grain boundary glass softens at temperatures >1200 °C, and causes degradation of mechanical properties at elevated temperatures.[4–6] It is known that high-temperature mechanical properties can be improved by decreasing the content of glass. This can be achieved by crystallisation of glassy phase with adequate post-sintering heat treatment.[7] Intergranular phase can be nearly completely crystallized, with the exception of a thin residual amorphous grain boundary film.[8] Formation of crystalline phases at grain boundaries and in triple pockets can further influence the creep in two ways. Firstly, the presence of crystalline phases in grain boundary junctions increases the creep resistance by increasing the energy required to initiate deformation by grain boundary sliding.[9] Secondly, a significant volume change can be observed during crystallisation, as a consequence of the formation of crystalline phases with specific volume smaller than the specific volume of original glass. The creep resistance (and also room temperature strength) is then impaired by the formation of cavities, and microcracks in triple pockets, and by debonding of crystals from the adjoining silicon nitride grains.[10] Alkaline-earth impurities, in particular Ca, strongly influence the high-temperature properties of the residual grain boundary glass, and hence, also the high-temperature properties of polycrystalline Si_3N_4.[2,8,11] The addition of Ca causes softening of glass at lower temperatures compared to Ca-free glass.[2,11]

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Moreover, the mismatch of thermal expansions of Si_3N_4 grains, of grain boundary glasses, and of secondary crystalline phases results in formation of internal residual stresses in silicon nitride composites, with corresponding consequences for the room-temperature mechanical properties.[6,12] Previous crystallisation studies indicate that the addition of Y_2O_3 and Al_2O_3 to Si_3N_4 ceramics results in crystallisation of yttrium silicate Y_2SiO_5, and of yttrium disilicate$Y_2Si_2O_7$ from grain boundary glass. These phases are usually accompanied by yttrium-aluminium garnet $Y_3Al_5O_{12}$ (YAG). With increasing time, and temperature of heat treatment Y_2SiO_5 is gradually replaced by $Y_2Si_2O_7$ and YAG.[1,7] Although potentially beneficial for high-temperature properties of silicon nitride ceramics through decreasing the total amount of grain boundary glass, crystallisation of YAG has detrimental effect on the room temperature strength. This decrease is attributed to the volume shrinkage associated with the formation of YAG, which results in microcracking, and debonding of the garnet crystals from the surrounding silicon nitride grains.[10]

The present work investigates the influence of the Ca^{2+} addition on the density, thermal expansion, and crystallisation properties of Y_2O_3–Al_2O_3–SiO_2 glasses, as the first, nitrogen-free approximation of model systems of grain boundary glasses in silicon nitride ceramics sintered with addition of Y_2O_3 and Al_2O_3, and with CaO as a model impurity. Possible implications for the mechanical properties of Si_3N_4 ceramics are discussed in terms of the observed compositional dependences of the physical properties of the glasses CaO–Y_2O_3–Al_2O_3–SiO_2.

2. Experimental

2.1. Preparation of glasses

Glasses were prepared by mixing the appropriate quantities of high purity powder reagents Al_2O_3 (99.9%), Y_2O_3 (PIDC, USA, grade 4N-99.99%), SiO_2 (pure, Reachim, St. Petersburg), and $CaCO_3$ (p.a., Lachema, Brno), to yield 100 g of glass. The powders were dry-mixed and melted in a 10%-RhPt crucible in air in an electric furnace, and held at the melting temperature for 5 h. Depending on the composition the melting temperature varied between 1570 and 1630 °C. The homogeneity of the glasses was ensured by repeated fritting and hand mixing in the course of melting. Each melt was poured onto a stainless steel plate, and annealed in a muffle furnace for 4 h. Depending on the composition the annealing temperature varied between 800 and 850 °C. After annealing, the samples were cooled down to room temperature in the furnace.

Table 1
Chemical compositions of studied glasses (expressed in mole fractions)

Sample	$x(CaO)$	$x(Y_2O_3)$	$x(Al_2O_3)$	$x(SiO_2)$	$\frac{x(NBO)}{x(Si)+x(Al)}$
YAGSiO$_2$	0.00	0.1417	0.2361	0.6222	0.1727
YAGSiCa1	0.05	0.1346	0.2243	0.5911	0.2207
YAGSiCa2	0.10	0.1275	0.2125	0.5600	0.2741
YAGSiCa3	0.15	0.1204	0.2007	0.5289	0.3338
YASiCa01	0.05	0.1229	0.2079	0.6222	0.2072
YASiCa02	0.10	0.1042	0.1736	0.6222	0.2465
YASiCa03	0.15	0.0854	0.1424	0.6222	0.2908
YASiCa04	0.20	0.0666	0.1111	0.6222	0.3419

The last column represents the molar ratio of non-bridging oxygens to network formers in the glass structure.

Two compositional series of calcium yttrium aluminosilicate glasses were prepared. The compositions of glasses are summarised in Table 1. The compositions of both series can be generally expressed as $(Y_3Al_5O_{12})_x(SiO_2)_y(CaO)_z$, $(x+y+z=1)$ with the Y_2O_3/Al_2O_3 molar ratio equivalent to that of crystalline YAG, and the silica content in the basic glass (i.e. $z=0$) corresponding to the eutectic composition of the pseudo-binary system YAG–SiO_2 [(37.78 $(Y_3Al_5O_{12})$·62.22 (SiO_2)]. The composition of the set I (specimens YAGSiCa1–YAGSiCa3), can be more specifically expressed by the general formula $[(Y_3Al_5O_{12})_x(SiO_2)_y]_{1-z1}(CaO)_{z1}$, where $x=0.3778$, and $y=0.6222$) with the constant yttria/alumina/silica molar ratio, and with variable CaO content. The composition of the set II (specimens YASiC01–YASiCa04) is expressed by the general formula $(Y_3Al_5O_{12})_{x-z2}(SiO_2)_y(CaO)_{z2}$ with variable YAG/CaO molar ratio and constant silica content. The studied range of compositions of prepared glasses is shown in the CaO–$Y_3Al_5O_{12}$–SiO_2 pseudoternary phase diagram in Fig. 1.

Thermal expansion coefficient α was determined using a Netzsch TMA-402 thermomechanical analyser. Rectangular bars with dimensions of approximately 20 mm × 5 mm × 5 mm were cut from a bulk glass, ground with a diamond grinding wheel, and then heated in the analyser in ambient atmosphere at the heating rate of 5 °C/min. The average coefficient of thermal expansion in the temperature range between 350 and 550 °C was calculated from the slope of linear temperature dependence of the relative linear expansion of the bars.

The density of glasses was measured by the Archimedes method of bulk specimens using water as a suspending medium. The density of crystallized glasses was measured on pulverised specimens by liquid pycnometry in hexamethyldisiloxane.

The glasses were devitrified by heating the bulk specimens in ambient atmosphere in an electric furnace at 1150 °C for 5 or 70 h. XRD analysis of crystallised glasses was carried out

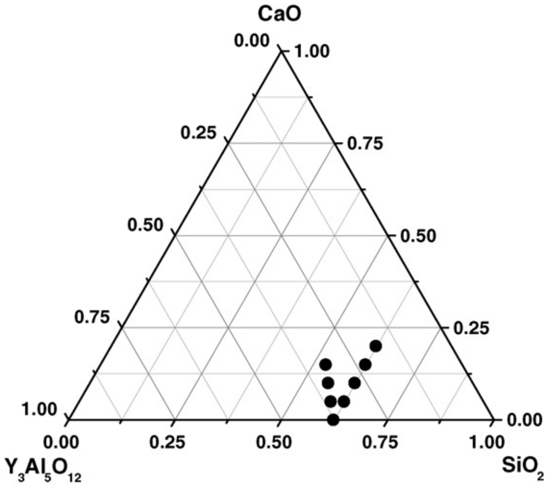

Fig. 1. Range of compositions of prepared glasses in the Y_2O_3–Al_2O_3–SiO_2 ternary phase diagram.

using a Siemens D5005 diffractometer operating at 40 kV and 30 mA in the 2Θ range 5–85°, and with Cu Kα radiation. The qualitative analysis was carried out using a standard software package Diffract Plus (Bruker-AXS, version 6.0). The contents of individual crystalline phases in devitrified glasses were estimated from relative intensities of diffraction peaks using the same software package. The more precise quantification with the use of Rietveld analysis was not possible: not all phases identified from diffraction patterns have known structures, and the content of residual amorphous phase could not be determined.

The crystallised specimens were further examined by TEM (JEOL 1200EX) in order to identify possible presence of microcavities, and/or crystalline phases.

3. Results and discussion

3.1. Thermal expansion

The thermal expansion was evaluated as the function of the content of impurities (CaO) in the basic glass (Fig. 2a). The thermal expansion increased with increasing content of CaO, but in quite a different way in the sets I and II glasses. This implies the influence of another network modifying ion Y^{3+} (SiO_2 and Al_2O_3 are known to be network forming oxides[13,14]), which decreases the number of bridging oxygens in the structure of glass, i.e. the degree of cross-linking of the glass structure. In some glasses this effect can be compensated with higher content of silica. Therefore, the thermal expansion coefficients of the set I glasses, where part of silica is replaced by calcia, were higher than the thermal expansion coefficients of glasses from the set II, where the concentration of silica is constant, and always higher than the content of silica in the set I glasses. With regard to these facts we have to emphasise that the structure and properties of glasses are complex functions of all their constituents. The dependences of glass properties on composition cannot be therefore simply described as dependences on the content of single oxide (CaO in our case). In the following text all dependences of measured parameters on composition are therefore expressed by taking into account the structural function of all oxide constituents in glass (Fig. 2b). The structural function of components is expressed as the ratio of molar fraction of non-bridging oxygens (NBO) to molar fraction of tetrahedrically coordinated central atoms of Si and Al, i.e. $x(\mathrm{NBO})/[x(\mathrm{Si})+x(\mathrm{Al})]$. The molar fraction of non-bridging oxygens is calculated as the sum of non-bridging oxygens from individual network modifying oxides (CaO, Y_2O_3) reduced by the number of oxygens spent for the transition $Al_2O_3 + O^{2-} \rightarrow 2AlO_2^{-}$. The molar fraction of non-bridging oxygens (NBO) to molar fraction of tetrahedrically coordinated central atoms Si and Al can be then expressed as follows:

$$\frac{[n(\mathrm{CaO}) + 3n(\mathrm{Y_2O_3}) - n(\mathrm{Al_2O_3})]}{[n(\mathrm{SiO_2}) + 2n(\mathrm{Al_2O_3})]}$$

The thermal expansion coefficients of both sets of glasses plotted within these coordinates then show similar trends, thus confirming combined network modifying function of both calcia and yttria. The thermal expansion coefficients of studied glasses varied between $5.54 \times 10^{-6}\,\mathrm{K}^{-1}$ (basic glass without CaO) and $6.56 \times 10^{-6}\,\mathrm{K}^{-1}$ (set I, YAGSiCa3, 15 mol.% CaO), and $6.58 \times 10^{-6}\,\mathrm{K}^{-1}$ (set II, YASiCa04, 20 mol.% CaO). Silicon nitride is the phase with relatively low thermal expansion ($3 \times 10^{-6}\,\mathrm{K}^{-1}$ in the temperature interval 20–1000 °C).[15] Then even the presence of the basic yttrium aluminosilicate glass with higher thermal expansion would result in formation of residual stresses within the silicon nitride matrix. These could relax by formation of microcracks along the grain boundaries, thus promoting crack propagation in the material. The presence of Ca^{2+} ions further increases the thermal expansion coefficient of grain boundary glass; the presence of calcia as an impurity can be therefore considered as deleterious. However, the overall increase of thermal expansion with increasing calcia content is relatively small: the expected influence on room temperature mechanical properties would be therefore only mild.

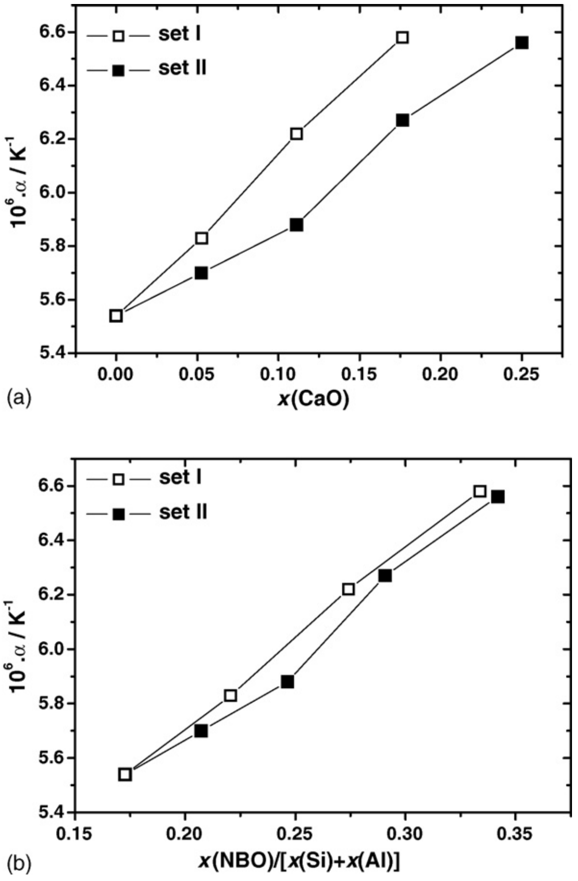

Fig. 2. The relationship between the thermal expansion coefficients and the molar fraction of CaO (a), and the ratio of molar fraction of non-bridging oxygens (NBO) to molar fraction of tetrahedrically coordinated central atoms of Si and Al (b) in the sets I and II glasses.

3.2. Density

Density measurements confirmed that the density of $YAGSiO_2$ glasses decreased with increasing CaO content in the structure of glass. However, this trend was not unambiguous, and was markedly influenced by the presence of the second modifying ion Y^{3+} (Fig. 3). In the set I glasses, with calcia added in

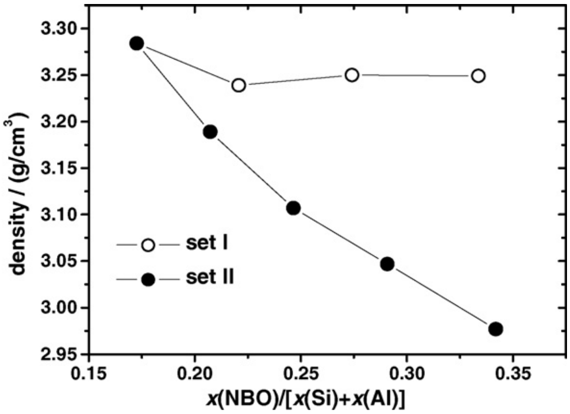

Fig. 3. Density of the sets I and II glasses as a function of the ratio of molar fraction of non-bridging oxygens (NBO) to molar fraction of tetrahedrically coordinated central atoms of Si and Al.

place of silica, and yttria content changing only slightly (from 14 to 12 mol.% for $YAGSiO_2$ and YAGSiCa3, respectively), the density decreased by 1.4% as 5 mol.% calcia was added to the basic glass. No further change was observed as the calcia content increased to 10, or 15 mol.%. In the set II glasses, the concentration of yttria decreased progressively with increasing calcia content. In this case the density decreased by more than 9% as the content of calcia increased to 20 mol.%.

Further experiments revealed that cavities were formed in studied glasses in the course of devitrification (Fig. 4). Such effect was too expected, as the crystalline phases are denser than the original glass. However, the extent of cavity formation was surprising, as the increase of density due to formation of denser crystalline phases was expected to be, at least in part, compensated by shrinkage of the specimen by viscous flow of residual glass. The first order estimates of the maximum extent of cavity formation have been made under the following assumptions: (I) no shrinkage of the specimens by viscous flow of glass takes place in the course of crystallisation: the difference between the volume of original glass and the glass-crystalline system after thermal treatment is then equal to the volume of cavities in the specimen; (II) the crystallization yields crystalline phases in molar ratios as estimated by semi-quantitative XRD measurements; (III) the UI phase, whose composition is unknown, is not considered; (IV) the process proceeds only as long as one of the oxides in glass (CaO, or Y_2O_3) is completely consumed by the formed crystalline phases. The results show that, with the stoichiometry given, between 13 and 77 mol.% of the original glass can crystallise (13 mol.% in YAGSiCa1, and 77 mol.% in YAGSiCa2). However, these are extreme values, and usually 30–40 mol.% of glass crystallises before CaO or Y_2O_3 are completely consumed. This leaves a significant mole fraction of residual glass with markedly altered composition, and somewhat lower density. Considering high density of crystalline phases, especially those, which contained yttria, the total increase of density due to crystallisation varies between 0.2 and 4.4%, which results in the total volume change between 0.05 and 1.4%.

The crystallisation of calcia-containing aluminosilicate grain boundary glasses can be thus expected to impair the room temperature properties of silicon nitride ceramics. Cavities can be formed in grain boundary junctions as a result of significant negative volume change, which may in turn result in formation of microcracks, debonding of crystalline phases from the surrounding glass matrix and decrease of the room temperature strength of the material.[10]

The density of thermally treated glasses was not measured by Archimedes method in water: the presence of cavities in the bulk glass would result in incorrect readings. The density was therefore measured by liquid pycnometry on pulverised samples. The results are shown in Fig. 5. Indeed, in accord with the results of estimations mentioned above an increase of density of crystallised samples was observed with respect to original glass. In the set I glasses, the density of all studied compositions increased after 5 h thermal treatment-induced devitrification. The increase was more pronounced after 70 h, indicating more extensive devitrification of glasses after extended isothermal treatment. The specimens with higher content of calcia achieved higher densities after thermal treatment. The observed trends serve as the indirect evidence that the presence of calcia increases the

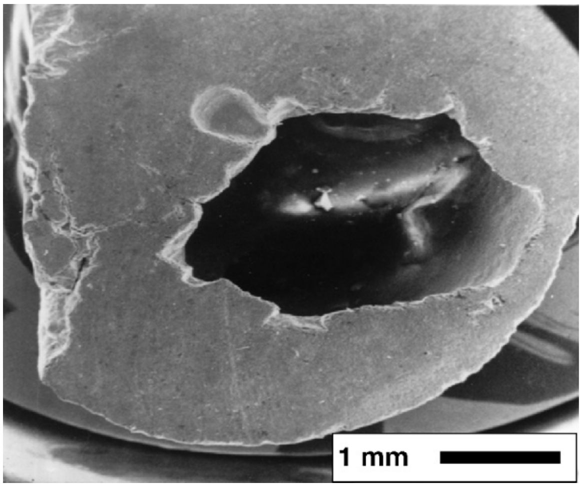

Fig. 4. A cavity in the sample of crystallised $YAGSiO_2$ glass after 5 h thermal treatment at 1150 °C.

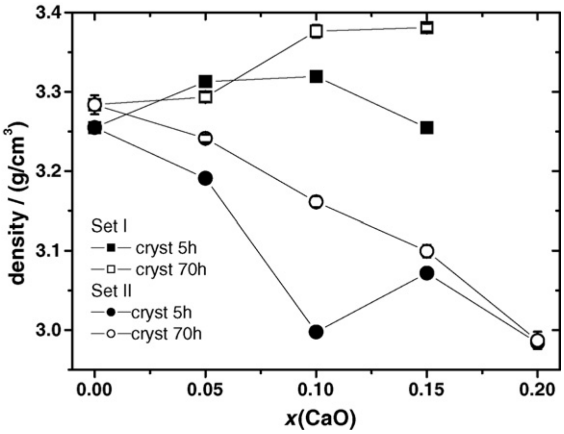

Fig. 5. The density-composition dependence of the sets I and II glasses after 5 and 70 h thermal treatment at 1150 °C.

tendency of the glass to crystallise: higher density after devitrification can be explained by higher fraction of crystalline phases with high density, and lower fraction of residual glass in thermally treated glasses.

Quite opposite trends were observed in the set II glasses. Devitrification of the glass leads to slight increase of density after 5 h thermal treatment, which increased further with prolonged devitrification time. However, the density of crystallised samples decreased linearly with increasing calcia content, following approximately the same trend as the original glasses. The only exception from the observed trend was the sample YASiCa02 after 5 h thermal treatment, where extreme decrease of density was observed. This anomaly was however minimised in glass of the same composition, but heat treated for 70 h.

These apparently inconsistent results can be viewed differently if one takes into account that the fraction of residual, not crystallised glass might vary significantly in thermally treated specimens with various composition. Generally, the tendency of glasses to crystallise tends to increase with increasing calcia content.[16] In the set I glasses where silica is progressively replaced by calcia the crystallisation can be expected to proceed to greater extent, and the content of residual glass after thermal treatment would be lower. On the contrary, the content of silica in the set II glasses is constant, and calcia is added on account of alumina and yttria. The extent of crystallisation is therefore expected to be lower than in the set I. For reasons, which are presently not clear, the crystallisation of the glass YASiCa02 appears to be very difficult, as indicated by anomalously low density shown in Fig. 5. This anomaly can be explained in part by high fraction of residual glass after 5 h devitrification, and very low contents of crystalline phases with high density. Seventy-hours thermal treatment appears to be sufficient for extended crystallisation even in this system and the observed anomaly is minimised. Further apparent inconsistency is that the density of the 5 h crystallised glass YASiCa02 is in fact *lower* than the density of the original glass before crystallisation. The possibility of an accidental error was excluded by repeated measurements, which always yielded identical result. Possible presence of cavities of micrometer dimensions in grains of pulverised glass, which could account for the observed anomaly, has been explored by transmission electron microscopy. However, the TEM examination identified only a relatively large fraction of microcrystals with dendritic morphology, but no microcavities (Fig. 6a and b). Some hints for explanation of the observed anomaly were provided by XRD semi-quantitative analysis of crystallised samples, as shown below.

With regard to the possible influence of devitrification on the mechanical properties of silicon nitride ceramics, no final conclusions could be drawn. The observed extensive formation of cavities could be expected to impair the room temperature mechanical properties, as discussed above. Some improvement of the creep resistance might occur as a consequence of the presence of crystalline secondary phases at the grain boundaries, which would increase the energetic demands for grain boundary sliding, and hence, limit the high-temperature deformation of the material.

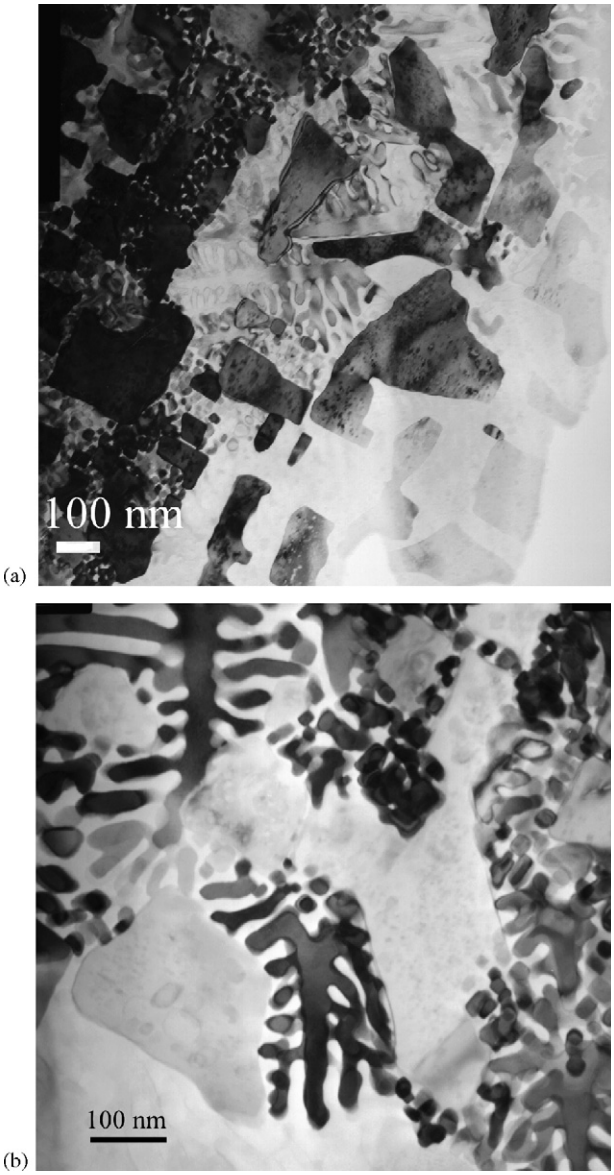

Fig. 6. The TEM micrograph of the YASiCa02 devitrified glass after 5 h isothermal treatment at 1150 °C (a), and the microcrystals with dendritic morphology observed in the sample (b). Dark regions represent crystalline phases, light areas are residual glass.

3.3. XRD analysis

XRD analysis revealed the existence of at least six different crystalline chemical species in annealed glasses. Some of them were present in more than one crystalline form, e.g. yttrium disilicate was detected in the form of γ-$Y_2Si_2O_7$, PDF No. 32-1448, and keivyite PDF No. 22–1103. Anorthite ($CaAl_2Si_2O_8$, PDF No. 09–0464 and 12–0301), tricalcium aluminate ($Ca_3Al_2O_6$, PDF No 32–0150), and calcium yttrium oxide silicate ($Ca_4Y_6O(SiO_4)_6$, PDF No 27–0093) were also identified. Despite the fact that the chemical composition of glass reflects the molar ratio Y2O3/Al2O3 equivalent to crystalline yttrium-aluminium garnet (YAG), no YAG was detected. This result is in part in accord with recent observations of Kolitsch et al. who concluded that under given experimental con-

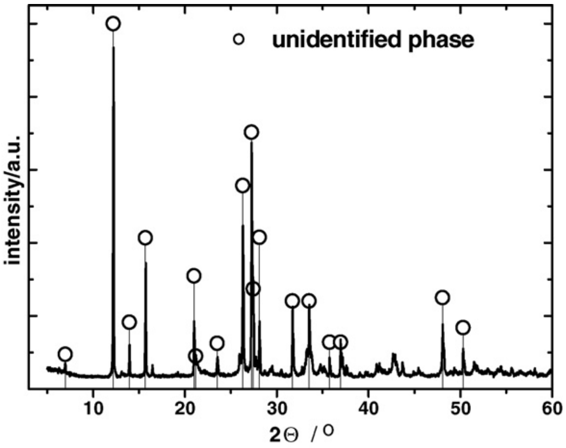

Fig. 7. The X-ray diffraction pattern of the UI phase.

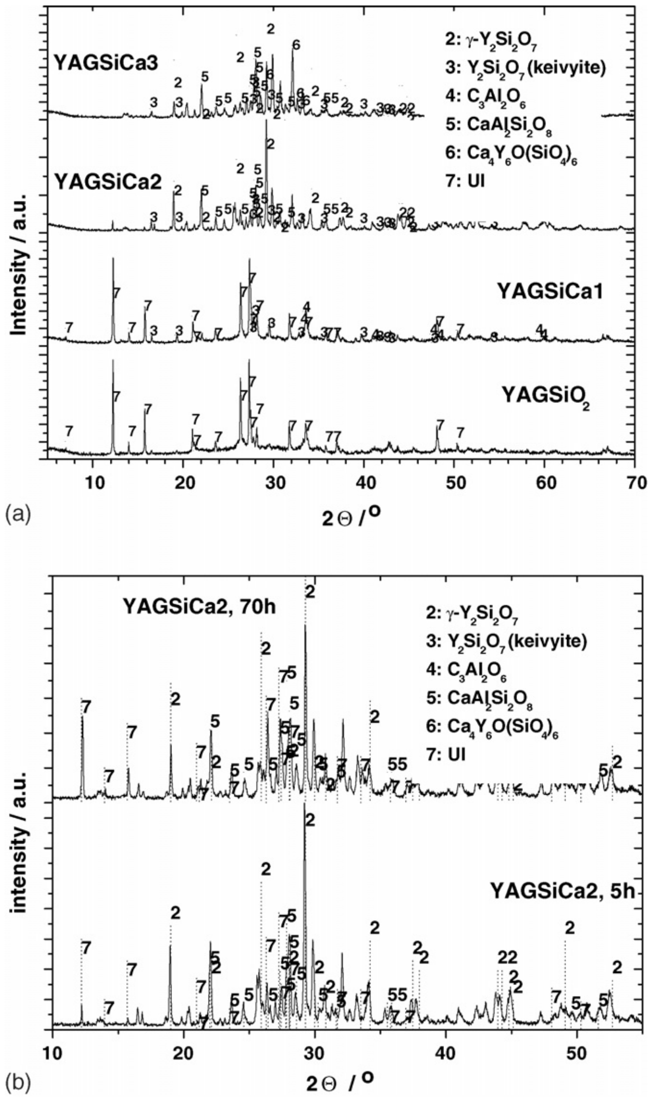

Fig. 8. X-ray diffraction patterns of crystallised glasses set I, illustrating the influence of the content of calcia (a) and of the time of isothermal treatment (b) on the content of the UI phase.

ditions no YAG can be formed and suggested that a ternary solid solution $Y_4Al_2O_9$–$Y_4Al_{2(1-x)}$ $Si_{2x}O_{9+x}$ is crystallised from yttrium-containing aluminosilicate glasses.[17] However, neither of these phases could be found in our specimens. Instead, a set of diffraction lines, which could not be attributed to any single, or combination of more, crystalline phases registered in the PDF database was found. This phase is referred to in the following text as the UI (unidentified) phase. The diffraction pattern shown in Fig. 7 indicates that the UI phase is created primarily by crystallisation of the basic $YAGSiO_2$ glass which, after 5 h annealing at 1150 °C, contains almost exclusively the UI phase. The attempts to synthesise it as a clean substance failed and the crystallised samples contained at the best estimated 95% of the UI phase. This prevented unambiguous identification of diffraction peaks and their attribution to some specific phase. We can only speculate that the phase is a crystalline yttrium aluminosilicate of unknown stoichiometry, or a solid solution of two or more yttrium aluminosilicate species. This view is further supported by the fact that the content of the UI phase is lower in calcia-containing specimens and decreases progressively with increasing mole fraction of calcia in glass (Fig. 8a), where it is replaced by the phase $Ca_4Y_6O(SiO_4)_6$ with high calcia content. The addition of calcia above 10 mol.% resulted in disappearance of the UI phase below the detection limit of the XRD analysis. Extended isothermal dwell at 1150 °C favoured the formation of the UI phase, and the intensities of its diffraction peaks after 70 h thermal treatment are stronger than after 5 h (Fig. 8b).

The estimated mole fractions of crystalline species are shown in Fig. 9a and b. For simplicity, different crystallographic phases of the same chemical composition (e.g. γ-$Y_2Si_2O_7$, and keivyite) were considered as a single phase. As the quantification of the UI phase was not possible, due to impossibility to attribute the diffraction peaks to some specific phase,[18] the substance was disregarded in the analysis, and only the mole fractions of the four known phases are shown. Some common trends can be however observed in both sets of studied glasses. Crystallisation of the basic, calcium-free glass results in the formation of a single phase UI. The UI phase disappeared gradually, as the calcia content increased. The major phases identified in crystallised glasses containing 5 and 10 mol.% CaO were various crystallographic modifications of yttrium disilcate, anorthite, UI, and in some cases, small amounts of tricalcium aluminate. In the set I glasses the content of yttrium disilicate increased as the content of calcia changed from 5 to 10 mol.%. This increase was accompanied by disappearance of tricalcium aluminate. Further increase of the content of calcia to 15 mol.% was reflected in decrease of yttrium disilicate content, which was then compensated by increase of the content of anorthite and formation of the phase $Ca_4Y_6O(SiO_4)_6$.

Purely qualitatively speaking, the increase of calcia content results in the shift of phase composition in both sets of glasses from yttrium disilicate and calcium trialuminate towards anorthite and $Ca_4Y_6O(SiO_4)_6$:

$$Y_2Si_2O_7 + Ca_3Al_2O_{12}(+\mathrm{UI}) \leftrightarrow CaAl_2Si_2O_8 + Ca_4Y_6O(SiO_4)_6$$

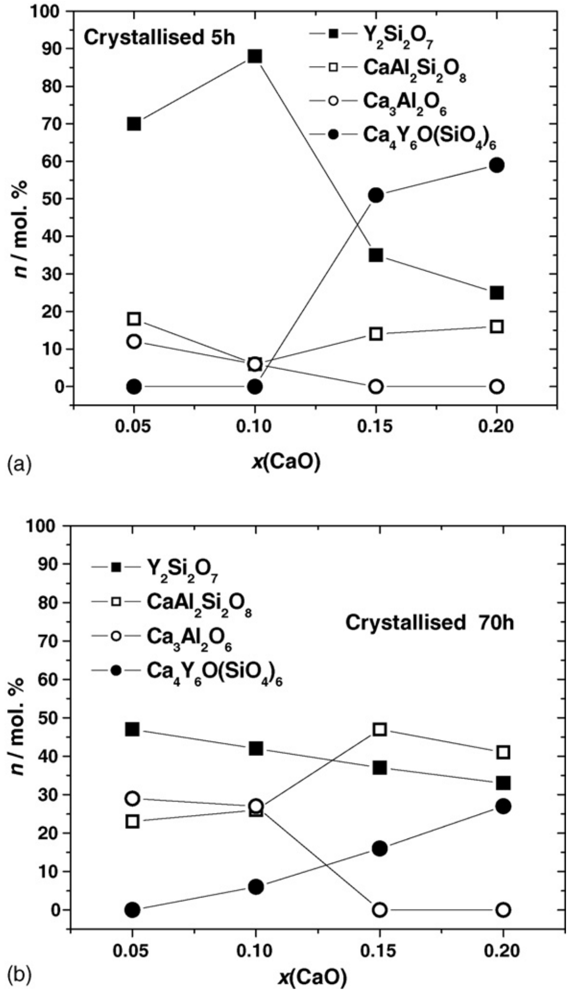

Fig. 9. Estimated mole fractions of individual crystalline chemical species in the set II glasses after 5 h (a) and 70 h (b) of thermal treatment induced crystallisation.

Extended dwell at annealing temperature of the set I glasses resulted in slight increase of the contents of yttrium disilicate and anorthite, accompanied by simultaneous decrease of tricalciumaluminate and $Ca_4Y_6O(SiO_4)_6$.

In the set II glasses the phase development was similar. The concentration of anorthite in both series of crystallized glasses increased after extended annealing at 1150 °C. It seems that in both sets of crystallised glasses the prolonged heat treatment promoted its formation, especially in glasses with high calcia contents. Generally speaking, the first phases to crystallise in the low-calcia glasses appear to be yttrium disilicate, the UI, anorthite, and tricalcium aluminate. Their contents increased, or changed only slightly as the time of isothermal treatment extended. In high-calcia glasses the first phases to crystallise were yttrium disilicate, anorthite, and $Ca_4Y_6O(SiO_4)_6$. However, with increasing time of isothermal treatment the $Ca_4Y_6O(SiO_4)_6$ phase disappeared gradually, and yttrium disilicate and anorthite remained as the main crystalline phases.

With respect to the specimen YASiCa02 with anomalously low density after 5 h crystallisation, it has to be noted that the major crystalline phase is yttrium disilicate (88 mol.% of all crystalline species). The exact extent of crystallinity of the specimen is not known; it can be however anticipated that the crystallisation of yttrium disilicate will result in significant depletion of silica and yttria, and marked increase of relative content of calcia in residual glass. Calcia as network modifier will "open" the structure of residual glass, significantly reducing its density. The glass of such composition at grain boundaries of silicon nitride ceramics can be then expected to form weak interfaces between Si_3N_4 grains resulting in intergranular propagation of cracks in the material, with possible positive effect on fracture toughness.

The data discussed above show that crystallisation of yttria and calcia containing aluminosilicate glasses is a complex process, which is strongly influenced not only by the content of impurities (calcia, in this case), but also by the total ratio of network forming and network modifying components in the structure of glass, and by the time of isothermal dwell. Moreover, in the real system of silicon nitride ceramics with grain boundary aluminosilicate glass the process of crystallisation will be further influenced by the presence of nitrogen in glass structure (which is known to dissolve in glass from Si_3N_4 and increase its viscosity), by the presence of minor impurities, which tend to concentrate in triple grain boundary junctions, and by steric constraints imposed to a nanometre thick film of grain boundary glass by surrounding crystalline ceramic matrix grains. There would be therefore no straightforward correlation between the crystallisation characteristics of the bulk glass and the crystallisation of glass systems in real ceramic materials, or their room or high-temperature mechanical properties.

4. Conclusions

The physical properties of calcia-containing yttria aluminosilicate glasses studied as model glasses for silicon nitride ceramics depend not only on the content of calcia as the model impurity, but rather on the total fraction of network modifying oxides (CaO, Y_2O_3) in the glass structure. The thermal expansion coefficients increased and the densities of glasses decreased with the increasing content of network modifiers. Crystallised glasses contained yttrium disilicate, anorthite, tricalcium aluminate, calcium yttrium oxide silicate, and one unidentified phase, most likely a crystalline yttrium aluminium silicate of unknown stoichiometry, or a solid solution of two or more yttrium aluminium silicate species. No YAG was detected. Prolonged dwell at annealing temperature, and increased CaO content promoted the formation of anorthite and calcium yttrium oxide silicate, and decreased the content of yttrium disilicate in crystallised glasses. Cavities were observed in crystallised glasses, as the consequence of formation of crystalline phases with the densities higher than the density of the original glass. The results implicate deleterious effect of crystallisation on room temperature mechanical properties of yttrium aluminosilicate containing silicon nitride ceramics through cavity formation, grain boundary microcracking and debonding of glass-silicon nitride interfaces. No unambiguous conclusions can be drawn from the crystallisation experiments for the high-temperature properties of silicon nitride ceramics, although the extent of crystallisation achieved by high-temperature isothermal treatment of bulk glasses suggests that significant reduction of the volume fraction of grain boundary glass, and hence, improved creep resistance can be achieved by suitable heat treatment of yttria-alumina sintered Si_3N_4 ceramics.

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