THE PREPARATION OF BINARY Al$_2$O$_3$–Y$_2$O$_3$ GLASS MICROSPHERES BY FLAME SYNTHESIS FROM POWDER OXIDE PRECURSORS

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The work deals with alternative way of preparation of binary aluminate glasses by flame synthesis of glass microspheres from powder precursors, and their subsequent sintering under mechanical pressure in viscous flow regime and in the temperature interval between the glass transition temperature T_g and the onset of crystallization temperature T_x. The flame synthesis yielded the microspheres with diameters between 10 and 40 µm: seven compositions in the pseudo binary system Al$_2$O$_3$–Y$_3$Al$_5$O$_{12}$ (YAG) were prepared. Except of the eutectic composition, all other compositions were partially crystalline, consisting of amorphous yttrium aluminate matrix containing YAG and α-Al$_2$O$_3$ as the main crystalline phases. The presence of crystalline phases was due to insufficient melting of the precursor powder in the flame and could be partially eliminated by re-melting. The results of DTA indicated hight tendency of the prepared glasses to crystallization, with narrow interval of 50 °C between the T_g and T_x. The sintering of microspheres under applied mechanical pressure of 30 MPa resulted in white non transparent glasses with residual porosity P = 0.12, and increased content of crystalline phases as the result of secondary crystallization of glasses during sintering.

INTRODUCTION

Aluminate glasses with high alumina content are considered as potential candidates for various applications ranging from transparent ballistic protections, through infrared transparent windows, to hosts for rare earth elements in materials used for solid state lasers. However, the preparation of aluminate glasses in bulk is not easy because Al$_2$O$_3$ is a difficult glass-former and the melts have high tendency to crystallize. The synthesis of aluminate glasses then requires high cooling rates in the order of magnitude 10^3 K/s to avoid crystallization but also, especially in case of binary rare earth aluminates, also extremely high melting temperatures. For example, in the system Al$_2$O$_3$–Y$_2$O$_3$ studied in this work the lowest melting temperature is the eutectic at 60 wt.% of Al$_2$O$_3$ at 1760°C. A score of various, mostly experimentally demanding, techniques aimed at preparation of aluminate glasses has been described in the literature. Containerless melting techniques with the use of an aero-acoustic levitator (AAL) or a conical nozzle levitator (CNL) are used to eliminate heterogeneous nucleation on melting container surfaces and thus to suppress crystallisation on cooling [1] Rare-earth aluminates can be thus prepared in the form of bulk single-phase glass or glass fibers [2-4]. McMillan et al. prepared CaO–Al$_2$O$_3$ glasses, containing 50 mol % Al$_2$O$_3$ via splat quenching technique [5]. Rosenflanz et al. [6] prepared bulk Al$_2$O$_3$–Re$_2$O$_3$ (Re = Y, La, Gd) glasses with hardness between 14.4 and 18.3 GPa and the fracture toughness between 2.1 and 4.2 MPa.m$^{1/2}$ by pressure-assisted sintering of glass microbeads prepared by spraying of suitable precursors into hydrogen-oxygen flame. The sintering was carried out at the temperatures, which were sufficiently high to facilitate densification by plastic flow, but still low enough to prevent crystallization of the glass.

The present work is aimed at preparation of Y$_2$O$_3$–Al$_2$O$_3$ glass microspheres with various Al$_2$O$_3$ content from oxide powder precursors sprayed into oxygen/methane flame. The work attempts to investigate the compositional range, in which the microspheres can be prepared in glassy state, reports on basic properties of prepared glasses, and on the attempts to prepare Y$_2$O$_3$–Al$_2$O$_3$ glasses in bulk by hot pressing.

EXPERIMENTAL

High-purity oxide powders Y$_2$O$_3$ (Treibacher Industrie AG, Austria), and Al$_2$O$_3$ (Taimicron TM DAR, Krahn Chemie GmbH, Germany) were used for preparation of precursors powders. The required amounts of oxide powders were homogenised in a PE bottle with

high purity alumina milling balls in isopropanol for 24 h. The suspension was then dried at continuous stirring under infrared lamp, and sieved through a 100 μm PE sieve. The powder was filled in a platinum crucible and calcined for 6 h in an electric furnace with $MoSi_2$ elements at the temperature of 1600°C in order to pre-react the individual components. The calcined mixture was then crushed and milled in a planetary agate mill (Fritsch Pulverisette) and sieved through a 100 μm PE sieve to prepare a reasonably free flowing powder. The as-weighted compositions of prepared samples are summarized in Table 1.

Glass microspheres were prepared from precursor powders by flame-spraying technique. Figure 1 shows a schematic drawing of the apparatus for the flame synthesis. Powders were fed into a high temperature CH_4–O_2 flame ($T \sim 2200$°C) by a stream of carrier methane gas, and then the molten particles were quenched by spraying them with distilled water. Glass microspheres were let to settle down in a sedimentation tank, collected, thoroughly washed with distilled water and acetone, and dried.
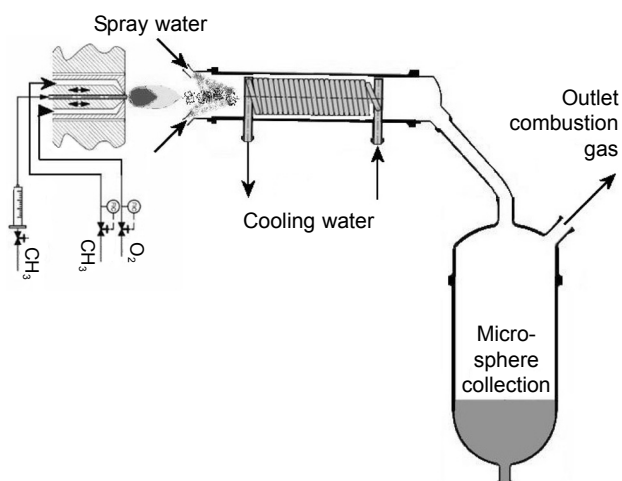

Figure 1. Schematic of the apparatus for preparation of glass microspheres by flame-spraying technique.

The density of microspheres was determined by liquid pycnometry with hexamethyldisiloxane as the immersion liquid. The morphology of prepared microspheres was examined by optical and scanning electron microscopy (SEM). In some cases differential thermal analysis was applied in order to determine the glass transition temperature and the onset of crystallization of prepared glasses. X-ray diffraction was applied in order to confirm the amorphous nature of prepared glasses, or to detect any crystalline phases present.
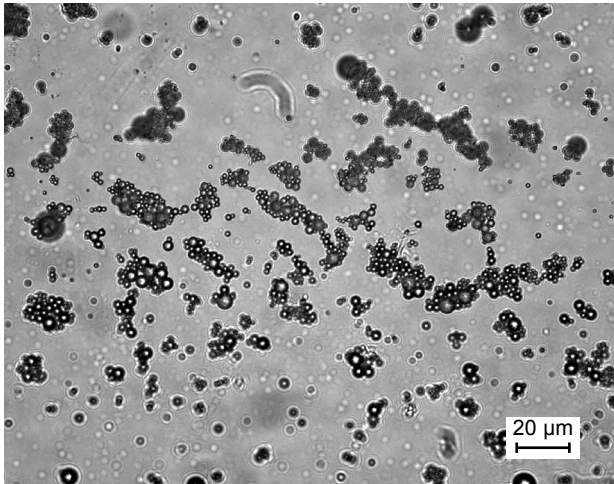
The microspheres of the composition A60Y40 (eutectic composition) were hot-pressed at the pressure of 30 MPa and two different temperatures (840 and 900°C) in vacuum. The mechanical pressure was applied from the start of the experiment; heating and cooling rates were 10°C/min. The hot pressed pellets were again examined by X-ray diffraction and the fracture surfaces by SEM.
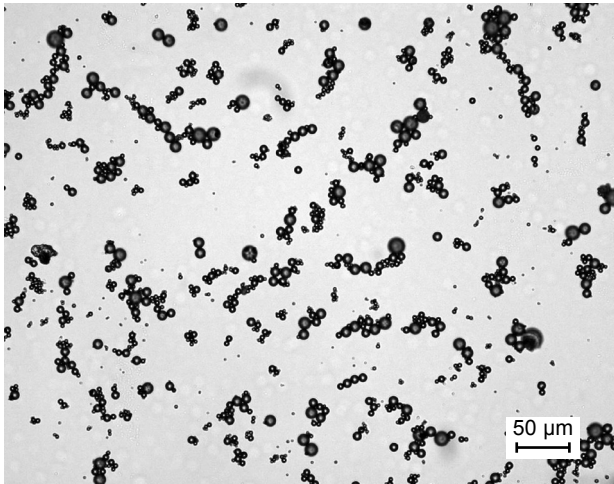
RESULTS AND DISCUSSION

Table 1 summarizes seven theoretical compositions of microspheres prepared in the system Al_2O_3–Y_2O_3 with various Al_2O_3 content and their basic characteristics. These comprise the eutectic composition A60Y40 in the pseudobinary system $Y_3Al_5O_{12}$–Al_2O_3, the composition of aluminium–yttrium garnet $Y_3Al_5O_{12}$ (YAG) A43Y57, the two compositions equal to the eutectic ± 3 wt. % of Al_2O_3 A57Y43 and A63Y37, and three glasses A67Y33, A70Y30, A75Y25 with alumina content exceeding 80 mol %. The compositions were selected to investigate the glass forming ability at the high alumina end of the binary system Al_2O_3–Y_2O_3. All prepared systems required high melting temperatures, from 1760°C for the eutectic composition, to 1925°C for the composition equivalent to YAG. The synthesis in the methane-oxygen flame satisfies the requirement of the high melting temperature: the temperature of the flame estimated from the measurement by optical pyrometer was ~ 2200°C. For virtually all compositions the prepared microspheres with diameters ranging between

Table 1. The as-weighed compositions of prepared glass samples and their basic characteristics: X_{YAG} (mol%) - theoretical molar content of YAG, T_m-melting temperature as determined from the phase diagram, T_g-glass transition temperature, T_x- onset of crystallisation, *THP*-hot pressing temperature, n.m. = not measured, a = amorphous, p - c = partly crystalline.
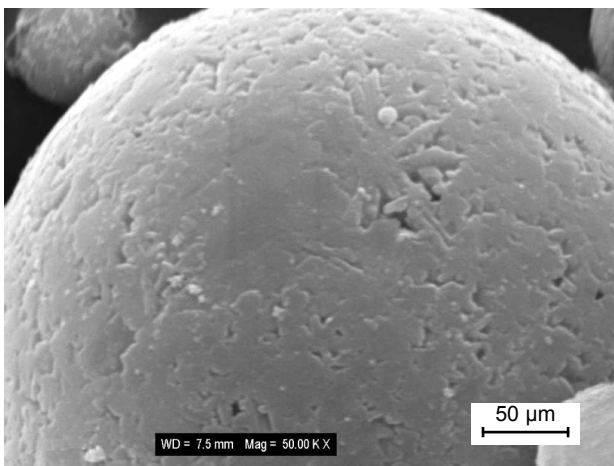
Sample	Al_2O_3 (mol%)	Al_2O_3 (wt.%)	X_{YAG} (mol%)	T_m (°C)	ρ (g/cm³)	XRD	T_g (°C)	T_x (°C)	T_{HP} (°C)
A43Y57	62.6	43	100	1925	4.165	p-c	n.m.	n.m.	-
A57Y43	74.6	57	67.89	1790	3.918	p-c	n.m.	n.m.	-
A60Y40	76.8	60	62.01	1760	3.856	a	870	910	900
A63Y37	79.0	63	56.13	1775	3.817	p-c	n.m.	n.m.	-
A67Y33	81.8	67	48.65	1825	3.811	p-c	n.m.	n.m.	-
A70Y30	83.8	70	43.30	1850	n.m.	p-c	n.m.	n.m.	-
A75Y25	86.9	75	35.02	1900	3.751	p-c	876	909	-

a)

b)

c)

Figure 2. Optical micrographs of microspheres prepared by flame synthesis: a) A43Y57, b) A60Y40, and the SEM micrograph of a A75Y25 microsphere.

10-40 μm were found to be transparent in visible wavelength range as confirmed by examination with optical microscope (Figure 2a,b), which indicates their glassy character. However, the SEM examination of micropsheres of the A75Y25 composition (86.9 mol. % Al₂O₃) show microspheres with regular surface features, indicating at least their partial crystallinity (Figure 2c).

The theoretical densities of all systems in the work were calculated by the rule of mixtures assuming zero volume change at mixing of two respective crystalline phases α-Al₂O₃ and YAG, while the amounts of the phases were estimated from the thermodynamical modeling of the Al₂O₃–Y₂O₃ system in reference [7] (Figure 3). The comparison of the real measured densities of glass micropshers with the theoretical calculated densities of these systems is shown in Figure 4. Although
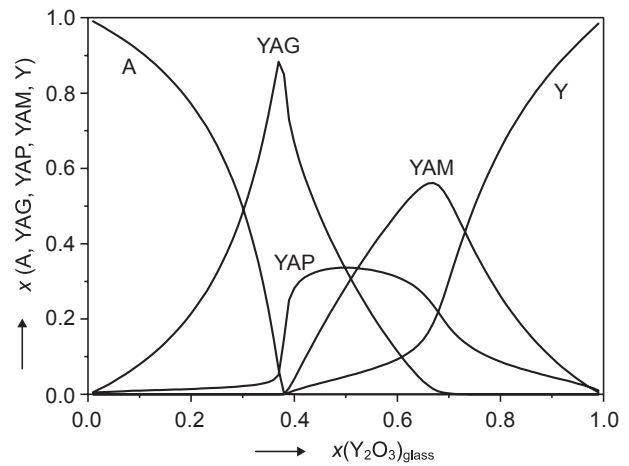

Figure 3. Calculated relative abundance of individual components in glass at 750 K. A = Al₂O₃, Y = Y₂O₃, YAG = Y₃Al₅O₁₂ (yttrium aluminium garnet), YAP = YAlO₃ (perovskite phase), YAM = Y₂AlO₉ (mellilite phase) [7].
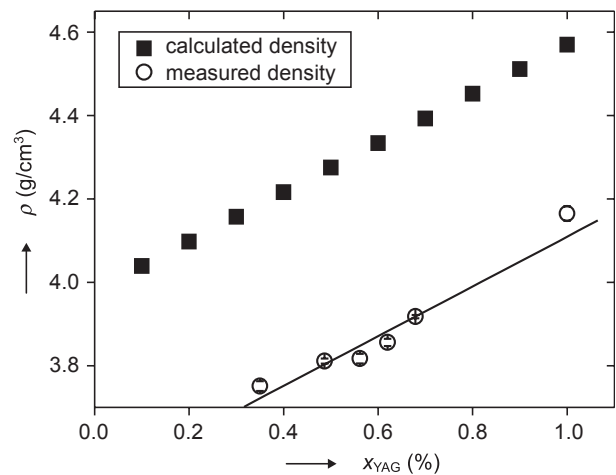

Figure 4. The comparison results of density measurements and theoretical calculated densities of Al₂O₃–Y₂O₃ systems.

both dependences follow approximately linear trends with similar slope, the real densities are much lower than calculated ones, indicating high content of amorphous phase (glass) in the microspheres.

The results of X-ray diffraction (Figure 5) show that except of the eutectic A60Y40 composition with the lowest melting temperature the microspheres of other compositions contain crystalline phases, especially YAG (those with lower alumina contents up to eutectic composition), and α-Al_2O_3 (those with higher alumina

contents). The A43Y57 microspheres of YAG composition contained, except of crystalline YAG, also traces of the $YAlO_3$ perovskite phase. Traces of crystalline δ-Al_2O_3 were also identified in the specimens with high alumina contents (A67Y33, A70Y30 and A75Y25).

The original hypothesis that the presence of crystalline phases is mainly the result of insufficient quenching rate and crystallisation of the melt was abandoned after it has been proved by the X-ray diffraction that repeated passage through the flame results in decrease of the intensity of YAG peaks in A43Y57 microspheres (Figure 6). The crystalline phases in glass spheres are then more likely the residua from insufficient melting of the precursor powder due to insufficient flame temperature, or short retention time in the flame, than crystalline phases newly formed from glass melt
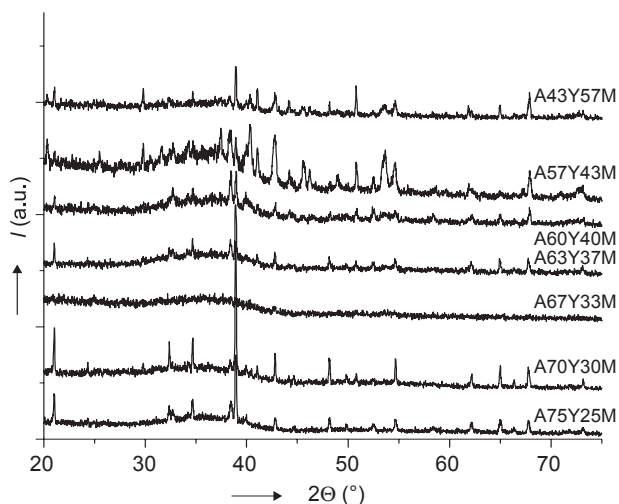

Figure 5. The results of X-ray powder diffraction analysis of microspheres of various compositions. Except of the A60Y40 eutectic composition all exhibit, apart from high background indicating the presence of amorphous phase, also fraction of crystalline phases.

Figure 7. The DTA curve of A60Y40 glass microspheres. Inset shows in detail the area of the curve used for determination of the glass transition temperature.
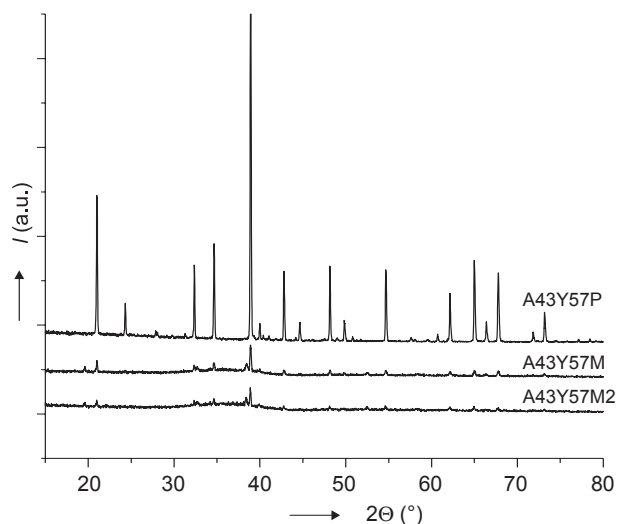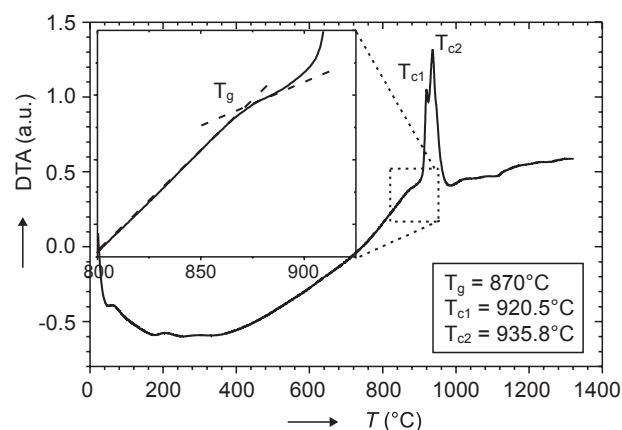

Figure 6. Comparison of the results of X-ray powder diffraction analysis of A43Y57 specimens: A43Y57P: pre-calcined precursor powder, A43Y57M: glass microspheres, A43Y57M2: re-melted microspheres. Note the decrease of intensity of diffraction lines in re-melted micro-spheres.
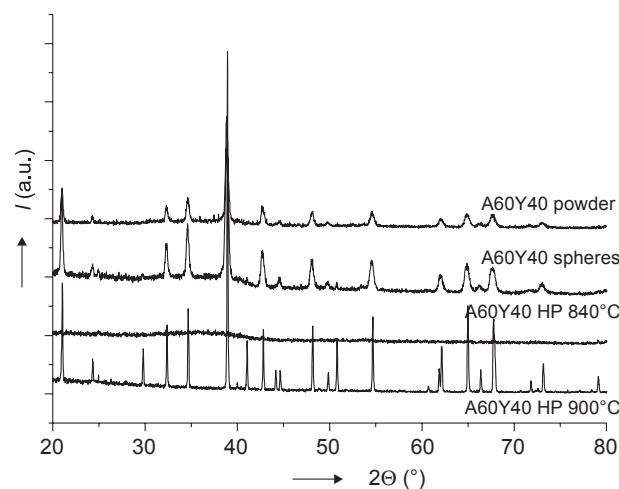

Figure 8. The results of X-ray powder diffraction analysis of A60Y40 specimens: pre-calcined precursor powder, microspheres, and hot pressed micropsheres.

upon cooling. Some exception in this case may be the perovskite phase, which was not detected in pre-calcined precursor powders. The presence of transition δ-Al$_2$O$_3$ is most likely the result of decomposition of hydrated aluminas formed in the course of quenching of high alumina melt with water.

The only X-ray amorphous A60Y40 sample was further characterized by DTA in order to determine the glass transition and the onset of crystallization temperatures (Figure 7). The results indicate very low thermal stability of the glass, with only 50°C temperature interval above the T_g before crystallization commences. The temperatures determined by DTA were used to propose a temperature regime, which was expected to facilitate densification of glass under pressure by plastic flow. However, both attempts to prepare fully dense transparent bulk yttrium aluminate glass of the A60Y40 composition by pressure assisted sintering at 30 MPa and temperatures 840°C and 900°C were unsuccessful. The resulting pellets were in both cases white and opaque. The XRD analysis (Figure 8) revealed partial crystallisation of glass in the course of sintering, with formation of yttrium aluminium garnet as the primary crystalline phase. The large width of YAG diffraction peaks suggests that the crystallites were very fine, most likely in nanometer range, and the high background indicates the presence of residual glassy phase. It is interesting that crystallization took place also at the temperature of hot pressing 840°C, which is well bellow the glass transition temperature, as determined by DTA. The reason of such behavior is unclear at the moment, and together with mechanisms of crystallization deserves further investigation.

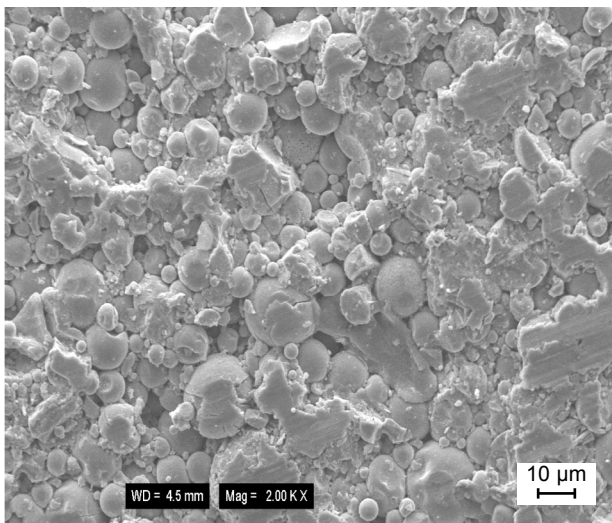The main reason for the opacity of hot pressed glasses is the presence of significant amount of light scattering residual porosity (12.8 %, as determined from density measurements). This result was confirmed also by SEM examination of fracture surfaces of the A60Y40 hot pressed pellet (Figure 9). This revealed not only the presence of residual porosity, but also preserved identity of original microspheres within the body, which were only partially deformed and formed only narrow necks at the points of mutual contacts. The conditions of hot pressing therefore appear too mild to facilitate sufficient densification (either the temperature or the pressure were too low), but further increase of the temperature is limited by severe crystallization of the glass.

CONCLUSION

Flame synthesis in methane-oxygen flame was tested as the means for preparation of binary yttria-alumina glasses with high alumina content. The method has restrictions related to the maximum flame temperature, retention time of powder particles in the flame, and maximum quenching rate depending from the size of molten droplets and efficiency of cooling by spraying with water: most of the prepared microspheres were therefore partly crystalline, with YAG and α-Al$_2$O$_3$ as main crystalline phases. The presence of crystalline phases is believed to be rather the result of insufficient melting of pre-calcined precursor powder than re-crystallization of melt due to insufficient cooling rate. Out of 7 prepared compositions, only the eutectic composition A60Y40 was completely X-ray amorphous. The A60Y40 microspheres were pressure-sintered in order to prepare fully dense bulk glass of the same composition: however the attempts were unsuccessful so far, as the sintering temperature is limited due to crystallization of the glass even at the temperature lower than the T_g.

Figure 9. SEM micrograph of fracture surface of the hot pressed A60Y40 specimen.

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PRÍPRAVA BINÁRNYCH Al₂O₃–Y₂O₃ SKLENÝCH MIKROGULIČIEK PLAMEŇOVOU SYNTÉZOU Z PRÁŠKOVÝCH PREKURZOROV.

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Práca sa zaoberá alternatívnou prípravou binárnych hlinitanových skiel plameňovou syntézou sklených mikroguličiek z práškových prekurzorov a ich následným spekaním viskóznym tokom za pôsobenia mechanického tlaku v teplotnom intervale medzi teplotou skleného prechodu T_g a teplotou začiatku kryštalizácie T_x. Plameňovou syntézou sa vo forme mikroguličiek s priemerom od 10 do 40 μm pripravilo sedem zložení v pseudobinárnom systéme Al₂O₃–Y₃Al₅O₁₂ (YAG). S výnimkou eutektického zloženia boli všetky mikroguličky čiastočne kryštalické, pozostávajúce z amorfnej ytrito-aluminátovej matrice s obsahom YAG a α-Al₂O₃ ako hlavných kryštalických fáz. Prítomnosť kryštalických fáz je spôsobená nedostatočným pretavením častíc prekurzora v plameni a je možné ju čiastočne eliminovať opakovaným pretavením. Výsledky DTA naznačujú vysoký sklon pripravených skiel ku kryštalizácii, so šírkou intervalu medzi T_g a T_x na úrovni 50°C. Výsledkom spekania mikroguličiek v tomto teplotnom intervale s aplikovaným tlakom 30 MPa boli biele netransparentné sklá s vysokým obsahom zvyškovej pórovitosti (P = 0,12) a zvýšeným obsahom kryštalických fáz v dôsledku sekundárnej kryštalizácie skiel počas spekania.