Preliminary Study of Thermal Properties of Al_2O_3-Yb_2O_3 Glass Microspheres

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Abstract. *Binary ytterbium-aluminate glass microspheres with eutectic (79.4 mol. % Al_2O_3, 20.6 mol. % Yb_2O_3) composition were prepared by flame synthesis in methan-oxygen flame. The starting powder was prepared by sol-gel method in order to obtain homogenous glass particles with a narrow interval of particle size distribution. Prepared microspheres were studied by optical microscopy, scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and differential thermal analysis (DTA). According to the XRD, small portion of YbAG, α-Al_2O_3 and non-identified phase were present in glass microspheres after flame synthesis. From DTA records, temperatures of onset of crystallization (T_c) and temperature of maxima of the exothermic crystallization peak (T_x) were determined. High temperature X-ray diffraction analysis (HT-XRD) in temperature range 750-1200 °C with 2h and 4h isothermal holding time at temperatures 933 and 1044 °C was performed for preliminary study of thermal behaviour of prepared system.*

Keywords: Ytterbium-Aluminate Glasses, Flame Synthesis, Thermal Properties

1. Introduction

Aluminate glasses with high alumina content have recently come to the attention both - technologists and researchers for their excepted excellent properties, as hardness, fracture thoughnes, chemical and thermal resistance. Due to good optical properties, these materials are also suitable for replacement of commercially used laser materials as corundum (monocrystalline α-Al_2O_3), PCA (polycrystalline alumina), YAG (yttrium-aluminium garnet), YbAG (ytterbium-aluminium garnet). However their main disadvantages are high melting temperatures, high crystallisation rates and high cooling rates required during preparation. The several works were focused on study of Re_2O_3-Al_2O_3 glasses, and various preparation method with using of splat quenching technique [1], AAL (aero-acoustic levitator), CNL (conical nozzle levitator) [2] devices and other were described. New approach was used in the work of Rosenflanz et al [3]. They prepare the glasses in form a small microspheres which were subsequently sintered by hot press technique. For successful preparation of larger pieces of glass or glassceramic materials, it is very important to know thermal behavior of aluminate glasses. In this work, ytterbium-aluminate glasses with eutectic composition were prepared by combination of sol-gel method and flame synthesis. The morphology of prepared glass

microbeads was studied by optical microscopy and SEM. DTA and HT-XRD were used for determination of phase evolution during heat treatment of prepared material.

2. Experimental

The Al_2O_3-Yb_2O_3 precursor powder with composition corresponding to the eutectics phase (AYbEM) was prepared by mixing aluminium nitrate and ytterbium nitrate solutions in deionised water. Ytterbium nitrate solution was prepared by dissolution of ytterbium oxide in diluted nitric acid. The water solution of citric acid and ethylene glycol were added to the nitrates solution (the molar ratios of citric acid and ethylene glycol to metal ions were 1:1). The solution was allowed to reflux at 85 °C for 2 hours. Polymerization was promoted by heating to 150 °C, at which the viscosity rapidly increased with accompanying solvent evaporation until aerated resins were formed. The organic compounds from the powders were removed by heating to 800 °C for several hours. Prepared powders were fed into methan-oxygen flame and molten particles were cooling by distilled water, collected, separated, dried and calcinated at 650 °C for 4h to remove of residua from flame synthesis. Prepared glass microbeads were examined by optical microscopy (Nicon ECLIPSE ME 600), SEM (Zeiss EVO 40HV at accelerating voltage 20kV) and X-ray powder diffraction analysis (Panalytical Empyrean, CuKα radiation, 2Θ range 10-80). HT-XRD in range of 750-1200 °C with step 5 °C and different isothermal dwell time was used for preliminary kinetics study of prepared glass microspheres. DTA measurements (Netzsch STA 449 F1 Jupiter) in nitrogen atmosphere, with heating rate 10 °C/min in temperature range of 35-1200 °C were performed for determination of T_c (onset of crystallization temperature) and T_x (temperature of maxima of the exothermic crystallization peak) of prepared glasses.

Table 1. The basic charasteristics of prepared system (p.c.-polycrystalline)

sample	Al_2O_3 (mol.%)	Yb_2O_3 (mol.%)	T_m (°C)	T_c (°C)	T_x (°C)	XRD
AYbEM eutectic composition	79,4	20,6	1750	929,2 1030,9 1074,3	933,8 1044,3 1089,6	p.c.

3. Results

Prepared glass microbeads were transparent, spherical and fully remelted with diameter size up to 10 μm (Fig. 1). Only small amount of fully or partially crystalline particles was observed by SEM (Fig. 2). Also XRD confirms predominantly amorphous character of prepared samples (high background in XRD patterns) with traces of YbAG, α –Al_2O_3 and non-identified phase (peaks with small intensities centered at 16,89, 28,62 and 45,23 in 2Θ range). The presence of this non-identified phase is probably associated with the transition of alumina and yttria to thermodynamically stable YbAG phase. The formation of this phase can be explained with high temperature in methan-oxygen flame and high cooling rates used in system [4] and also with existence of non-homogenous temperature field and short dwell time of particles in methan-oxygen flame during flame synthesis. One strong exothermic peak with onset at 929,2 °C and maximum at 933,8 °C; which can be attributed to the crystal growth of YbAG, and two smaller broad exothermic peaks at 1044,3 °C and 1089,6 °C (onset temperatures 1030,9 °C and 1074 °C)were observed in DTA records of prepared glass microspheres (Fig. 3). The basic characteristics of prepared sample are in Table 1.

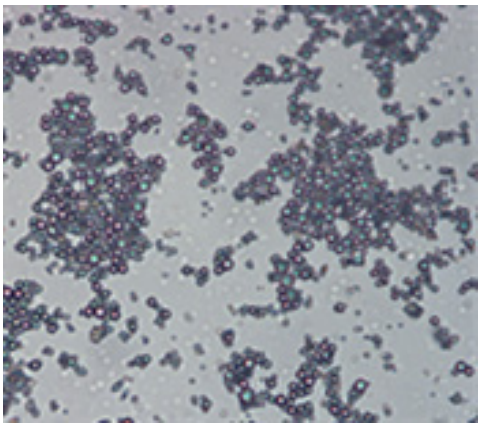

Fig. 1 The optical micrograph of sample AYbEM

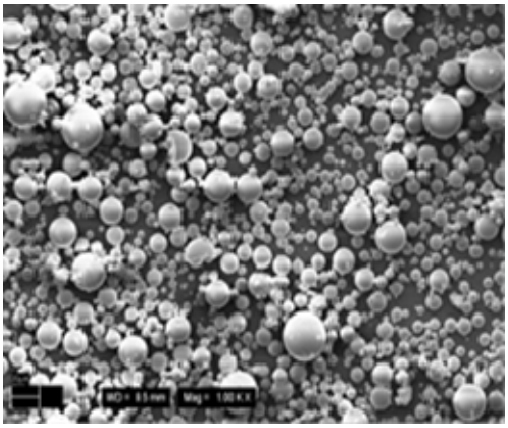

Fig. 2 SEM micrograph of sample AYbEM

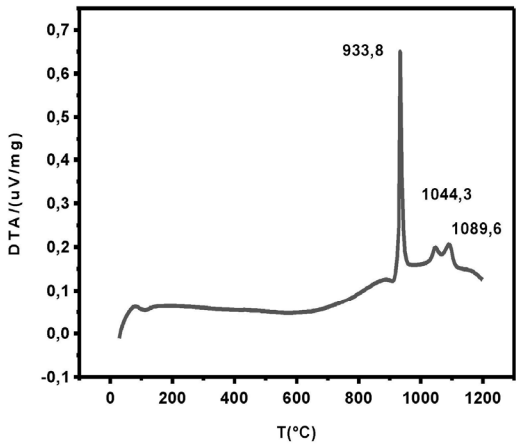

Fig. 3 DTA records of sample AYbEM

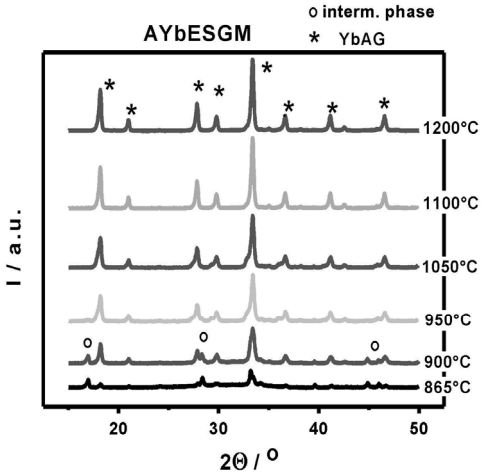

Fig. 4 HT XRD patterns of sample AYbEM in temperature range 865-1200 °C

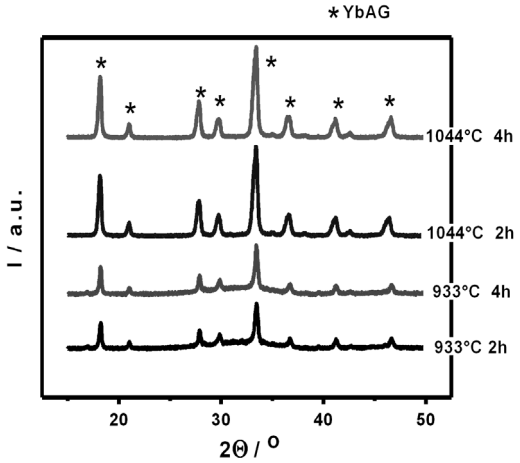

Fig. 5 The comparison of results of HT XRD after 2h and 4h dwell time at 933 °C and 1044°C.

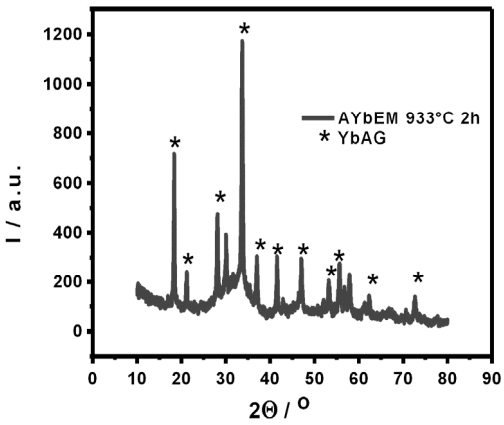

Fig. 6 HT X-ray patterns of sample AYbEM recorded after 2h dwell time at 933 °C

For better understanding of thermal behavior of prepared sample, HT-XRD was performed. From results of this HT-XRD, it is clearly seen, that traces of non-identified phase, were converted to YbAG phase in temperature range of 865-1050 °C (Fig. 4). However, with further increasing of temperature (1050-1200 °C), observed YbAG peaks become higher and sharper, which can be explained by crystal growth of YbAG phase in prepared sample. The next HT XRD experiments with isothermal hold of 2 and 4 hours at first two exothermic maxima (933 °C and 1044 °C), show only crystallisation of YbAG phase, with conversion of non-identified phase to YbAG during the first ten minutes at 933 °C and ≈ 7 minutes at 1044 °C. Higher content of YbAG crystalline phase was observed in sample held at 1044 °C after 2 hours of dwell time and fully crystalline material was obtained after 4 hours (Fig. 5). The HT XRD spectra after 2h and 4h at 933 °C with persistent amorphous background between 20-40 in 2Θ range, indicated incomplete crystallisation of eutectic glass sample (Fig. 6). This observed slow crystallization at 933 °C opens the possibility of preparation of glassceramics materials in system Al_2O_3-Yb_2O_3 by controlled crystallization of glass microspheres. The further DTA analysis and HT-XRD study focused on nucleation of prepared glass microspheres is necessary for better understanding of crystallisation behavior of prepared glass microspheres.

4. Conclusions

The partially crystalline glass microspheres with high alumina content in system Al_2O_3-Yb_2O_3 were prepared with diameter ≤ 10μm. DTA and HT-XRD for preliminary study of crystallisation behaviour of prepared glass were performed. The crystallisation of YbAG phase in prepared sample was studied at temperatures 933 °C and 1044 °C with different isothermal holding time. As shown results this work, for preparation glass-ceramics materials is interesting slowly crystallization of pure YbAG phase at 933 °C.

Acknowledgements

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