

Preparation and Characterization of $\text{Yb}_2\text{O}_3 - \text{Al}_2\text{O}_3$ Glass Microspheres with High Alumina Content

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Abstract. *In the paper we report on the preparation of ytterbia-alumina glass microspheres with high alumina content by flame synthesis. The microspheres with various alumina contents were prepared by using starting powders prepared by conventional mixing of aluminium oxide and ytterbium nitrates in appropriate proportions. The precursor powders were fed into methane-oxygen flame and after melting in the flame quenched by spraying with distilled water. The prepared microspheres were examined by optical microscopy, SEM, XRD, DTA and IR, in order to analyse the influence of experimental conditions and the way of preparation on homogeneity and the fraction of crystalline phases in prepared glasses, and to determine the temperature of maximum rate of crystallization of prepared systems. Mostly homogeneous glasses with low degree of crystallinity were prepared as microspheres in the pseudo-binary system $\text{Yb}_3\text{Al}_5\text{O}_{12}$ - Al_2O_3 . The presence of $\text{Yb}_3\text{Al}_5\text{O}_{12}$ (YbAG) crystalline phase together with two non-equilibrium orthorhombic and hexagonal YbAlO_3 (YbAP) phases was confirmed by XRD in prepared samples.*

1. Introduction

Modern solid state laser technology especially DPSSL (diode-pumping solid state laser) technology has become a very intense field of research in Physics. The replacement of flash-lamp pumping systems by direct laser-diode pumping systems requires development of new special and efficiency materials. Traditionally used host material – YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$ -yttrium aluminium garnet) is supplied by new materials such as YAP (YAlO_3 - yttrium-aluminium perovskite) and YAM (monoclinic yttrium-aluminate $\text{Y}_4\text{Al}_2\text{O}_9$), ytterbium-aluminium garnet (YbAG), and others, which have better thermal properties (for example low thermal conductivity $\sim 0.13 \text{ W/mK}$)[1], high hardness and elastic modulus, greater chemical durability and very good non-hygroscopic properties. To produce high average power DPSSL, two rare-earth ions dominate: neodymium and ytterbium. At the beginning of the high-power laser development, the Nd-doped materials were preferred to the Yb-doped ones. It was mainly because of the four level nature of Nd ions and their many absorption lines, which are more convenient as far as flash lamp pumping is concerned. However, it seems obvious for more than one decade now, that Yb-doped materials are more suited for very efficient and very high-average-power diode-pumped lasers [2]. As it is clear from previous research [3, 4], Yb^{3+} ions with more simple energy level construction than Nd have some important advantages: low level of quantum defects (8.6%) between the pump and the laser photons, long storage lifetime of the upper laser level (1.3 ms) and no excited state absorption or up conversion loss. Due to the benefits of Yb^{3+} ions we expect better properties in doped single crystals and polycrystalline materials over other materials used for laser application, such as low thermal load, long upper state lifetime, large absorption width around the InGaAs laser emission range, relative large emission cross section, low thermal conductivity and strong

energy storing capacity [5 - 8]. However, these materials are commonly used in single crystal forms and their preparation is highly time, energy and financially consuming. Development of glass or polycrystalline transparent ceramic materials based on cubic oxides (YAG, YbAG) appears to be a highly economic solution, because fabrication of these materials is relatively easy and cheap. In recent years a number of works concerning preparation of very fine powders and their sintering was published [9]. These new materials are promising not only for laser applications but also as TBCs materials, or as oxidation and erosion resistant materials for design in military and commercial gas turbine engines or as optically active coating materials [5, 7, 10]. The aim of this work was preparation of fully amorphous or partially crystalline glass microspheres in systems Al_2O_3 - Yb_2O_3 by flame synthesis and their characterisation.

Starting powders for flame synthesis were prepared by mixing of high purity Al_2O_3 with $\text{Yb}(\text{NO}_3)_3$ solution, which was prepared by dissolving Yb_2O_3 in HNO_3 . For flame synthesis methane-oxygen flame was used. All prepared binary, mostly glassy samples of various composition were examined by OM, XRD, SEM and DTA. The glass microspheres prepared in this way can be used as precursors for fabrication of transparent ceramic and glassceramic materials with good thermal, mechanical and optical properties.

2. Experimental

The compositions of the synthesized specimens (as weighed) are summarised in the Table 1. The samples A30Yb70M, A43Yb57M, A45Yb55M, A50Yb50M, and A54Yb46M were prepared using high-purity oxide powders (Yb_2O_3 - Treibacher Industrie AG, Austria, Al_2O_3 - Taimicron TM DAR, Krahm Chemie GmbH, Germany). The alumina powder was mixed with ytterbium oxide dissolved in nitric acid. The prepared mixture was homogenised by ball milling for 1 h. Then the ytterbium nitrate was converted to hydroxide by the addition of NH_4OH and the mixture was homogenized for another 1 h to complete the hydrolysis reaction. The precursor powders were finally dried, sieved, and pre-reacted for 4 h in order to increase the homogeneity of the mixture and form chemical bonds among individual components. The powders were fed into methane-oxygen flame. Molten particles were quenched by distilled water, separated, dried and calcined at 650°C in air for elimination of residues (e.g. soots from combustion process) from flame synthesis. Prepared microspheres were examined by optical microscopy (Nikon ECLIPSE ME 600) and SEM (Zeiss EVO 40HV at accelerating voltage 20kV). X-ray powder diffraction analysis (STOE Stadi-P, Germany, $\text{CuK}\alpha$ radiation, 2θ range 20 - 80°), IR spectroscopy (FTIR spectrometer Nicolet Magna 750, in the wavenumber range 400 - 4000 cm^{-1} , standard KBr technique) and density measurement (by liquid pycnometry in hexamethyldisiloxane) were used for confirmation of amorphous or polycrystalline nature of prepared starting powders and glass microspheres. DTA measurements (DTA-TGA –simultaneous analyzer SDT 2960) were applied for determination of temperature of maximum rate of crystallization (T_x) of prepared samples.

3. Results and discussion

Composition and basic characteristics of prepared precursor powders and glass microspheres are summarized in Tab. 1. All prepared precursor powders were polycrystalline. The main phases identified in samples with higher alumina content (above 74.5 mol. %) were YbAG and α - Al_2O_3 . The X-ray diffraction data of the starting powders A30Yb70M, with lower alumina content (62.5 mol. %) showed the presence of YbAG together with traces of YbAlO_3 perovskite (YbAP). The α - Al_2O_3 was not detected. The XRD patterns (Fig. 1) of glass microspheres were characteristic by high background, indicating highly amorphous nature of

prepared samples, but also contained separate diffraction peaks showing the traces of YbAG and YbAP crystalline phases. The presence of YbAP crystalline phase in the Al_2O_3 - Yb_2O_3 binary system was unexpected: the stability of perovskite structure decreases with decreasing ionic radius. Moreover, increasing stability of monoclinic structure with decreasing ionic radius is assumed [12]. Also, the equilibrium binary phase diagrams Al_2O_3 - Yb_2O_3 as published by various authors [11, 12, 13] recognize, apart from the YbAG crystalline phase, the existence of only one other thermodynamically stable binary compound, monoclinic ytterbium aluminate of the composition $2\text{Yb}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (YbAM) in the temperature interval between 874 °C [12] and 1675 °C [11]. We therefore propose that the observed YbAP structures are non-equilibrium unstable phases associated with the transition of alumina and yttria to thermodynamically stable YbAM and YbAG phases. The traces of the YbAP phase in glass microspheres can be explained also by high temperature of methane-oxygen flame $\geq 2000^\circ\text{C}$, and high cooling rates applied during preparation of these systems. The prepared microspheres can be therefore considered as highly non-equilibrium system which, together with the presence of inhomogenities (Yb rich regions with the Y_2O_3 : Al_2O_3 molar composition close to 1:1 similar to those observed during preparation of YAG)[14], give rise to formation of YbAlO_3 perovskite structures. The preliminary study of the structure of prepared glasses by IR spectroscopy (Fig. 2) revealed that the IR spectra of prepared glass microspheres contained two broad poorly resolved bands. The first band at $400\text{--}800\text{ cm}^{-1}$ corresponds to Al-O vibrations of tetrahedrally coordinated Al atoms in YbAG, the second one at $900\text{--}1100\text{ cm}^{-1}$, and observed also in the Yb_2O_3 spectra, could be attributed to Yb-O vibrations of octahedrally coordinated Yb atoms in the YbAG structure[5]. However, similar band with maximum at 1028 cm^{-1} was observed also in the spectra of yttrium aluminate glasses and could be attributed to change of coordination number of Al atoms from 4 to 6 in aluminate glasses[15].

Table 1. Prepared composition and their basic characteristic, p-c: partly crystalline, o-orthorhombic, h-hexagonal. The content of alumina is expressed both in weight and mole %. The content of Yb_2O_3 is the difference to 100 %.

sample	mol. % Al_2O_3	weight. % Al_2O_3	XRD	XRD quality		Tx [°C]
				powders	Microspheres	
A30Yb70	62.4	30	p-c	YbAG, YbAP h	YbAG, YbAPo	923.1
A43Yb57	74.5	43	p-c	YbAG, α - Al_2O_3	YbAG, YbAPo, YbAPh	942.8
A45Yb55	75.9	45	p-c	YbAG, α - Al_2O_3	YbAG	942.8
A50Yb50	79.4	50	p-c	α - Al_2O_3 , Yb_2O_3	YbAG, YbAPo	924.7 945.8
A54Yb46	81.9	54	p-c	YbAG, α - Al_2O_3	YbAG	926 944

The morphology of prepared glass microspheres was examined by optical microscopy and SEM. Prepared particles were transparent (Fig. 3), fully remelted, with particle size $\leq 15\mu\text{m}$. However, detailed SEM examination (Fig. 4) revealed that some microspheres were fully or partially crystalline as can be seen from regular features and facets at the surface of microspheres with larger diameters ($\geq 10\mu\text{m}$). This feature is considered as undesirable, as the presence of crystallites might significantly influence the properties of prepared glasses, including the density, transparency, crystallization characteristic, or ability to densify by

viscous flow. The temperatures of maximum rate of crystallization T_X (Tab. 1) were determined by DTA.

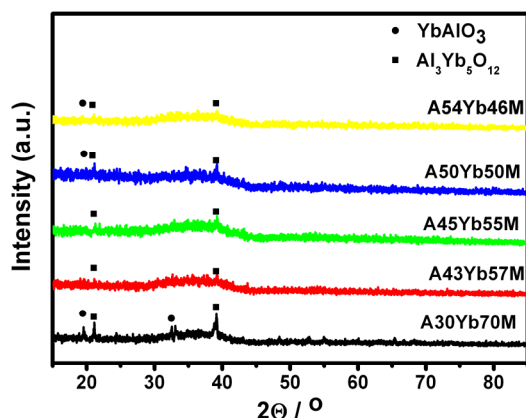


Fig. 1. XRD spectra of prepared glass microspheres

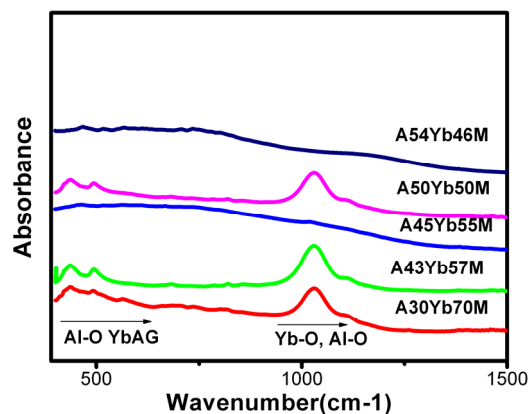


Fig. 2. IR spectra of prepared glass microspheres

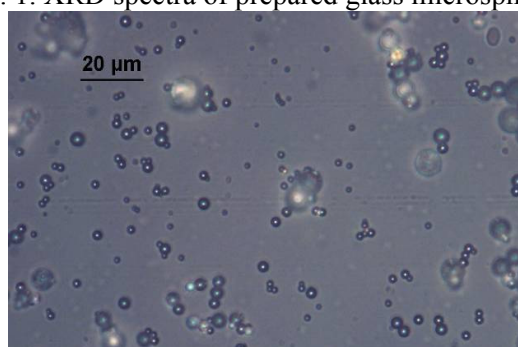


Fig. 3. Optical micrograph of the sample A50Yb50

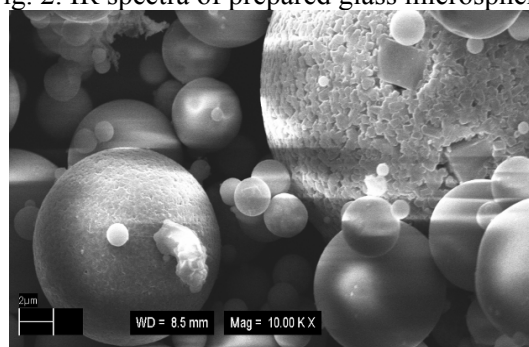


Fig. 4. SEM micrograph of the sample A50Yb50

While the compositions A30Yb70M, A43Yb57M and A45Yb55M showed only one crystallization peak on DTA records, the compositions with higher alumina content, such as A50Yb50M and A54Yb46M showed the presence of two closely spaced exothermic peaks. Based on the measured data or the information from the literature we could not find any plausible explanation for such behavior. Therefore, for detailed study of the structure and crystallization properties of these systems further examination of prepared microspheres by various methods, such as ^{27}Al MAS NMR, and high temperature XRD and DTA will be necessary. These will be further extended using fully amorphous glasses prepared by sol-gel methods, which contain no nuclei of the crystalline phases.

4. Conclusion

Glass microspheres in the system $\text{Al}_2\text{O}_3\text{-Yb}_2\text{O}_3$ with very low degree of crystallinity were prepared by flame synthesis. Examination of the microspheres revealed the presence of YbAG and traces of non-equilibrium phase YbAP. The IR spectra of studied systems contained only two broad unresolved bands between $400\text{-}800\text{ cm}^{-1}$ and $900\text{-}1100\text{ cm}^{-1}$. These were attributed to Al-O and Yb-O vibrations in the structure of YbAG, and to the change of Al coordination number in the structure of glass.

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