Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Preparation and Characterization of Basic and Er^{3+}-Doped Glasses in the System Y_2O_3-Al_2O_3-ZrO_2

R. Klement[a,*], B. Hruška[a], V. Hronský[b], D. Olčák[b]

[a]Vitrum Laugaricio–Joint Glass Centre of the IIC SAS, TnU AD, FChPT STU and RONA, a.s., Študentská 2, SK-911 50 Trenčín, Slovakia

[b]Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice, Park Komenského 2, SK-042 00 Košice, Slovakia

The undoped, and Er-doped yttrium aluminozirconate (AYZ) glasses were prepared by flame synthesis in the form of transparent glass microbeads. The ZrO_2 content was in the range between 5 and 20 mol. %. The prepared glass microbeads were characterised by optical microscopy, SEM, XRD, DSC, ^{27}Al MAS NMR, UV–VIS–NIR and fluorescence spectroscopy. The thermal stability of AYZ glasses, expressed in terms of the difference between the glass transition temperature, T_g, and the onset of crystallization, T_x, was not affected by the increasing ZrO_2 content. The ^{27}Al MAS NMR spectra of studied glass samples reveal that Al atoms are predominantly 4-coordinated in glasses. The AYZ5 and AYZ10 basic glasses were doped with Er^{3+} at the level of 1–5 mol. % of Er_2O_3. The UV–VIS–NIR/fluorescence spectra show characteristic absorptions/emissions, due to the optically active Er^{3+} ions in the host glasses. The absorption/emission properties of guest ions are not significantly affected by the glass host.

DOI: 10.12693/APhysPolA.126.302

PACS: 42.70.Hj, 42.70.Ce, 78.55.Qr

1. Introduction

Rare earth (RE) aluminate glasses have been of great interest due to their high elastic modulus and hardness, high refraction index, excellent optical properties, and good corrosion resistance [1]. When doped with photoactive RE ions (e.g. Nd^{3+}, Er^{3+}, etc.), these glasses are potential candidates for applications in solid state lasers, optical waveguides and optical amplifier hosts [2].

In the present study we report on the preparation and characterization of glasses in the system Y_2O_3-Al_2O_3-ZrO_2 (AYZ) and their Er-doped analogues. The selected properties of the prepared glass hosts and rare-earth ions doped analogues are discussed and compared.

2. Experimental

Glass microspheres of the studied compositions were prepared from precursor powders by the flame-spraying technique as reported earlier [3]. Instrumentation: Optical microscopy (Nikon Eclipse ME600); Scanning Electron Microscopy–SEM (JEOL JSM-7600 F/EDS); Powder X-ray diffraction–XRD (Panalytical Empyrean, CuK_α radiation, 2Θ range 10–80°) equipped with a high temperature (HT) cell; Differential scanning calorimetry–DSC (Netzsch STA 449 F1 Jupiter TG/DTA/DSC), the heating rate 10 °C/min; ^{27}Al MAS NMR spectra (MAS–12kHz)–NMR spectrometer Varian 400 MHz, spectra simulation by the program DM-Fit [4]; UV–VIS–NIR spectra–Cary 5000 equipped with external DRA accessory; Photoluminescence spectra–spectrometer Fluorolog 3 FL 3–21 (Horiba).

*corresponding author; e-mail: robert.klement@tnuni.sk

3. Results and discussion

The theoretical composition of basic glasses is summarized in the Table. The composition of Er-doped glasses is derived from basic analogues AYZ5 and AYZ10 by substitution of Y_2O_3 by Er_2O_3 at the level of 1, 3 and 5 mol. %.

TABLE

Theoretical composition of basic glasses in mol. %.

Sample	Al_2O_3	Y_2O_3	ZrO_2
AYZ5	73.02	21.98	5.00
AYZ10	69.15	20.82	10.00
AYZ15	65.33	19.67	15.00
AYZ20	61.49	18.51	20.00

The prepared glass microspheres were transparent with composition close to the theoretical values, as determined by SEM/EDS.

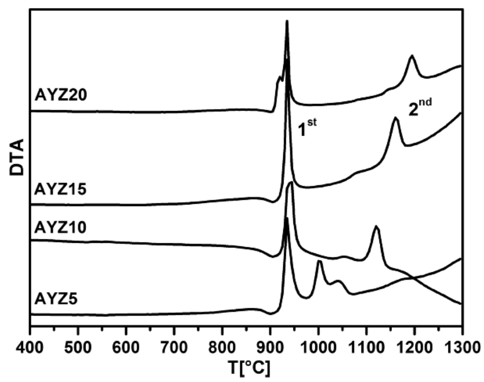

Fig. 1. DSC traces of prepared basic glasses.

The powder XRD patterns of the glass samples AYZ15 and AYZ20 revealed besides the broad amorphous background, the presence of crystalline phase of zirconium yttrium oxide (YSZ). Samples AYZ5 and AYZ10 were found to be XRD amorphous. The Er^{3+}-doped AYZ5 and AYZ10 glasses were found to be almost XRD amorphous, containing only traces of YAG ($Y_3Al_5O_{12}$) phase. The DSC records of glass microbeads are shown in Fig. 1. The T_g of studied glasses was found to be ~ 865 °C. As documented by HT XRD experiments, the first sharp crystallization peak observed at ~ 940 °C corresponds to crystallization of YSZ phase, except for the sample AYZ5. The second crystallization peak, observed for AYZ10, AYZ15 and AYZ20, which is compositionaly dependent, corresponds to the crystallization of YAG phase as documented by HT XRD. However, in the case of AYZ5 glass, only YAG phase crystallizes from the glass system. The thermal stability of basic glasses, expressed in terms of the difference between the glass transition temperature, T_g, and the onset of crystallization, T_x (observed at ~ 920 °C), was not affected by increasing ZrO_2 content. For Er^{3+}-doped glasses, the T_g is not significantly affected by glass doping ($T_g \sim 865$ °C) and the thermal behaviour was also found to be similar to un-doped glasses.

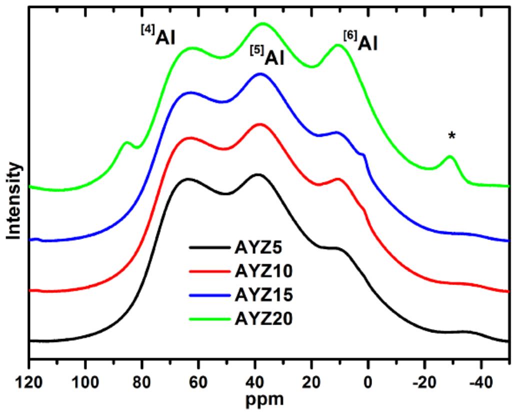

Fig. 2. The ^{27}Al MAS NMR spectra of basic glasses.

The structure of prepared glasses has been inspected by ^{27}Al MAS NMR spectroscopy (Fig. 2). The spectra of all studied AYZ glasses show very similar features and contain three broad lines observed at ~ 63 ppm, ~ 38 ppm and ~ 10 ppm, corresponding to four ($^{[4]}$Al), five ($^{[5]}$Al) and six-coordinated ($^{[6]}$Al) Al species, respectively; asterisk denotes rotational side band. For sample AYZ20, another signal of $^{[4]}$Al species at ~ 85 ppm was observed. The broad lines are due to the distribution of quadrupolar coupling and chemical shifts inherent to the structural disorder that is observed in glasses. The simulation of the NMR spectra revealed, that relative abundance of the $^{[4]}$Al, $^{[5]}$Al and $^{[6]}$Al species changes with composition of the glasses; predominant Al species are $^{[4]}$Al and with increasing content of ZrO_2 increases the abundance of $^{[5]}$Al and $^{[6]}$Al, while content of $^{[4]}$Al decreases.

The photoluminescence (PL) spectra of the Er^{3+}-doped AYZ5 glasses are shown in Fig. 3. The visible PL spectra of glasses under excitation at 380 nm exhibit strong green emission at 547 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) with weaker green emission at 524 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$). In NIR region, the weak emissions at 855 nm ($^4S_{3/2} \rightarrow {}^4I_{13/2}$), 980 nm ($^4I_{11/2} \rightarrow {}^4I_{15/2}$) and strong emission at 1530 nm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) were observed. The intensity of the emissions decreases with increasing concentration of Er^{3+} ions due to concentration quenching. The photoluminescence properties (emission band position and intensity) are not significantly affected by glass hosts when the doped AYZ5 and AYZ10 glasses with different ZrO_2 content are compared.

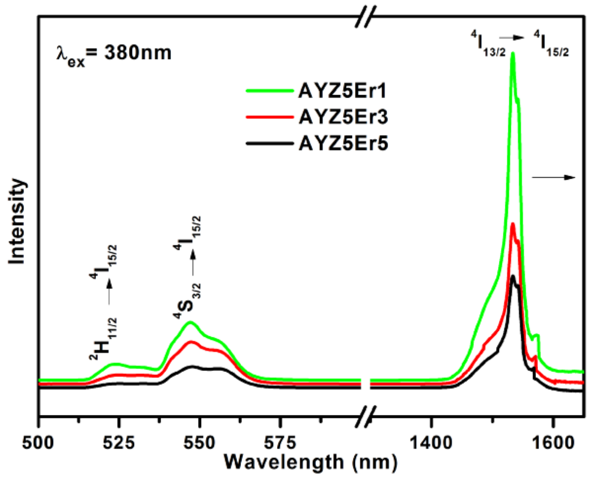

Fig. 3. Emission spectra of Er-doped AYZ5 glasses.

4. Conclusions

The basic (undoped) and Er^{3+} glasses in the system Y_2O_3-Al_2O_3-ZrO_2 were successfully prepared by flame spraying method and characterized by physico-chemical techniques. The thermal properties of basic glasses point to the relatively low thermal stability of prepared glasses which is not significantly affected by ZrO_2 content.

The prepared AYZ glasses are able to accommodate high concentrations (up to 10 at.% of Er^{3+} or more) of optically active RE ions.

Acknowledgments

This publication was created in the frame of the projects "Centre of excellence for ceramics, glass, and silicate materials" ITMS 262 20120056, and "Centre of Excellence for Integrated Research & Exploitation of Advanced Materials and Technologies in Automotive Electronics", ITMS 26220120055, funded from the EFRD.

References

[1] J.E. Shelby, J. Kohli, *J. Am. Ceram. Soc.* **73**, 39 (1990).

[2] P. Jander, W.S. Brocklesby, IEEE, *J. Quantum Electron.* **40**, 509 (2004).

[3] A. Prnová, R. Karell, D. Galuse, *Ceram. Silik.* **52**, 109 (2008).

[4] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, *Magn. Reson. Chem.* **40**, 70 (2002).