Optical Materials 45 (2015) 121–130

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Lead-gallium glasses and glass–ceramics doped with SiO_2 for near infrared transmittance

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ARTICLE INFO

Article history:
Received 3 February 2015
Received in revised form 9 March 2015
Accepted 16 March 2015
Available online 3 April 2015

Keywords:
Lead-gallium glass
BaF_2
Transparent glass-ceramics
UV–Vis
FT-IR
^{71}Ga MAS NMR

ABSTRACT

Lead–gallium glasses, due to the absence of typical glass-forming components, are characterized by an increased tendency to crystallization. Despite this, they are interesting materials due to a shift of IR absorption edge up to 6–7 μm. The paper considers how the SiO_2 dopant affects thermal stability and the UV–VIS and IR transmittance of lead-gallium glasses. The base lead-gallium glass ($0.75PbO{\cdot}0.25Ga_2O_3$) was modified by the addition of 5, 10 and 15 mol% SiO_2, respectively. DTA/DSC data showed that the glasses are characterized by the multi-stage crystallization, which is changed with the amount of silica doped. The XRD analysis confirmed that: (i) different forms of lead oxide crystallize after heat treatment of the glass, and (ii) the Ga_2PbO_4 phase is formed at higher temperatures.

The silica admixture allowed inserting a few percent of BaF_2 into the lead–gallium glass structure. It was found that a transparent glass–ceramic based on the lead-gallium glass with a low phonon barium fluoride phase can be obtained during the thermal treatment.

The study of UV–VIS–IR transmittance shows that 10–15 mol% SiO_2 in the lead-gallium glasses diminishes the absorption band in the range of 2.6–4 μm due to the presence of hydroxyl groups and simultaneously reduces transmittance in the range of 5–6.5 μm from 10 to 20%. Introduction of SiO_2 to the glass results in the increase of transmittance in the shorter wavelength region and the UV-edge shift is observed. It was also confirmed that the BaF_2 nanocrystallites exerts no effect on the transmittance of the spectrum analyzed.

1. Introduction

The properties of glass materials used in the infrared technology focus on obtaining the maximum transmittance in the desired IR range of the spectrum, an appropriate refractive index as a function of wavelength, coupled with good mechanical and chemical resistivity. Among the new materials produced specifically for the use in optoelectronics and fiber optics a broad group of amorphous glassy materials can be distinguished. In this group research interests are focused in particular on [1–14]:

- Oxide glass synthesized with lead and bismuth oxides.
- Halide glasses containing halides of zinc, cadmium, bismuth and thorium.
- Fluoride glasses made on the basis of ZrF_4, ThF_4 and AlF_3.
- Chalcogenide glasses, e.g. As_2S_3, As_2Te_3 and As_2Se_3.
- Halide–chalcogenide glasses from systems: $HgS—PbBr_2—PbI_2$ and $Sb_2S_3—HgS—PbBr_2$.
- Photochromic glass containing SiO_2, Na_2O, Al_2O_3, B_2O_3 and the silver halides and copper oxide.
- Polychrome glass made on the basis of $SiO_2—Al_2O_3—ZnO—Na_2O$ using CeO_2 as an optical stabilizer.

Preparation of optical fibers operating in the IR region met a number of difficulties due to the high susceptibility to crystallization of glasses, low viscosity during fiber drawing, fiber coverage problems with another material to form a core-cladding structure, low chemical resistance, and poor mechanical properties of the fibers, as well as, in some cases, toxicity of the components. Technological problems with practical application of waveguides based on heavy metal chalcogenides and halides containing glass were considered previously as cumbersome and have led to the search for materials based on oxide glasses with a simple production technology and good physical properties. A shift of the

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http://dx.doi.org/10.1016/j.optmat.2015.03.018
0925-3467/

absorption edge further into infrared region is in line with prerequisites for oxide glass [1]. The absorption edge is increasingly moving toward IR for traditional glasses based on boron, silicate and germanium, reaching finally a maximum of about 5–5.5 μm for the last-mentioned component. Another possibility to shift the red cut-off is the use of non-oxide glasses, chemical resistance and low mechanical strength limits however their application, despite their good transmittance characteristics up to 8 μm for fluoride glass, and even up to about 40 μm for iodine and bromide based glasses [2,3].

Theoretical predictions indicate that the shift of the absorption edge toward longer wavelengths should be observed for the glasses which include ions of high atomic weight and low field strength. For the elements forming oxide glass lead and bismuth have the highest mass, and at the same time the smallest field strength of non-radioactive elements, which suggests achieving a significant shift in the infrared absorption edge. The stable Bi_2O_3—PbO- based glass can be obtained when gallium oxide is a component of the glass [3,4]. Lead–bismuth glasses containing gallium or cadmium oxides are characterized by better infrared transmittance in comparison to other oxide glasses. Their characteristics obey: lower thermal expansion coefficient, higher resistance against chemical agents, as well as high density and high refractive index [2,3].

Glass containing heavy metal oxides, due to their unique physical properties such as the wide range transmittance, a high refractive index, and low dielectric losses have been of much interest and a number papers were devoted to the glassy state systems [5–7], infrared transmittance [15,16] and structural studies [17–21]. These glasses were also admixed with rare earth elements [22–26]. Optical properties, especially refractive index were studied for the R_2O—Ga_2O_3—SiO_2 and RO—Ga_2O_3—SiO_2 systems [27].

In this work the influence of SiO_2 dopant on thermal stability and transmittance range of lead-gallium glasses is presented. Additionally, a possibility of BaF_2 incorporation into the structure of the glass is studied for inducing formation of the low phonon phase. Such materials with low phonon nanophase of BaF_2 doped lanthanides should present better luminescence properties while maintaining good transmittance. The materials were studied due to their application as nonlinear photonic crystal fibers (PCFs) and supercontinuum generation. Moreover, such materials can be alternative for silica glasses which cannot operate above 2.5 μm. Improvement of luminescence properties can be achieved only if optical active ions are incorporated into the low phonon phase which is formed during crystallization. Due to the process of glass crystallization which must be precisely controlled the information about the thermal stability of each glass becomes very important.

Table 1
Nominal compositions of the lead-gallium glasses prepared.

Sample	The glass composition (mol%)			
	PbO	Ga_2O_3	SiO_2	BaF_2
A0	75	25	–	–
ASi5	75	20	5	–
ASi10	70	20	10	–
ASi15	65	20	15	–
ASi15F	63	20	15	2

2. Experimental

2.1. Synthesis of glass

Five lead-galium glasses of good quality were prepared (Table 1, Fig. 1). The base glass composition of $0.75PbO{\cdot}0.25Ga_2O_3$ was modified by the addition of 5, 10 and 15 mol% SiO_2, respectively. For the glass with 15 mol% SiO_2 it was also possible to introduce up to 2 mol% BaF_2. Otherwise, crystallization was observed during glass casting. To induce the crystallization in the glass matrix a specific heat treatment was applied using an electric furnace, following the DTA data obtained for each kind of glass.

The glass was prepared by melting a batch in a platinum crucible in the electric furnace in air atmosphere holding it at the highest temperature of 1000 °C for 15 min to obtain 0.05 mol of glass. The crucible was covered with a platinum lid to reduce material vaporization. The melt was poured out onto a brass plate forming a layer 2–4 mm thick, followed by annealing at a temperature near the transformation temperature (T_g) ca. 350 °C.

2.2. Methods of experiments

The ability of the glass to crystallization was determined by DTA/DSC measurements conducted on the Perkin Elmer DTA-7

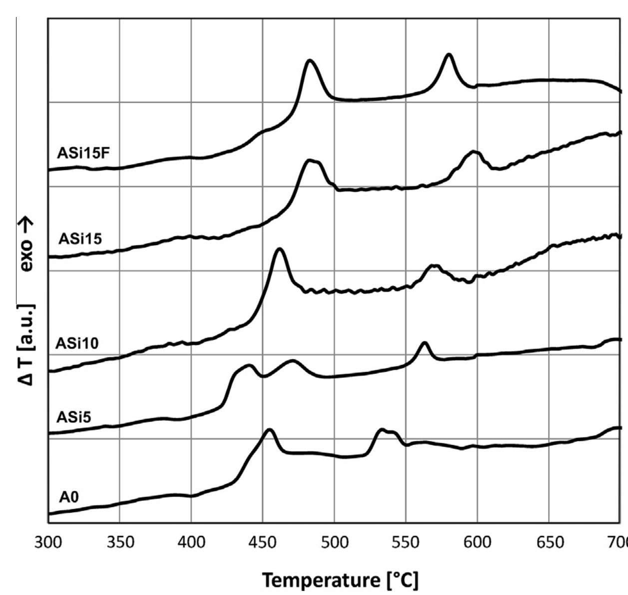

Fig. 2. DTA curves of the lead-gallium glasses.

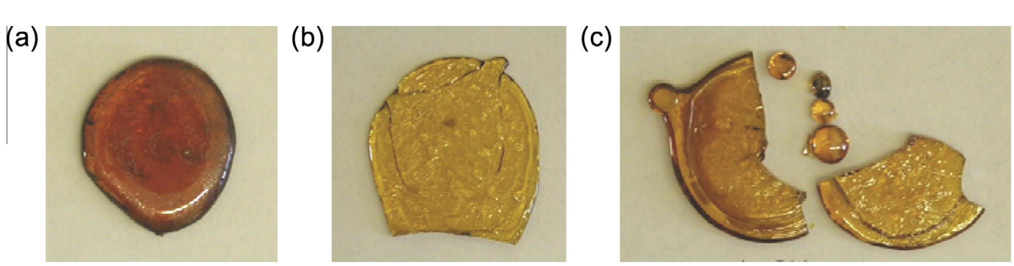

Fig. 1. Lead-gallium glasses: (a) A0, (b) ASi15 doped with 15 mol% SiO_2, (c) ASi15F doped with 15 mol% SiO_2 and 2 mol% BaF_2.