THERMAL PROPERTIES OF FLUORIDE GLASSES AND THEIR GEL PRECURSORS

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Abstract

Xerogels were prepared from zirconium, barium, aluminum, lanthanum and lithium acetates, corresponding to a Li containing ZBLA composition. The study of their thermal properties (DSC, TG/DTG, FT-IR) showed that they might be used as chemically stable precursors in the preparation of fluoride glasses. Hydrofluoric acid in solution was chosen as a mild fluorinating agent. This newly proposed technique of fluorinating allowed to obtain high quality ZBLALi glass which presents the advantage of higher thermal stability and homogeneity in comparison with the glass obtained using individual commercial fluorides.

Introduction

The extended transmission window, low phonon energy and high solubility of rare earth compounds in fluoride glasses make them suitable for creating passive as well as active optical systems such as fiber lasers, optical amplifiers, ultra-low loss optical fibers, planar waveguide and upconversion devices [1–3]. Nonetheless, conventional melt-quenching techniques have certain limitations as to the fabrication of glasses with the required high purity and specific geometry. In the case of oxide materials, the sol–gel method provides a simple way to prepare high purity glasses with a wide assortment of shapes, from thin films and layers to large monolithic blocks [4]. Hybrid materials in the form of xerogels are used for obtaining coatings with special optical and mechanical properties [5]. In the case of fluoride glasses, however, the sol–gel technique is far from perfect as any perceptible change of precursor, composition, solvent or fluorinating agent alters significantly not only the properties of the final glass but also influences the parameters of the chemical process itself. Glasses

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and thin films prepared using alkoxides, oxychlorides, crown esters and acetates are generally used in the preparation of fluoride glasses by this method. Soon after obtaining xerogels, fluorination by $NH_4F \cdot HF$, gaseous HF, trifluoroacetic acid or NbF_5 is carried out [6–9]. All these agents have certain disadvantages: $NH_4F \cdot HF$ always leaves ammonium groups trapped in the network, gaseous HF is a poisonous and hazardous material, CF_3COOH does not permit a complete fluorination and NbF_5 contaminates the final product with undesirable niobium. The aim of the present work is to study thermal stability and some properties of fluoride glass ZBLALi and its gel precursors. The latter were prepared using acetates as starting materials in order to compare a newly proposed fluorination method, using hydrofluoric acid solution, with a conventional one using $NH_4F \cdot HF$. Thermal analysis (DSC and TG/DTG) provide a simple technique of characterizing gels-precursors and glasses within the required interval of temperatures.

Experimental

Starting materials and methods

The gels were prepared using the following acetates: $Ba(CH_3COO)_2$ (Fluka), $La(CH_3COO)_3$ (Fluka), $Li(CH_3COO)$ (Fluka), $Zr(CH_3COO)_4$ was used in the form of 14% solution in acetic acid (Aldrich). All reagents were of analytical grade purity. Hydrofluoric and acetic acids were purchased from Merck. $NH_4F \cdot HF$ was purchased from Nuclear. Both LaF_3 and BaF_2 were of fiber glass purity purchased from BDH. Aluminum acetate loses its solubility quickly after preparation owing to its ageing, so a commercial reagent might not be used. Fresh $Al(CH_3COO)_3$ solution was prepared precipitating $Al(OH)_3$ from the solution of double aluminum-ammonium sulfate; the hydroxide was filtered out and quickly dissolved in a calculated volume of glacial CH_3COOH. The composition of gel matrix was calculated in order to produce the final glass with the following proportions of constituents: $47ZrF_4$, $14BaF_2$, $4LaF_3$, $5AlF_3$ and $30LiF$, in mol%. They are represented as fluorides in order to make comparisons. An identical composition was also prepared directly by mixing up pure commercial fluorides.

The starting components were combined and resulting solutions were left for evaporation under the flux of air. Gelation came into being during 24 h, the resultant gels were homogeneous and optically clear. X-ray diffraction investigation showed no reflections. After drying at 60°C for 72 h, two methods of gel treatment were tested:

a) fluorination by adding hydrofluoric acid to the gels at room temperature with consequent drying and heating at ca. 200°C;
b) fluorination by adding $NH_4F \cdot HF$ heating firstly at 300°C and then to 500°C (for elimination of ammonia and excessive NH_4HF).

Melting of fluorinated materials, as well as the reference sample containing commercial fluorides, was carried out in a platinum crucible at 850°C for 20 min. All operations were carried out in a dry box under nitrogen atmosphere. Samples were quenched by pouring into a brass mould and then annealed at 260°C for 30 min.

Differential scanning calorimetry (DSC), was performed using a DSC/50-Shimadzu instrument under the following conditions: sample mass ~15 mg, gas flux 100 mL min^{-1} of both synthetic air and nitrogen. Heating rate varied: for the study of gels it was 4°C min^{-1}, while for the glass samples it was 10°C min^{-1}. Thermogravimetric analysis (TG) of the gels was performed under synthetic air atmosphere, with a heating rate of 4°C min^{-1}. A TGA/50H-Shimadzu instrument was employed. FT-IR spectra of gaseous products which were released during heating were registered using a Brucker instrument, model Vector 22, HgCdT detector with resolution of 4 cm^{-1} and 32 scans. In order to evaluate crystallinity and identify the compounds resulting from thermal events, X-ray diffraction study was performed using a Kristalloflex-Siemens diffractometer, CuK$_\alpha$ radiation, Ni filter. The identification was achieved with a set of DIFFRACT programs and ICSD (International Centre for Diffraction Data) data files.

Results and discussion

DSC curves of gel (Fig. 1) presented three endothermic effects due to successive dehydration. The third one is partially superposed with the first of the two following exothermic peaks, at approximately 323 and 380°C. This pattern was observed when synthetic air was used as a gaseous carrier (Fig. 1a). On the contrary, they disappear when the experiment is held using nitrogen atmosphere (Fig. 1b), proving the fact that both effects reflect only the oxidation and do not indicate any crystallization processes. In this case, the incineration of organic components would occur around 323°C and the carbon particles formed would be burnt at 380°C. Meanwhile, nitrogen acts only as a neutral carrier.
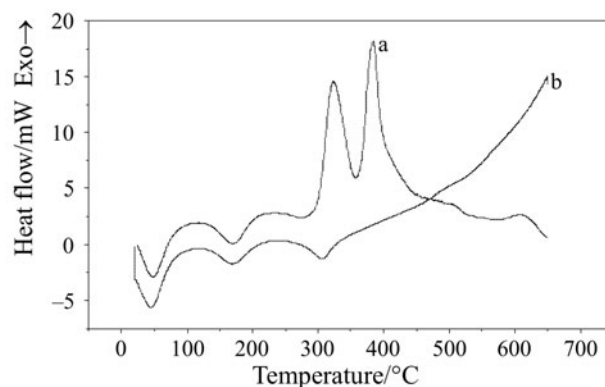
Fig. 1 DSC curves of gel ZBLALi prepared by using a – synthetic air and b – nitrogen

TG curves reported in Fig. 2 show four significant mass losses. That around 70°C corresponds to the elimination of absorbed water and that at 150°C reflects the release of water retained within gel pores. The mass loss observed at 320°C makes manifest gel network decomposition. The small peak at 389°C is due to the oxidation of the afore-

mentioned carbon particles. Another small mass loss after it seems to be due to the decomposition of trace carbonates.

The FT-IR spectra of gaseous products released during the gel thermal treatment (Fig. 3) shows intensive bands around 3400–3800 and 1645 cm^{-1} corresponding to water desorption from differently bonded H_2O populations (absorbed water and water contained in the pores), as it occurs in the case of silica gel and coprecipitated ferrite powders [10, 11]. An intensive band at 2450 cm^{-1} is attributed on the bases of classical data [12] to antisymmetric vibrations in gaseous CO_2. Carbon dioxide starts to form above 300°C, exactly corresponding to the onset of third exothermic effect in
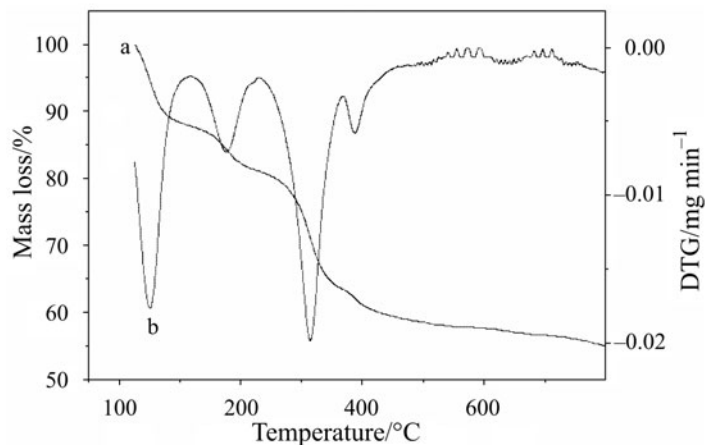

Fig. 2 TG and DTG curves of gel ZBLALi
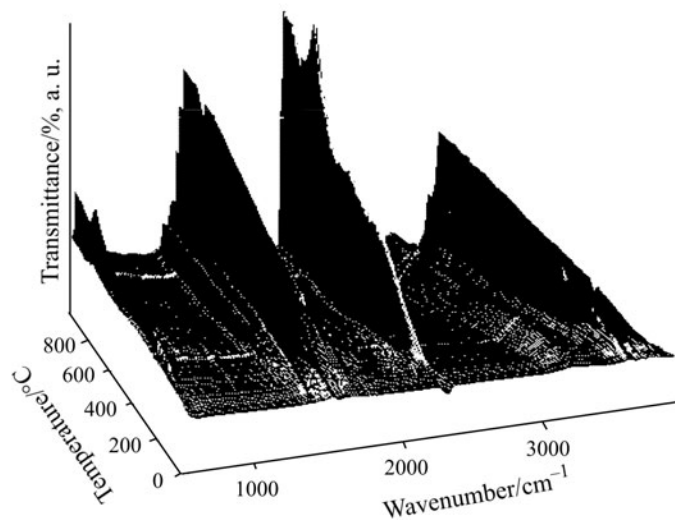

Fig. 3 Gaseous FT-IR specter of gel ZBLALi

Figs 1 and 2. We must assume that we are dealing with two different sources of CO_2: the first one, according to the temperature interval corresponds to oxidation of the organic ligand while the second confirms the decomposition of metal carbonates, principally those of lanthanum and barium.

According to X-ray patterns, the samples of gels treated up to 200°C are amorphous. They commence to crystallize after heating at 300–400°C showing the presence of ZrO_2 (ICSD file 37-1413) (Fig. 4). For treatments above 500°C the presence of barium carbonate could also be observed. These crystalline phases have high melting temperatures representing serious impediments to fluorides fusion at 850–900°C. Hence, the temperature of gels treatment should not go above 200–280°C.
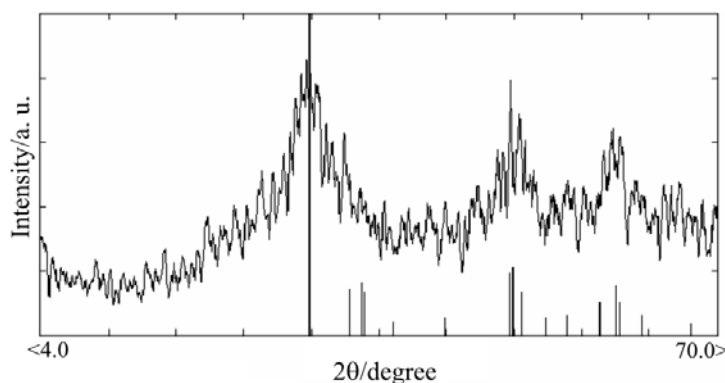

Fig. 4 X-ray diffractogram of gel ZBLALi thermally treated at 400ºC

The first fluorination method tested was the addition of $NH_4F \cdot HF$ to the gels. All attempts to melt the samples failed. The impossibility of fluoride glass preparation by this technique must be related to the necessity of working at temperatures above 300°C, which leads to the formation of zirconia, as showed above. This stable phase cannot be melted at the temperature at which the fluoride glasses are usually prepared, as even low ZrO_2 contents induce further nucleation and crystallization.

On the contrary, the second method, e. g. fluorination of gels dried at 200°C using the solution of hydrofluoric acid, could have been easily carried out at room temperature, later melting resulting in homogeneous, transparent glass samples. Thermal characteristics of this glass were compared with the characteristics of a reference sample obtained directly by fusion of commercial fluorides.

The reference curve (Fig. 5a) presented T_x–T_g=72°C and three crystallization peaks: the first (medium) at 340°C, the second at 382°C (strong) and the last (shoulder) at 405°C accompanied by endothermic melting peaks of 522 and 542°C, respectively, with comparable intensity (1:1.1).

The curve registered with the sample prepared by sol–gel (Fig. 5b) had greater thermal stability (T_x–T_g=86°C) presenting a single crystallization peak at 380°C. Meanwhile, the relative intensity of melting peaks at 507 and 528°C was drastically changed (1.0:3.0).
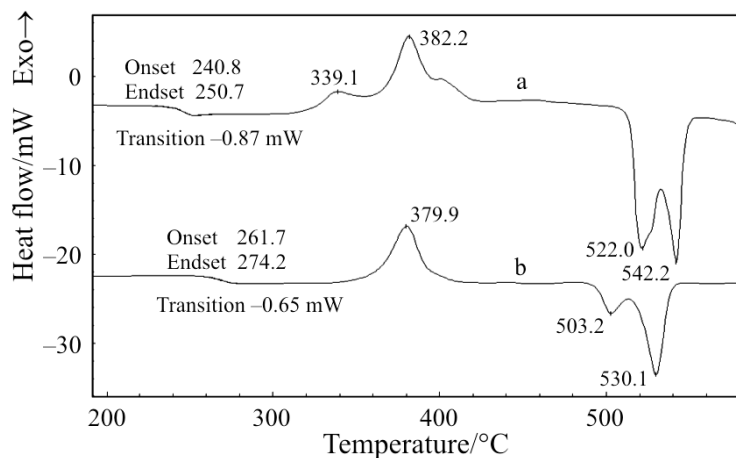
Fig. 5 DSC curves of ZBLALi glasses obtained by two different routes

The lack of compositional homogeneity within the vitreous phase favors the formation of various crystalline species to which correspond different temperatures of crystallization and melting. Hence, the presence of only one crystallization peak and the reduction of the first melting peak strongly confirm an increase in homogeneity of the glass prepared from the gel precursor.

Conclusions

Gels synthesized from acetates corresponding to ZBLALi composition proved to be proper precursors of fluoride glasses. The investigation of their thermal properties allowed the choice of operational conditions and a suitable fluorinating agent: hydrofluoric acid in solution. The ZBLALi glass successfully obtained by the newly proposed technique is similar to the glass obtained from commercial fluoride but presents the advantage of higher thermal stability and homogeneity.

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