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The effect of nitrogen addition on certain properties and structure of fluorozirconate glasses

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The effect of nitrogen on the properties and structure of fluorozirconate glasses in the system ZrF_4–BaF_2–LaF_3–AlF_3 (ZBLA) was investigated. Nitrogen was introduced by means of aluminium nitride. The substitution of fluorine by nitrogen in ZBLA glasses resulted in a considerable increase of microhardness, reduction of the linear expansion coefficient, and a small increase in characteristic temperatures. Structural investigations comprised RDF and Fourier transform–infrared (FT–IR) examinations. From radial distribution function (RDF) it followed that the introduction of nitrogen caused an increase of the mean distances Zr–F(N), Ba–F(N), La–F(N). From FT–IR spectra, it followed that nitrogen became incorporated into the bridging fluorine atoms which was evinced by a shifting of bands deriving from the bending vibrations between the $[ZrF_6]^{2-}$ octahedra towards higher wave numbers.

1. Introduction

Fluorozirconate glasses are new materials which may find many applications in optoelectronics and electronics. They may be used as laser windows, infrared domes, laser hosts, lenses, filters, and mid-infrared optical fibres. Nitrogen is introduced to improve their mechanical and thermal properties and chemical resistance. The improvement is the result of the fact that the zirconium and lanthanium nitrides have an interstitial structure (NaCl-type of octahedra). The metallic character of the bonds in nitrides is responsible for the high value of electrical and thermal conductivity as well as great mechanical strength [1–3]. The improvement of the properties results from the difference in the covalence of the Zr–F and Zr–N bonds. A knowledge of the effect of nitrogen on the structure makes it possible to account for the changes in these properties.

The replacement of oxygen by nitrogen in oxide glasses resulted in the formation of stronger, more compact, structure and an increase in the properties [4–8]. A similar effect of nitrogen on the properties and structure of fluorozirconate glasses has been reported by other authors [9–12].

The present study comprised investigations of microhardness, linear expansion coefficient and structural investigations including RDF and Fourier transform–infrared (FT-IR) examinations of fluorozirconate glasses modified with nitrogen. The effect of nitrogen on certain properties and structure of fluorozirconate glasses was defined.

2. Experimental procedure

Fluoride raw materials, ZrF_4, BaF_2, LaF_3, AlF_3 and AlN, were used to produce the glasses. Samples for the investigation of properties were in the shape of plates, 20 mm × 10 mm × 2 mm. Microhardness was determined on PMT-3 microhardness testing machine by measuring the size of the indentation of a loaded pyramid. The pyramid was loaded with a 20 g bob and pressed into a glass sample for 5 s. The coefficient of linear expansion was measured on Netsch type 412E dilatometer. RDF measurements were performed on Siemens diffractometer type 2500 with high stable detector K 800. Mo K_α radiation of mean wavelength $\lambda = 0.071\,07$ nm was used. The detector was the Si [Li] semiconducting meter. The intensity curve was measured by the step method with varying steps of 0.2°, 0.5°, 1° in the angle interval 2θ from 6°–164°.

Infrared absorption spectra were registered in the region 100–400 cm^{-1} for polyethylene pellets and in the region 400–4000 cm^{-1} for KBr pellets, with a FTS60 Digilab Fourier Spectrometer. The spectral resolution was 2 cm^{-1} over the whole spectral region.

3. Results and discussion

Microhardness and the linear expansion coefficient of fluorozirconate glasses modified with nitrogen, were measured and their structure examined. Table I lists the composition and microhardness of the glasses.

The introduction of 0.034 wt% nitrogen into fluorozirconate glasses causes an almost 28% increase of microhardness (for glass 1 without nitrogen, microhardness = 2.02 GPa; and for glass 2 containing 0.034 wt% N it amounts to 2.58 GPa). This is probably due to the introduction of an ion of higher valency (valency of fluorine = 1, that of nitrogen = 3) and stronger, more covalent Zr–N bonds with regard

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TABLE I Composition and microhardness of glasses

Glass	Glass composition					Nitrogen analysis (wt %)	Microhardness (GPa)
	ZrF_4	BaF_2	LaF_3	AlF_3	AlN		
1	58	36	6	10	0	0	2.02
2	58	36	6	0	10	0.034	2.58
3	58	32	10	10	0	0	2.16
4	58	32	10	0	10	0.035	2.78

TABLE II Linear expansion coefficient and characteristic temperatures of fluorozirconate glasses modified with nitrogen (compositions as in Table I)

Glass	$\alpha_{20-200°C}$ ($10^5\,°C^{-1}$)	$\alpha_{20-250°C}$ ($10^5\,°C^{-1}$)	T_g (°C)	T_m (°C)
1	2.0913	2.0568	292.0	306.4
2	1.6551	1.7704	293.1	306.8

TABLE III Interatomic distances obtained from RDF measurements in fluorozirconate glasses modified with nitrogen (composition as in Table I)

Glass	r_1 (nm) Zr–F(N)	r_2 (nm) Ba–F(N), La–F(N), F–F(N)	r_3 (nm) Ba–Ba, Zr–Zr, Zr–Ba
1	0.2086	0.2638	0.4290
2	0.2209	0.2700	0.4295
3	0.2025	0.2570	0.4230
4	0.2056	0.2608	0.4326

to Zr–F bonds (the difference in electronegativity for Zr–N = 1.4, and for Zr–F = 2.4).

The values of linear expansion coefficients and characteristic temperatures of the glasses are given in Table II.

The introduction of nitrogen into fluorozirconate glasses is followed by a decrease in their linear expansion coefficients. For glass 1 (without nitrogen) it is equal to $2.0568 \times 10^{-5}\,°C^{-1}$ and for glass 2 it becomes reduced (the nitrogen content is 0.034 wt %) to $1.7704 \times 10^{-5}\,°C^{-1}$, i.e. by about 16%. The linear expansion coefficient is the smaller the greater the bond energy and the higher the melting temperature. The nitrides whose melting temperature is high should reduce α. The bond energy is associated with valency and the ionic radius (the valency of nitrogen is -3, that of fluorine -1, and the ionic radii are 0.212 nm and 0.133 nm, respectively [13]). A slight increase in the transformation and of dilatometric softening temperatures, determined from the dilatometric curves, was observed.

Structural investigations comprised RDF and FT–IR examinations. Table III lists the values of interatomic distances obtained from RDF measurements. Fig. 1 shows illustrative $P(r)$ functions of glasses 1 and 2. The values of distances r_1 and r_2 in glasses containing nitrogen are higher. In ZrN these values are as follows: Zr–N, 0.231 nm; Zr–Zr, 0.327 nm; in LaN these distances are: La–N, 0.264 nm; La–La, 0.373 nm [1]. This observation might be interpreted as an indication that the distances in fluorozirconate

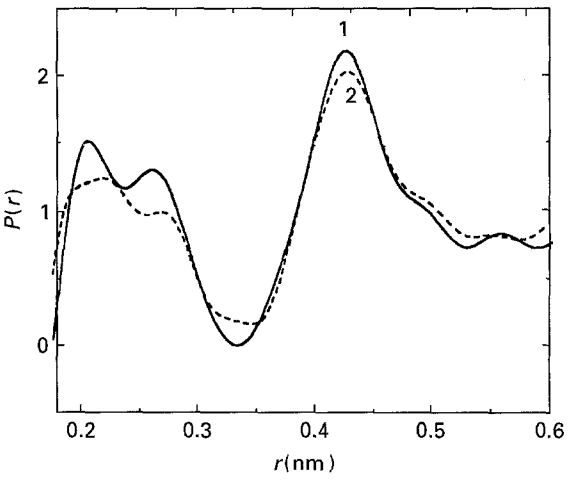

Figure 1 $P(r)$ functions of fluorozirconate glasses 1 and 2, modified with nitrogen (compositions as in Table I).

TABLE IV FT–IR spectra of fluorozirconate glasses modified with nitrogen (compositions as in Table I)

Glass	Positions of bands (cm^{-1}) (KBr pellets)	Positions of bands (cm^{-1}) (polyethylene pellets)
1	500	359 262 (width 103) 130–140
2	500	265 (width 109) 130–140
3	500	273 (width 133) 130–140
4	500	280 (width 137) 130–140

glasses modified with nitrogen are shifting towards the distance values observed in nitrides. Besides shifting of the two first bands as a function of $P(r)$, a broadening of these bands is observed. The broadening of the Zr–F peak after the introduction of nitrogen might be an indication of the deformation of the $[ZrF_6]^{2-}$ groups, associated with the incorporation of nitrogen (the radius of the nitrogen ion is 0.212 nm) taking the positions of the smaller fluorine ion (0.133 nm).

The positions of bands of the FT–IR spectra are listed in Table IV. After nitrogen has been introduced into the glasses, the band at 500 cm^{-1} does not undergo any change, while the band deriving from the bending octahedral vibrations, $[ZrF_6]^{2-}$, is shifted towards higher wave numbers and is broadened. The shifts are from 262 cm^{-1} for glass 1 to 265 cm^{-1} for glass 2 and from 273 cm^{-1} for glass 3 to 280 cm^{-1} for glass 4. Introduction of only 0.034 wt % nitrogen causes the broadening of the band by 6 cm^{-1} (glasses 1 and 2). Fig. 2 shows, by way of example, the FT–IR spectrum in the range 100–400 cm^{-1} for glasses 3 and 4

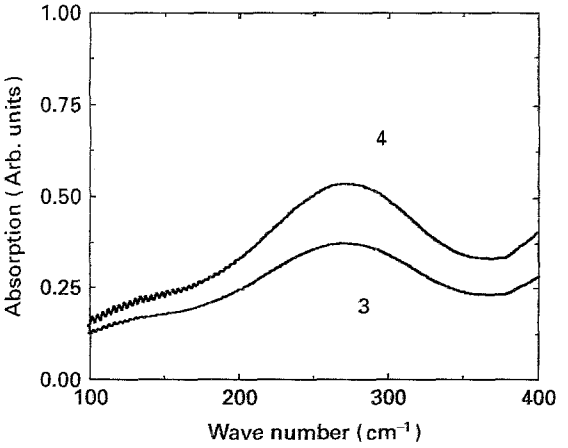

Figure 2 FT–IR spectrum of fluorozirconate glasses 3 and 4 performed in the range 100–400 cm^{-1} (compositions as in Table I).

(compositions as in Table I). Shifting and broadening of the bands might be an indication of nitrogen taking the positions of bridging fluorine.

4. Conclusions

The introduction of nitrogen into fluorozirconate glasses brought about an increase of their microhardness. This is probably due to the replacement of fluorine ions of lower valency (-1) by nitrogen ions of higher valency (-3) and a stronger, more covalent Zr–N bond when compared with the Zr–F bond.

The value of the linear expansion coefficient of the glasses is also reduced by the introduction of nitrogen into fluorozirconate glasses. Nitrides characterized by high melting temperature may reduce α. This effect is also connected with the valency and the ionic radius. The ionic radii are F = 0.133 nm, N^{3-} = 0.212 nm.

The subsequent investigations were concerned with the glass structure. Results of RDF examinations showed a shifting of bands relating to the distance of Zr–F, Ba–F, La–F, F–F towards greater distances and broadening of bands in fluorozirconate glasses containing nitrogen. It has been found that these distances shift towards those in nitrides. The Zr–F distance in a glass without nitrogen was 0.2086 nm, with nitrogen 0.2209 nm and in nitrides it was 0.231 nm.

FT–IR analysis has revealed the shifting of bands connected with the bending vibrations of octahedra, $[ZrF_6]^{2-}$, towards higher wave numbers after nitrogen has been incorporated into the glass. This might be interpreted as indicating that nitrogen is taking some of the positions of fluorine around the zirconium atom.

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