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Characterization of ZBGAN glasses

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The physical and electrical properties of a ZrF_4–BaF_2–GdF_3–AlF_3–NaF (ZBGAN) glass have been studied. The addition of NaF increases the glass-forming ability of the base composition glass yet does not degrade the optical characteristics. The viscosity decreased with increasing NaF, suggesting that the increased glass-forming ability was due to the confusion principle. The electrical conductivity decreased with increasing NaF for low temperatures but increased at higher temperatures. The activation energy showed an increase with increasing NaF. The data suggest that the conductivity is not due to the total fluorine ion concentration.

1. Introduction

Fibre-optic transoceanic telecommunication cables are currently based on silica glass compositions. The attenuation of these fibres has progressed to near the theoretical limit of 0.1 dB km^{-1}. Rapid progress in laser light sources has put pressure on the materials science community to develop materials which can transmit at longer wavelenghs with very low attenuation levels. The discovery of zirconium-based fluoride glasses in the mid-1970s seemed to meet these requirements [1]. These glasses have excellent transmission characteristics to approximately 7–8 μm and their theoretical attenuation is of the order of 10^{-2}–10^{-3} dB km^{-1} [2-4]. These attenuation levels have made repeaterless transoceanic cables a distinct possibility. To date, the lowest attenuation levels achieved have been of the order of 1 dB km^{-1} [5]. Of the zirconium-based glasses, ZrF_4–BaF_2–LaF_3–AlF_3–NaF (ZBLAN) and ZrF_4–BaF_2–GdF_3–AlF_3 (ZBGA) compositions seem to be the most promising for fibre-optic applications. The major obstacles to rapid commercialization are due to the inherently poor glass-forming ability of the fluoride glasses, and narrow glass-forming regions. These problems have been alleviated in part by the addition of sodium fluoride (NaF), as in the case of ZBLA glass compositions. This presence of NaF has enhanced the glass-forming ability of the ZBLA compositions by modifying the viscosity, and together with improved raw material purification and the use of a reactive atmosphere, has allowed the production of good optical fibres.

The ZBGA compositions show excellent transmission properties [6, 7] but like the ZBLA glasses they also tend to crystallize on cooling from the melt. In this paper the physical and electrical properties of a series of ZBGA glasses doped with NaF will be reported.

2. Experimental procedure

All glasses were prepared from commercially available fluoride precursors purchased from Cerac (P.O. Box 1178, Milwaukee, Wisconsin, USA). A 10-g batch of component fluorides was mixed with excess ammonium bifluoride and melted at 800 °C for 1 h in a platinum crucible under an argon atmosphere. After homogenization the melt was cast in a preheated carbon mould, annealed for 30 min just below the glass transition temperature and cooled slowly to ambient temperature.

Density measurements were made on parallel lapped samples by determination of the dimensions and weight. The glass transition T_g, crystallization T_x and melting T_m temperatures were determined by differential thermal analysis (DTA) using a DuPont 1090 instrument and a heating rate of 10 °C min^{-1}. Index of refraction of the glasses was determined by the Becke line method. Infrared absorption (IR) of polished glass samples was measured on a Beckman IR 4260 research spectrometer.

Viscosity of the glasses was measured using a parallel plate viscometer. Samples were core drilled from as-prepared glass and subsequently polished by parallel lapping. The change in specimen height was measured with digital micrometers. The viscosity was calculated according to the equation [8]:

$$\eta = \frac{2\pi M g h^5}{3V(\mathrm{d}h/\mathrm{d}t)(2\pi h^3 + V)} \qquad (1)$$

where η is viscosity (poise), M is the applied load (g); g, the gravitational constant (980 cm sec^{-2}); t, time (s); V, specimen volume (cm^3); h specimen height (cm); and $\mathrm{d}h/\mathrm{d}t$ is the deformation rate (cm sec^{-1}).

Direct current (d.c.) conductivity was determined by the alternating current (a.c.) technique (Fig. 1) [9, 10]. An Apple IIe microcomputer was used to control a Hewlett-Packard 4192 impedance analyser via the

IEEE–488 bus. The temperature was set and monitored using a Cyborg data acquisition system. This configuration was used to determine the real and imaginary components of impedance from which the resistance at d.c. could be calculated.

3. Results and discussion

Table I lists the glass compositions studied, the sodium content was varied from 0 to 24 mol %. The acronym N*n*, where N refers to sodium and *n* refers to the molecular per cent of sodium will be used. The physical appearance of the glasses are shown in Fig. 2. It can be seen from the figure that high-quality glasses were obtained within the range examined. The dark coloration appearing in some glasses has been attributed to a thin carbon layer formed at the interface during quenching.

The variation in density with NaF is shown in Fig. 3 and it decreases with increasing alkali content. All the glasses exhibited excellent transmission up to 8 μm. A typical i.r. transmission curve is shown in Fig. 4. The absence of any significant absorption in the region near 2.9 μm indicated the low hydroxyl content of the glasses. The variation in the spectra have been ascribed to the difference in thickness, clarity, degree of crystallization and polishing. There was no apparent correlation between the optical characteristics and the NaF content.

The variation of index of refraction decreases with increasing sodium, and is similar to variations reported for other compositions (Fig. 5). These results show that a core-cladding structure for the glasses based on the variation of refractive index can be obtained by appropriate variation of alkali content between the core-cladding regions.

The glass transition temperature (T_g), crystallization temperature (T_x), centre of crystallization peak (T_c) and melting temperature (T_m) derived from the DTA curves are tabulated in Table II. Fig. 6 shows the variation in glass transition and crystallization temperature with sodium content. The glass-forming ability is given by T_x–T_g; the greater the difference the more stable the glass composition (Fig. 7). It is evident from the figure that sodium contributes to the stability of the glass; glass without sodium has a lower T_x–T_g by approximately 20.

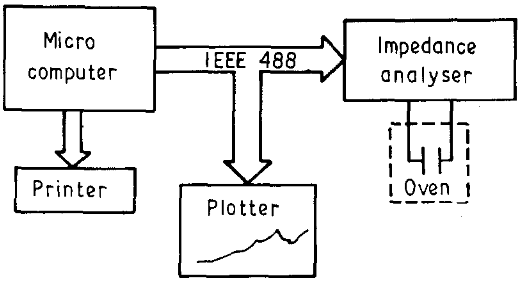

Figure 1 Schematic of experimental arrangement used for electrical measurements.

TABLE I Composition of ZBGAN glasses (in molecular per cent)

Acronym	ZrF_4	BaF_2	GdF_3	AlF_3	NaF
N0	60	32	4	4	–
N2	59	31	4	4	2
N4	58	30	4	4	4
N8	56	28	4	4	8
N12	54	26	4	4	12
N16	52	24	4	4	16
N20	50	22	4	4	20
N24	48	20	4	4	24

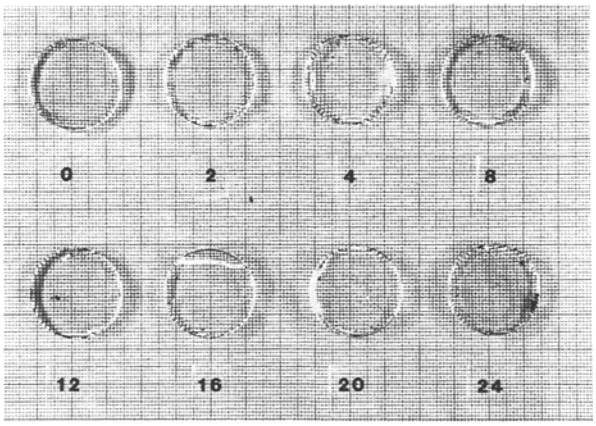

Figure 2 Physical appearance of ZBGA glasses with varying amounts of NaF (the numbers indicate molecular per cent of NaF).

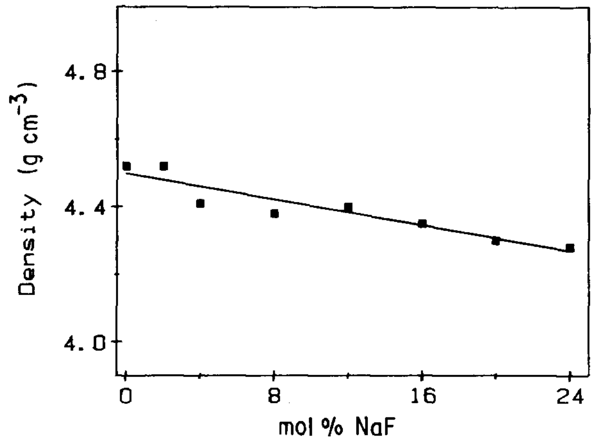

Figure 3 Variation of density with NaF content.

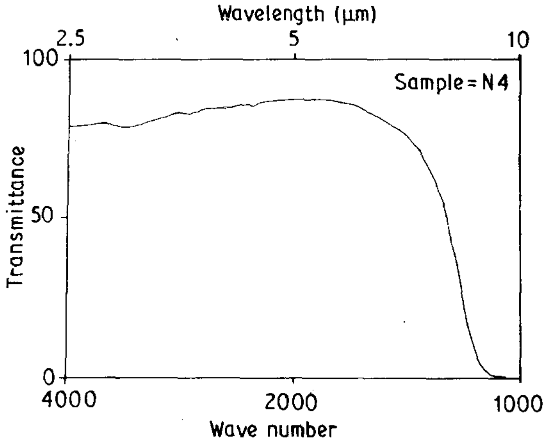

Figure 4 Typical IR curve for ZBGAN glass.

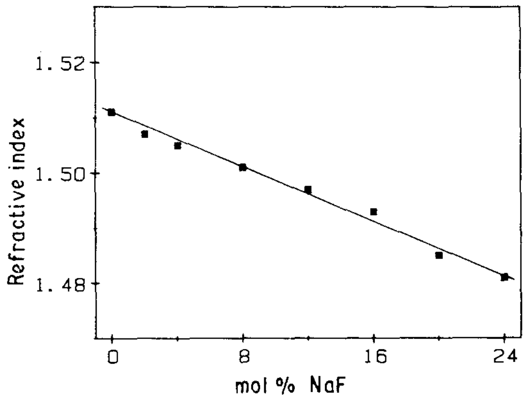

Figure 5 Variation of index of refraction with NaF (at 0.5893 μm, sodium D line).

TABLE II DTA DATA

Sample	T_g	T_x	T_c	T_m
N0	315	382	398	556
N2	305	393	410	557
N4	298	385	405	550
N8	296	380	406	524
N12	288	372	394	514
N16	280	368	386	469
N20	271	354	378	470
N24	264	352	375	470

The stability criterion has also been estimated [11]

$$S = (T_c - T_x)(T_x - T_g)/T_g \qquad (2)$$

where S is given in K (Fig. 8). Although the difference in parameter S is slight, glasses containing NaF appear to be more stable in agreement with the T_x–T_g criterion.

3.1. Viscosity

The viscosity of the glasses was determined using the parallel plate viscometer technique. The equipment was calibrated using a standard reference material (SRM) glass sample, SRM711 [12]. The rate of change of height (dh/dt) was determined from the displacement curve (Fig. 9). The height of the specimen at a particular temperature was obtained by subtracting the micrometer reading from the initial thickness of the sample. Fig. 10 shows the variation in viscosity against temperature for the SRM711 glass. The solid curve represents the expected value of viscosity which is in good agreement with the experimental data. The viscosity data are in excellent agreement with the expected values in the temperature range of 550–650 °C, the difference being approximately 10%. The viscosity deviates from the expected values at low

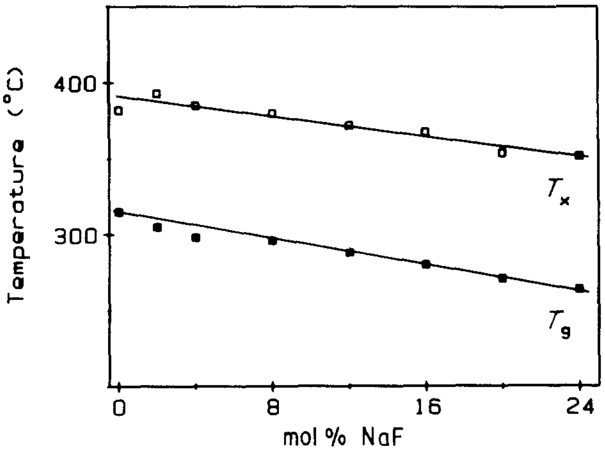

Figure 6 Variation of glass transition temperature T_g and crystallization temperature T_x with NaF.

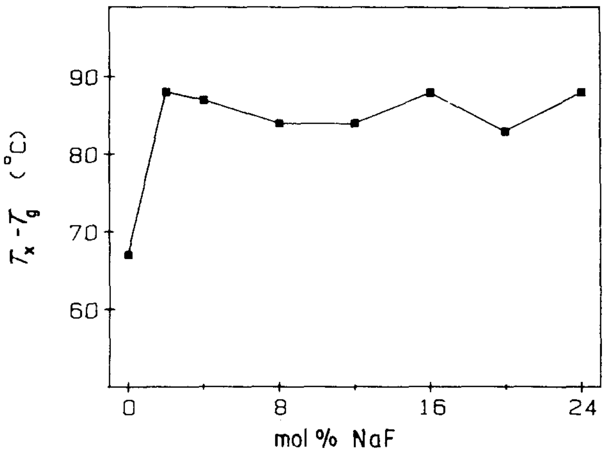

Figure 7 T_x–T_g against NaF content.

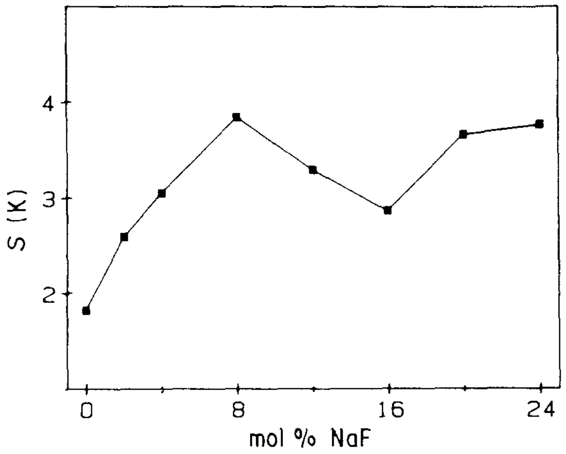

Figure 8 Variation of stability criterion S with NaF.

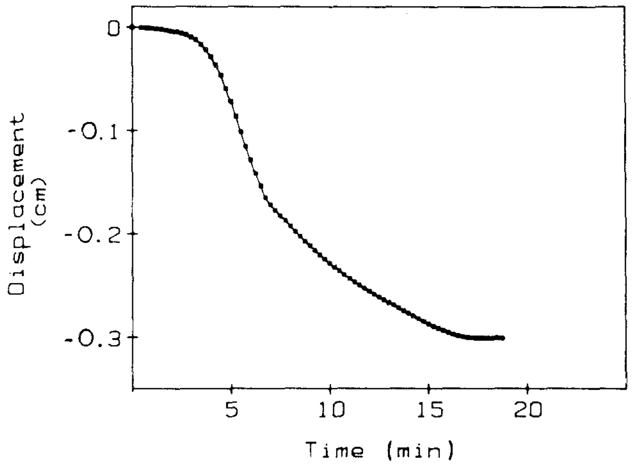

Figure 9 Typical curve for variation of sample thickness against time.

and high temperature: the former due to the small creep of the sample, and the latter has been attributed to the increased plasticity of the glass as the softening point is approached which leads to a large error in the derivative dh/dt.

A plot of viscosity as a function of temperature is given in Fig. 11. The results show that the viscosity decreases with increasing sodium and obeyed an Arrhenius law:

$$\eta = \eta_0 \exp(E/kT) \qquad (3)$$

where E is activation energy; T, temperature; and k, Boltzmann's constant. The activation energy against sodium content plotted in Fig. 12 indicates a decrease with increasing sodium in a similar trend to the viscosity results.

The decrease in viscosity indicates a depolymerization of the basic glass structure suggesting that the number of corner-sharing fluorine atoms is decreased by the addition of NaF. The glass-forming ability increased because of the 'confusion principle' rather than viscosity modification. The relation between the confusion principle and stability of the glass has also been verified for other glass systems [4].

The absolute values of activation energies obtained in this study are approximately four times less than those obtained on ZBLA glasses [13–15] but have the same order of magnitude as those reported for BeF_2 (81 kcal mol^{-1}). The activation energy for ZBLA compositions doped with PbF_2 was 88 kcal mol^{-1}. Since the viscosity values obtained for the SRM711 glass only differed 10% from the expected values, one would not anticipate an error of more than 10–20%. Thus the activation energy for the ZBGA glass is of the same order of magnitude as BeF_2- and PbF_2-doped ZBLAN glasses. The slightly lower values obtained in this study might be due to the fact that these glasses were of higher impurity content as they were prepared from commercial powder, and this would lead to structural and viscosity modifications.

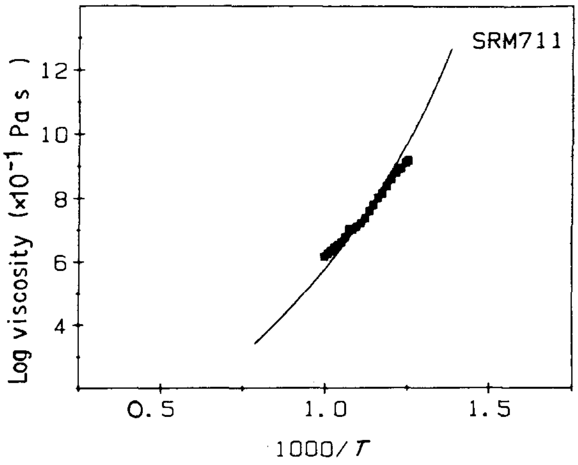

Figure 10 Variation of viscosity with temperature for NIST sample.

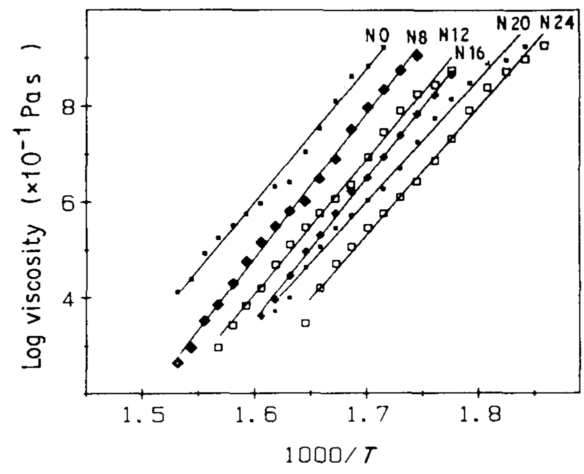

Figure 11 Variation of viscosity with temperature for ZBGAN glasses.

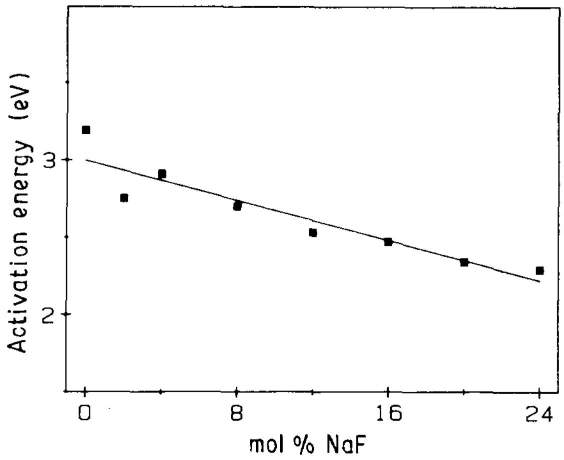

Figure 12 Variation of viscous activation energy with NaF.

3.2. Electrical properties

The d.c. conductivity as a function of temperature is shown in Fig. 13, the arrow indicating the direction of increasing sodium content. The conductivity obeyed an Arrhenius law of the form

$$\sigma = \sigma_0 \exp(-E/kT) \qquad (4)$$

where E is activation energy; k is Boltzmann's constant; and T is temperature. The addition of up to 24 mol % NaF produced only a slight change in

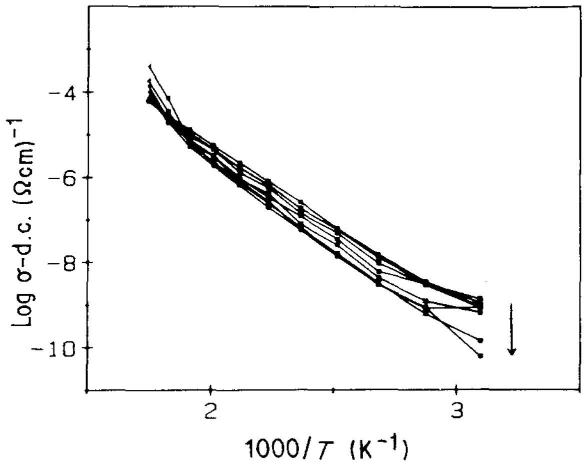

Figure 13 Variation of d.c. conductivity as a function of temperature (the arrow indicates the direction of increasing NaF content).

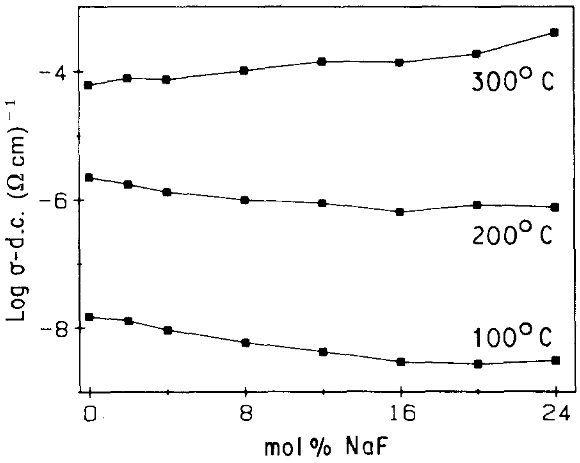

Figure 14 Variation of d.c. conductivity with NaF content.

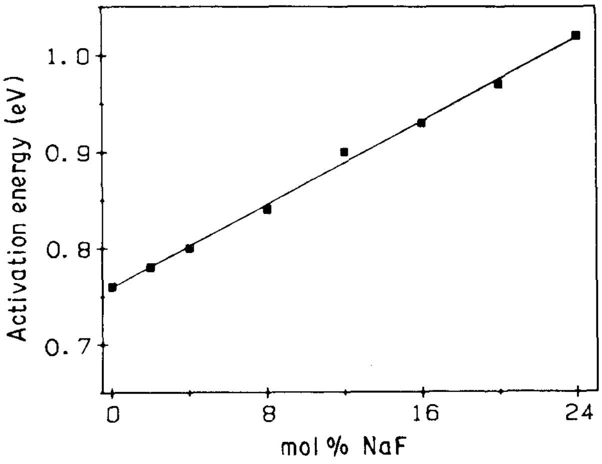

Figure 15 Variation of electrical activation energy with NaF.

TABLE III Calculated fluorine ion concentration

Sample	$[F^-]$ cm^{-3} × 10^{22}
N0	5.30
N2	5.31
N4	5.20
N8	5.20
N12	5.27
N16	5.25
N20	5.23
N24	5.25

conductivity. The conductivity at 200 °C was approximately $10^{-6}\,\Omega\,\text{cm}^{-1}$ for the samples studied, in agreement with other studies [16–27]. The conductivity for the ZBGA sample was greater than the ZBGAN samples and behaves similarily to the ZBLA and ZBLAN glasses [27].

There are two distinct conductivity regions observed: a low-temperature and a high-temperature region (Fig. 14). In the low-temperature region, the conductivity decreases with increasing sodium content, confirming that the conduction is due to the fluorine ions and that the sodium ions do not contribute to the conductivity. The addition of sodium decreases the glass-transition temperature, and therefore at high temperatures the increased conductivity can be attributed to structural changes occurring at the glass transition as well as thermal activation. The activation energy against sodium content is shown in Fig. 15 to increase with decreasing conductivity.

Chandrashekhar and Shafer [17] found that conductivity decreased when sodium replaced barium, but when sodium replaced zirconium there was no systematic variation with either conductivity or activation energy. In this study, however, the barium and zirconium atoms were simultaneously substituted by sodium as indicated by a systematic decrease in conductivity and an increase in activation energy (Figs 14 and 15). The concentration of F^- ions calculated from the composition and density are given in Table III, and varies slightly with composition. The conductivity is due only to non-bridging fluorine which is consistent with the present data.

There is no evidence of phase separation as revealed by a.c. impedance measurements. The decrease in conductivity, as well as the narrow temperature operating range due to the lowering of T_g for increased sodium content, make incorporation of these glasses into electric devices impractical.

4. Conclusions

The viscosity of a ZBGA base glass has been modified by the addition of sodium fluoride. The transmission properties of the glasses were not altered as a result of alkali fluoride addition. The index of refraction showed a gradual decrease with increasing sodium content. The viscosity and electrical conductivity decreased with increasing sodium. The glass-forming ability has been attributed to the confusion principle. Electrical and viscosity measurements indicate that depolymerization of the basic glass structure occurred.

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