INFLUENCE OF PREPARATION
OF FLOUROZIRCONATED GLASSES
ON THEIR ELECTRICAL AND DIELECTRICAL PROPERTIES

JÁN KALUŽNÝ, DMITRIJ LEŽAL*, EMIL MARIANI

Department of Physics, Faculty of Materials Science and Technology,
Paulínska 16, 917 24 Trnava, Slovak Republic

*Laboratory of Inorganic Materials,
Academy of Sciences of the Czech Republic and Institute of Chemical Technology
Pelleova 24, 160 01 Prague

Both the electrical and dielectrical properties of multicomponent flouroziconated glasses are usually sensitive to the thermal history of their preparation and to their content of impurities. A non-uniform distribution of the glass components could lead to the creation of clusters in the glass lattice. These are the cause of phase separation, or in other words the inchoate centres of crystallization. It was found from measured temperature and frequency dependences of both DC and AC conductivities and permitivity that the content of OH⁻ groups (more than 1 ppm) has a considerable effect on the properties associated with the glass structure. The presence of OH⁻ groups can not only affect optical properties but they may also be the centres of recrystallization. The way the type of glasses free of OH⁻ groups is prepared does not affect the electrical and dielectrical properties measured. The paper shows that the glasses are very stable up to temperatures of about 300 °C.

INTRODUCTION

Continuous attention has been paid to glasses by research. Glasses are metastable solids so that in some special cases their recrystallization must be avoided and their stability ensured. In order to solve this problem it is necessary to deal with the issues of glass microstructure by studying the forces acting over short distances. Their effects over medium distances should be considered when larger structural units (grains, inhomogeneities) are taken into account. Such units bound together by weaker but nevertheless defined coupling forces. These in many cases act as recrystallization nuclei.

Microstructure, and thus also the resulting performance properties, are affected not only by the thermal regime of glass preparation (melting temperature) but also by the annealing regime and the presence of impurities such as OH⁻ groups, metals etc.

Both electrical and dielectrical properties of glasses are affected by the thermal history of manufacture within the glass transition region [1,2]. Non-uniform distribution of individual components of glass can lead to the occurrence of clusters in the lattice and to phase separation. Also the presence of anions can be crucial in terms of the disposition of glass to create clusters or cause phase separation. The presence of clusters or phase separation usually affects electrical and dielectrical properties of glasses.

In general, the physical methods usually used for crystalline solids [3] can also be employed for non-ordered systems such as glasses. One can thus apply their results and concepts to non-ordered systems, for example relations and conceptions holding for ionic migration in the lattice. Owing to the short-range ordering of the glass lattice this approach is justified. But the differences are in the concentrations of defects and in the medium where the charge carriers migrate.

EXPERIMENTAL PART

The electrical and dielectrical properties were studied on multicomponent fluoride glasses having the composition 58ZrF - 33BaF - 5LaF - 4AlF (mol.%), which corresponds approximately to the middle of the glass forming area of the given system [4].

The glasses were prepared by melting the starting fluorides in a covered crucible made of glass carbon within the temperature interval (820, 955) °C in the atmospheres of dry nitrogen and in the reactive atmosphere obtained by thermal decomposition of type R 113 freon. The melting proper took 30 minutes and then the melt was cooled down in two steps. The melt in the crucible was first cooled to the temperature interval (610, 750) °C and then the molten glass was poured into a mould heated at (200, 300) °C where it was slowly annealed down to room temperature (tables 1, 2).

Absorption spectra in the infrared region were also measured on some of the samples and the corresponding content of OH⁻ in the glasses was calculated (table 2) [5].

The specimens 0.4 cm × 0.4 cm × 0.1 cm in size were polished to optical gloss and the contact surfaces coated with colloidal graphite before measurement. Direct

Table 1. Glasses free of OH⁻ prepared in different ways.

sample no.	temperature of glass melting (°C)	melting point before pour into mould (°C)	stabilization time of melting (min.)	permitivity ε′ at T ≥ 100 °C	activation energy within the temperature interval (30, 250) °C (eV)
O1	955	610→175	30	14.1	0.72
●2	820	685→315	30	14.3	0.75
□3	865	670→290	30	14.2	0.72
+4	860	625→325	20	14.3	0.72
×5	865	610→285	10	14.3	0.73

Table 2. Glasses containing OH⁻ prepared in different ways

	temperature of glass melting (°C)	melting point before pour into mould (°C)	stabilization time of melting (min.)	permitivity ε′ at T ⟨ 100 °C	ε′ at T ⟩ 100 °C	activation energy within the temperature interval (30, 250) °C (eV)	concentration (ppm OH⁻)
□6	850	650→300	30	10.4	14.2	0.75	7.1
O7	850*	650→300	30	12.7	14.1	0.76	2.6

* glass melted for second time

●8	850	750→300	30	10.9	14.2	0.75	4.7
×9	850**	750→300	60	11.4	14.1	0.77	3.3

**glass prepared with a different stabilization time

current conductivity dc was measured by the standard method over the temperature interval (-30, +300) °C. The measurements of both temperature and frequency dependence of alternate conductivity ac and permitivity ε were performed over the same temperature interval using frequencies within the (0.05, 100) kHz interval.

The glasses can be to a certain degree characterized by the measurements of dc, ac and ε. However, at the same time it is necessary to quantify the data in a way which would allow the processes influencing the values being measured.

RESULTS

Arrhenius equation holds for the temperature dependence of dc over the temperature range measured:

$$\sigma_{dc} = \sigma_0 \exp\left(- \frac{E}{kT} \right).$$

where σ_{dc}, σ_0, E, k, T are dc conductivity, pre-exponential factor, activation energy, Boltzman constant and temperature in K, respectively.

It follows from the measurements of temperature dependences of dc, ac, ε of glasses prepared in different

ways (tables 1,2) that within the given temperature range (-30, +250) °C there exists only one conductivity mechanism due to anions, with an activation energy of about 0.7 eV (figures 1,2) [7,8]. With all the samples, the activation energy increases to 1.1 eV at temperatures between 250 °C and 300 °C, i.e. just below the softening point T_g = 305 °C. Actually it is the self-conductivity of glasses which is already in play at these temperatures. Apart from determining the OH⁻ content we also measured dc over the temperature interval (-30, +150) °C on the glasses given in table 2. For the temperature interval (-30, +30) °C we found that all four samples had an activation energy of 0.83 eV. This value differs by about 0.1 eV from the activation energies established for the temperature interval (30, 250) °C. This difference is due to "freezing-up" of some of the structural bonds. In figures 1, 2, the dc dependences are plotted for samples given in tables 1 and 2, and one can see that they are identical. For reasons of clarity only some of the dependences are shown.

One can characterize to a considerable degree the processes related to the changes in structure by determining the temperature and frequency dependences of ac and permitivity ε. Usually employed the impendance
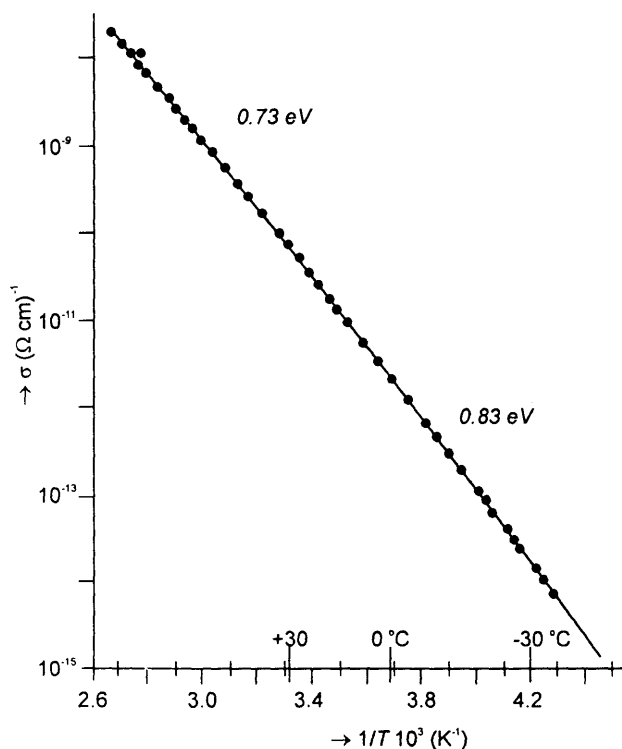
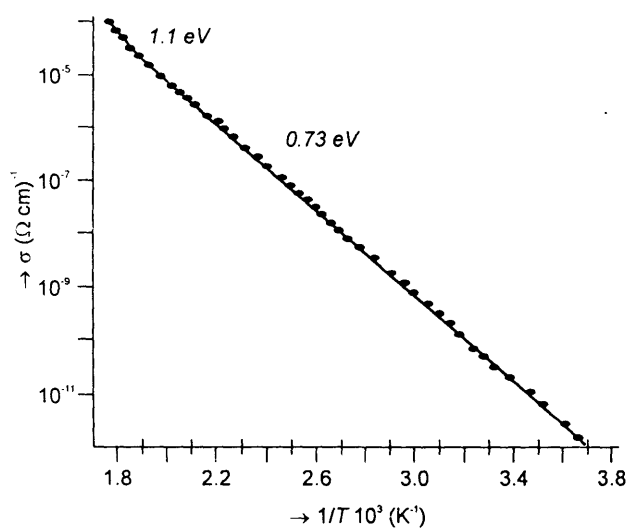Figure 1. Temperature dependence of dc for glasses free of OH^- groups.

Figure 2. Temperature dependence of dc for glasses containing OH^- groups.

and admittance diagrams usually eemployed for this purpose give information mainly about the effects taking place at the electrodes, but cannot be used for these glasses as these exhibit high dc values and a strong frequency dependence of ac. The values of ac and ε measured were therefore analyzed by means of the complex electric modulus M^* [9], for in this case the results are not affected by dc. M^* is given by the equation

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' + i\varepsilon''} = M' + iM''$$

where ε' is determined from the intersection of the modular diagrams, $\varepsilon'' = (\sigma / \omega \, \varepsilon_0)$ is proportional to dielectric losses, ε_0 is the permitivity of vacuum and $\omega = 2\pi f$.

The modular diagrams M'' vs. M' plotted in a complex plane reflect very sensitively the influence of the preparation of glasses on processes which are associated with relaxation and migration effects.

With respect to specific hygroscopic properties of fluorides, OH^- groups are built into their structural skeleton during the preparation of glasses. Their concentration is considerably affected by the technological processes employed.

A certain amount of water can get into the melted flourozirconated glasses if technological regime is not precisely followed. The molecules of H_2O dissociate into H^+ and OH^- ions by the process of hydrolysis and they are get built into the glass lattice. The concetration of OH^- had the values of (2.6, 7.1) ppm (table 2) and did not affect the measured temperature dependences of dc (figures 1, 2). On the hand, the presence of OH^- built into the lattice of glass (table 2) substantially changed the values of ε' for temperatures lower than 100 °C (figure 3). The permitivity of glass is known to be strongly affected by inhomogeneities. One can therefore assume, with respect to the experimentally established dependences plotted in figures 3, 4, 5, 7, that the OH^- groups present in the glass lattice were responsible for the inhomogeneities of the glass structure. This assumption was confirmed by the modular diagrams (asymmetric shape with the considerable elongation of the tail, figure 4). One can also follow the influence of changes in the technological process by means of the dependences measured (the same glass melted twice, or a different time of melt stabilization, figure 4). The influence of OH^- groups was not so marked at temperatures above 100 °C (figure 7).
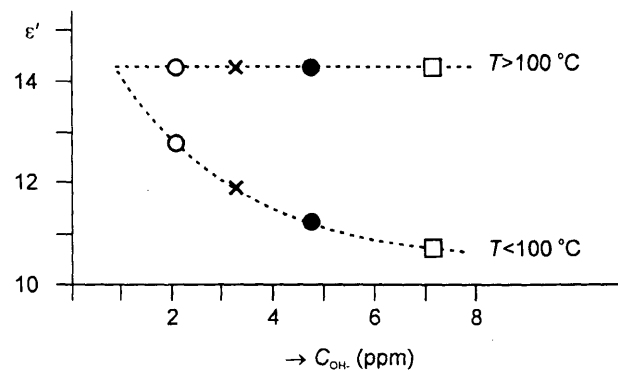

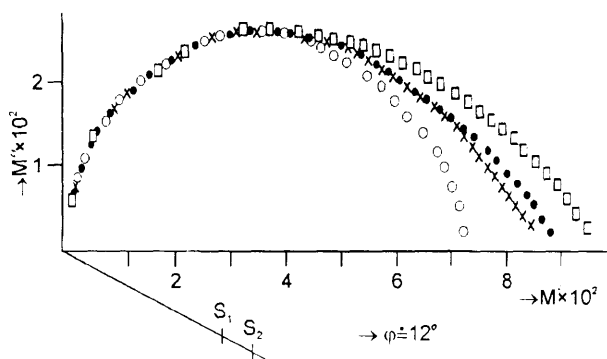Figure 3. The influence of OH concentration on permitivity for glasses of table 2.

Figure 4. Modular diagram M'' vs M' for glasses of table 2 below 100 °C.
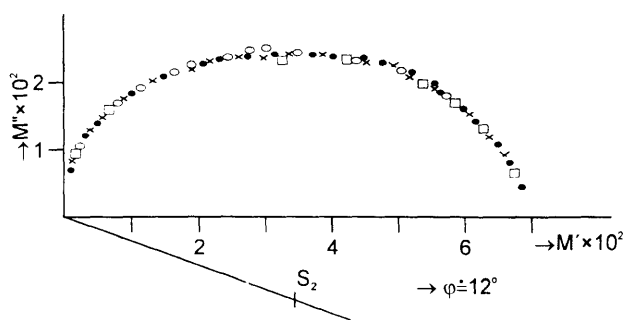

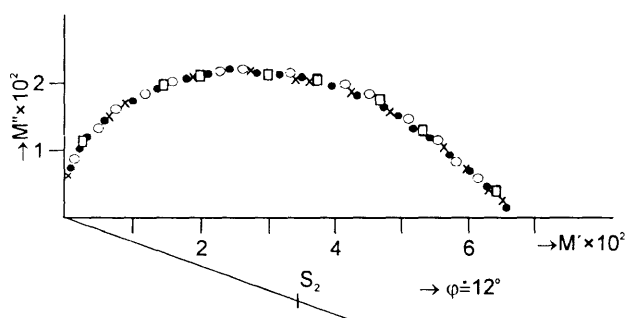Figure 6. Modular diagram M'' vs M' for glasses of table 1.

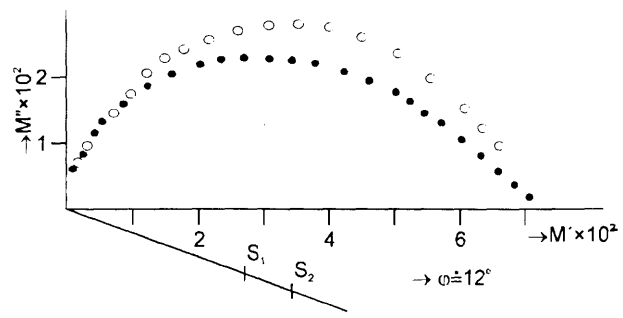Figure 5. Modular diagram M'' vs M' for glasses of table 2 above 100 °C.

Figure 7. Modular diagram M'' vs M' for glasses of table 2 containing OH⁻ groups and for glasses of table 1 free of OH⁻ groups , both for temperatures above 100 °C.

The influence of different technologies of glass preparation did not appear in the complex modular diagrams measured on samples containing less than 1 ppm of OH⁻ groups (figure 6).

DISCUSSION

Conductivity of the investigated glasses is due to F⁻ anions which move within the "holes" in the lattice. Although the model was worked out for oxygen glasses [4] it nevertheless holds in our case. According to the model there are always many more vacancies available in glass for migrating ions than is the actual number of free migrating ions, while the concentration of vacancies constant for a wide temperature interval. There exists only one migration mechanism, as confirmed by the fact that there was found out only one activation energy (of about 0.73 eV) for the *ac* temperature dependences (figures 1, 2). The relatively low activation energy indicates that the glass structure is fairly loose. The activation energy established represents the average distribution of potential barriers which the migrating ion must overcome. The different concentrations of OH⁻ groups (figure 3) occurring in glasses (table 2, figures 1, 2) were not indicated by the *dc* dependences. Measu-

rements of the glasses over the temperature interval (-30, +150) °C showed that the activation energy mildly varied to the extent of 0.1 eV. This phenomenon is caused by "freezing-up" of some of the structural bonds.

The experimentally established dependences of modular diagrams M'' vs M' (figures 4 - 7) enable one to explain the differences between the processes over the temperature interval both below and above 100 °C.

The dependences of modular diagrams M'' vs M' do not form an ideal circular line, the centre being shifted below the real axis (S_1, S_2 φ = 12 °). This means that the relaxations under the effect of the electric field are caused by migrating ions in the volume of glass but cannot be described by means of a single relaxation time only. Such a description requires a spectrum of relaxation times when the individual time values do not show great differences.

The main "arch" rising from the origin belongs to conductivity relaxations, while the high frequency "tail" belongs to localized relaxations of the larger units.

CONCLUSION

- There is one mechanism involved in the charge transport performed by F⁻ ions with an activation energy

of about 0.73 eV in the fluorozirconated glasses studied over the whole temperature interval investigated (-30, +250) °C. The mechanism depends neither on the way of the glass preparation nor on the content of OH⁻ groups.
- From the dependences of the modular diagrams it was found that the content of OH⁻ groups has a significant influence on those properties of glass which are associated with its structure. The presence of OH⁻ groups affects greatly the values of permitivity at temperatures below 100 °C. Only a small amount of OH⁻ groups (> 1 ppm) is capable of modifying to a substantial extent the structure of the given glass. The groups may act as nuclei of recrystallization. When OH⁻ groups are present, the shape of the spectrum M'' vs M' at temperatures up to 100 °C is broadened. It is asymmetrical with a considerable elongation of the arm towards the range of the short relaxation times. It confirms the relaxation of bigger groups. The extension is proportional to the content of OH⁻ groups in glass (7.1 ppm) and it changes the shape up to 27 % (figure 4).

– The way the glass was prepared did not affect the dependences of modular spectra when the glass was free of OH⁻ groups. Glasses with built-in OH⁻ groups exhibit a different course of modular diagrams also at temperatures above 100 °C, which substantiates the idea of a slightly different glass "structure" (figure 7).

– We ruled out the possibility of the influence of an absorbed layer of surface water by obtaining identical dependences from repeated measurements.

– All of the processes are reversible because identical dependences were obtained from multiple measurements. This confirms the conclusion that the glasses of the given compositions exhibit a strong structural stability up to about 300 °C.

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VPLYV PRÍPRAVY FLUOROZIRKONIČITÝVH SKIEL NA ICH ELEKTRICKÉ A DIELEKTRICKÉ VLASTNOSTI

JÁN KALUŽNÝ, DMITRIJ LEŽAL*, EMIL MARIANI

Katedra fyziky, Materiálovotechnologická fakulta STU, 917 24 Trnava, Slovenská republika.

Laboratoř anorganických materiálů ÚACH AV ČR a VŠCHT, Pelléova 24,160 00 Praha

Elektrické a dielektrické vlastnosti viaczložkových fluorozirkoničitých skiel sú zvyčajne citlivé na históriu ich prípravy a obsahovú čistotu. Nerovnaké rozloženie komponentov skla vedie k vytváraniu klasterovej siete v skle. Spôsobujú fázovú separáciu, alebo inými slovami počiatočné centrá kryštalizácie. Z nameraných teplotných a frekvenčných závislostí jednosmernej a striedavej vodivosti a permitivity sa zistilo, že obsah OH⁻ skupín (viac než 1 ppm) má značný vplyv na vlastnosti skla. Prítomnosť OH⁻ skupín nevplýva iba na optické vlastnosti, ale tiež môže byť zdrojom rekryštalizačných centier.

Z realizovaných meraní možno usudzovať, že skúmanie v fluorozirkoničitých sklách v teplotnom intervale (-30, +250) °C transport náboja je uskutočnený F⁻ iónmi, pričom mechanizmus je nezávislý na príprave skla, ako aj na obsahu OH⁻ skupín.

Z nameraných modulárnych diagramov sa usudzuje, že obsah OH⁻ skupín nemá podstatný vplyv na vlastnosti skla spájané s jeho štruktúrou. Prítomnosť OH⁻ významne ovplyvňuje hodnoty permitivity pod 100 °C. Za prítomnosti OH⁻ skupín tvar spektra M" vs M' sa zošíruje pri teplotách nad 100 °C. Je asymetrický s výrazným predĺžením do oblasti kratších relaxačných časov.

Vylučujeme myšlienku vplyvu absorpcie vrstvy povrchovej vody na základe identických závislosti získaných pri opakovaných meraní. Merania potvrdzujú tvrdenie, že sklá uvádzaných zloženi sú silne štrukturálne stabilné až do teploty 300 °C.