ELECTRICAL TRANSPORT PHENOMENA IN ZrF_4-BaF_2-LaF_3-AlF_3 GLASSES

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Electrical conductivities of ZrF_4-BaF_2-LaF_3-AlF_3 glasses in the d.c. and a.c. electrical fiedls were studied. The d.c. conductivity measurements showed, that only single mechanism of charge transport with the activation energy approximately 0.76 eV exists in the temperature range of 20–250° C. The results of a.c. conductivity measurements proved, that the dielectric relaxation of larger groups of ions appears within the temperature interval of 20–100° C. These groups are completely dissociated at the temperature around 100° C. The studied glasses are very stable at the temperatures lower than T_g.

INTRODUCTION

Fluorozirconate glasses were prepared for the first time in 1975 [1]. At the beginning they have been studied especially from the point of view of the influence of the preparation on the optical losses, and only later [2] the investigation of their ionic conductivity started. Many studies proved, that the charge transport is caused by fluoride anions [3–8]. For examining electrical and dielectric properties and relaxation mechanism of ZrF_4-BaF_2-LaF_3-AlF_3 glasses the composition of 58-33-5-4 mol. %, corresponding approximately to the middle of the glass forming region was chosen.

The information about electrical and dielectric properties of glasses of the similar composition are already available, but the relaxation mechanisms are not yet satisfactorily explained. The study of the electrical and dielectric properties of glass materials enables to understand some of the structural processes carrying out in the given compound. The information about these processes is essential for the glass production as for their application in the technical practice, in this case for the production of optical fibres.

EXPERIMENTAL

The fluoride mixture was melted in the covered glassy carbon crucible at the temperature of 850°C for 0.5–1.0 hour in the flowing dry N_2 with freon R113 (see Table I). After the stabilization at the temperature of 650°C or 750°C (see Table I) the melt was cast in the brass form preheated to 300°C. For all the samples the infra-red absorption spectra were measured and from the absorption band intensity at the wavelength 2.9 μm (using the absorption coefficient obtained for similarly composed glasses [10]), the content of OH^- groups was calculated (see Table I).

The samples of dimensions 0.4 × 0.4 × 0.1 mm were polished to the optical gloss and the electrical contacts from colloid graphite (DAG 580) were applied. The d.c. conductivity was measured in a vacuum in the temperature range from 20 to 250°C. The frequency dependence measurements of a.c. conductivities and permittivities were performed in the frequency range of 0.5–100 kHz within the same temperature interval.

Based on the measured results of d.c. and a.c. conductivities we can characterize glass considerably. It is necessary for this purpose to perform the classifica-

Table I

The preparation conditions of the glasses

Glass	Concentration of OH^- [ppm]	Melting period	Temperature before casting
1[a]	2.6	0.5 h	650°C
2	3.3	1.0 h	750°C
3	4.7	0.5 h	750°C
4	7.1	0.5 h	650°C

[a] 2 × remelted

Table II

The measured values of the activation energies

Glass	W_{dc} [eV]	W_{ac} [eV] $T > 100°C$	W_{ac} [eV] $T < 100°C$
1	0.76	0.80	0.28
2	0.77	0.80	0.30
3	0.77	0.79	0.26
4	0.75	0.76	0.26

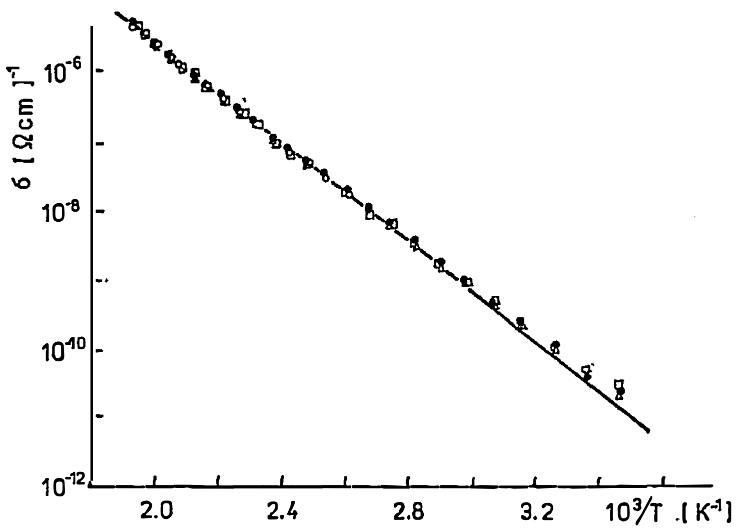

Fig. 1. The temperature dependence of d.c. conductivity. □ Glass No. 1; Glass No. 2; Glass No. 3; Glass No. 4.

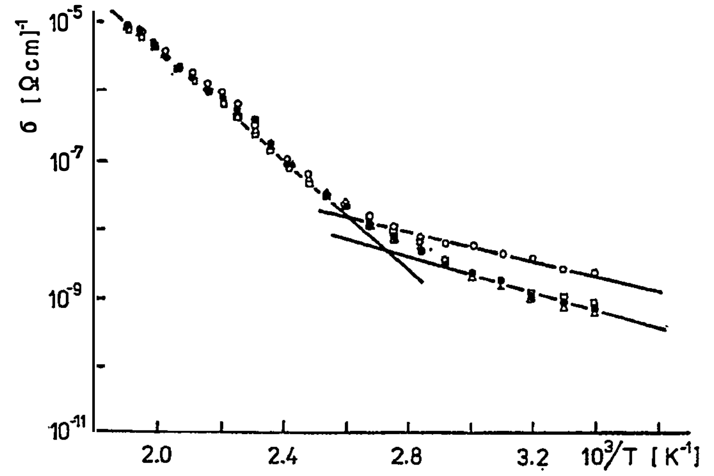

Fig. 2. The temperature dependence of a.c. conductivity ($f = 1.6$ kHz). □ Glass No. 1; ○ Glass No. 2; △ Glass No. 3; ● Glass No. 4.

tion of the data that would allow to identify processes contributing to the measured values.

For the temperature dependence of d.c. conductivity, the Arrhenius relationship (see Fig. 1) is valid in the whole measured temperature range:

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{W_{dk}}{kT}\right) \tag{1}$$

where W_{dc} is the activation energy, σ_0 is an experimental exponential factor, k is the Boltzmann constant and T is the absolute temperature. The measured values are placed in the Table II.

The results of the temperature dependence measurements of a.c. electrical conductivity at the frequency of 1.6 kHz are shown on the Fig. 2. From the measured values it can be seen, that the dependence course has the sharp change at 100°C. Below this temperature the activation energy of a.c. conductivity is $W_{ac} = 0.26$ eV and above 100°C the activation energy is approximately 0.8 eV. The small differences of the activation energies above 100°C determined by the measurements of the d.c. and a.c. conductivity are caused by the polarization effects.

The frequency dependence of a.c. conductivity (see Fig. 3) confirmed the validity of the Jonscher general relationship for this investigated case and can be

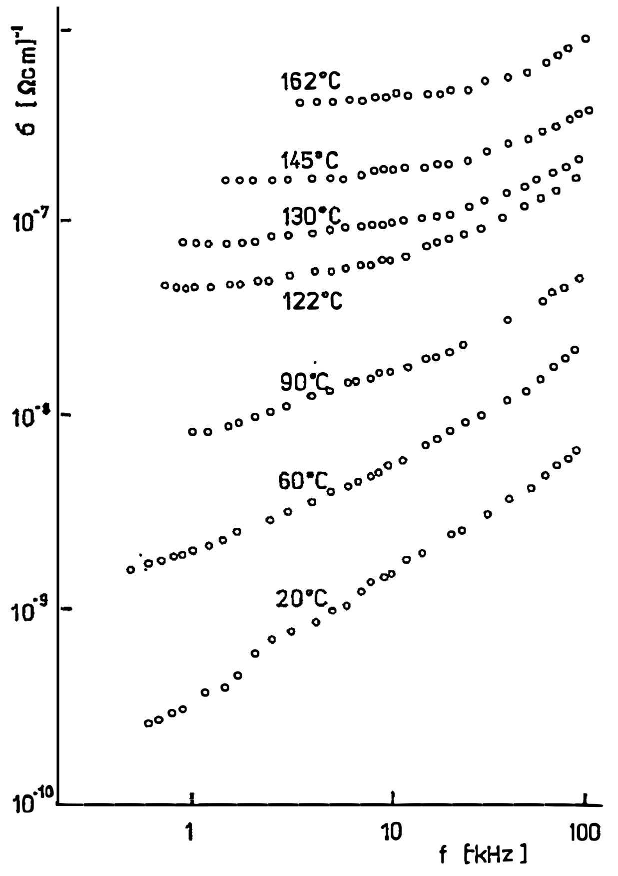

Fig. 3. The frequency dependence of the conductivity for the glass No. 2.

described by the simple expression:

$$\sigma_f = \sigma_{\mathrm{dc}} + Af^s \tag{2}$$

where σ_{dc} is d.c. conductivity, s is the charge parameter (for the studied glasses the value is 0.5–0.9 and it is typical for multi phase materials with the different conductivity of individual phases, see Fig. 4), A is the experimentally determined constant and f is the frequency.

The permittivity is also an important criterion for the judging the glass properties. Directly measured temperature and frequency dependencies of permittivity do not show any special properties, they only slightly increase as the temperature is increased (see Fig. 5 and 6). The values of the temperature dependence of permittivity measured at the frequency of 1.6 kHz can be strongly influenced by a polarization appeared close to electrodes or by the polarization on the crystal boundary. Therefore it is suitable to use the analysis for obtaining the information about the structural configuration of the studied material by the complex electrical module as it was established by Macedo [11]. This analysis enables us to determine

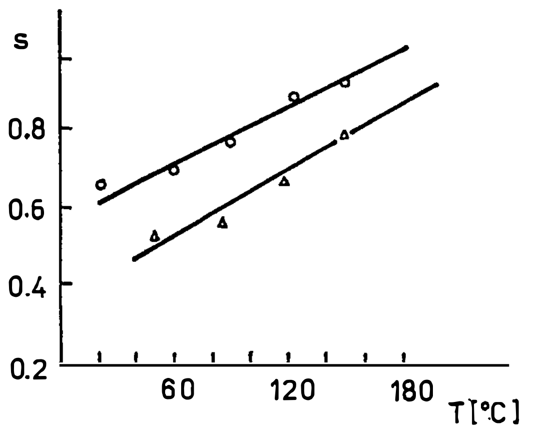

Fig. 4. The temperature dependence of the charge coefficient's; ○ Glass No. 2; △ Glass No. 3.

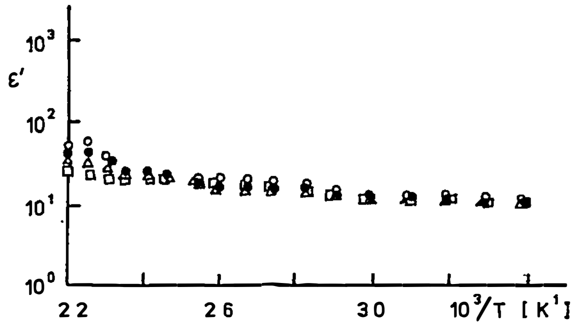

Fig. 5. The temperature dependence of real part of permittivity (f = 1.6 kHz); □ Glass No. 1; ○ Glass No. 2; △ Glass No. 3; ● Glass No. 4.

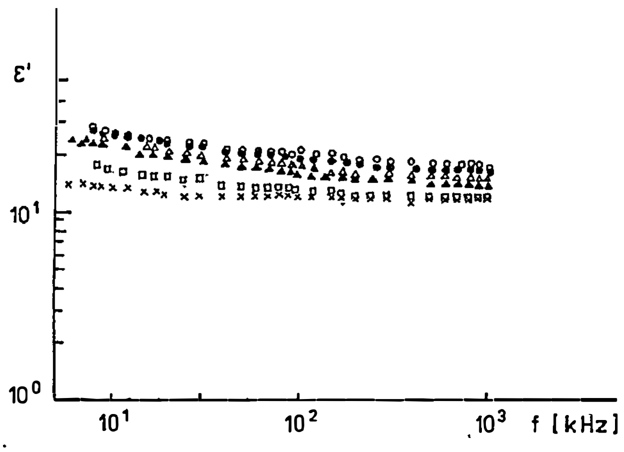

Fig. 6. The frequency dependence of real part of permittivity of the glass No. 2.; × 20° C; □ 88° C; ▲ 105° C; △ 118° C; ○ 136° C; ● 150° C.

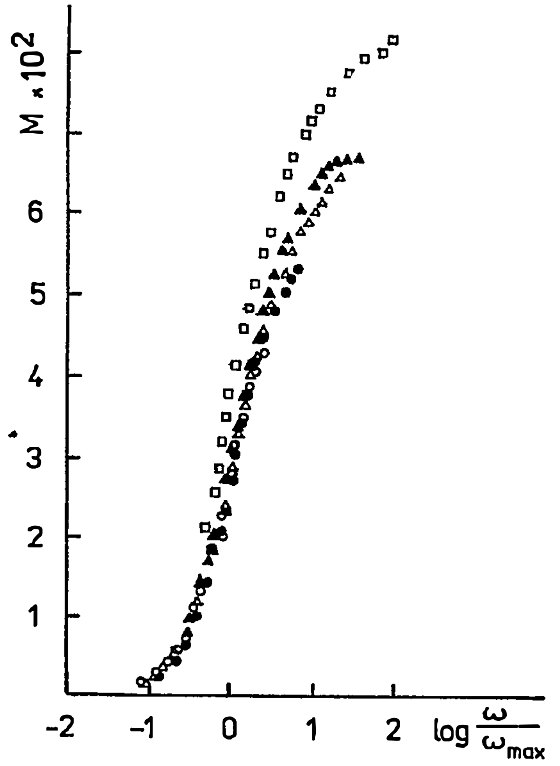

Fig. 7. The frequency dependence of real part of electrical module of the glass No. 2.; □ 88°C; ▲ 105°C; △ 118°C; ○ 136°C; ● 150°C.

the relaxation time and the relaxation energy spectra from the frequency dependence of complex permittivity ϵ^*:

$$\epsilon^* = \epsilon' - i\epsilon'' \tag{3}$$

$$M^* = \frac{1}{\epsilon^*} = \frac{1}{\epsilon' - \epsilon''} = M' + iM'' \tag{4}$$

where ϵ' is the relative permittivity (it decreases as the frequency is increased by the influence of the polarization effect) and ϵ'' is the factor proportional to the dielectric losses.

The courses of M'' and M' depending on the frequency for the various temperatures show the existence of the relaxation time spectrum in the measured glasses (see Fig. 7 and 8). The averaged activation energy of relaxation processes (the same for all the measured glasses; $W_{\text{rex}} = 0.71$ eV) can be determined from the temperature dependence of the maximum shift of the M'' (Fig. 9). Further information about the processes manifesting themselves in the glasses can be obtained from the course of the modular diagrams plotted in the complex plane M'' versus M' (see Fig. 10). It is obvious from all courses, that the conductivity relaxation being the main process are distinguished by the whole relaxation.spectrum.

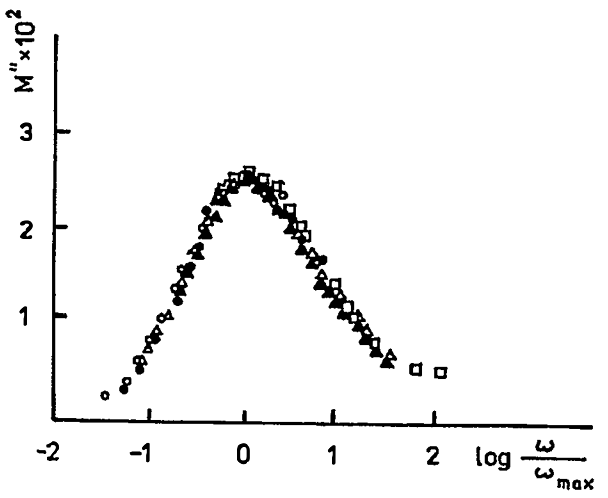

Fig. 8. The frequency dependence of imaginary part of complex electrical module of the glass No. 2.; □ 88°C; ▲ 105°C; △ 118°C; ○ 136°C; ● 150°.

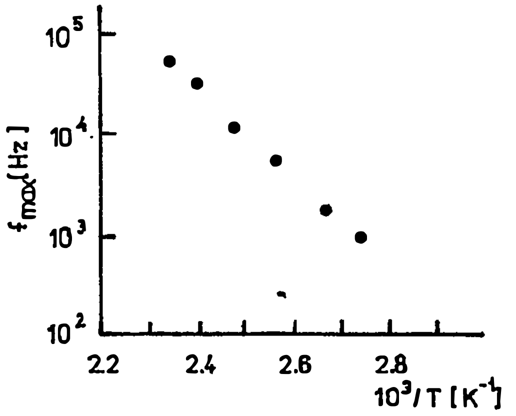

Fig. 9. The temperature dependence of the shift of the maximum in the frequency dependence of imaginary part of complex electrical module.

The spectrum is asymetrical with the expressive high-frequency tail strongly extended comparing it with the Debye course. For the temperatures higher than 100°C the relaxation time distribution is changed, the course approaches more the circle with the centre shifted under the real axis. The main "arch" started from the beginning belongs to the conductivity relaxation and on the other hand high frequency "tail" belongs to the local relaxation, for example the relaxation of larger groups of ions, individual phases and so on.

In the case of glasses with the statistical distribution of conductivity relaxation processes, it is efficient to use the extrapolation M'' versus M' for the exact determination of ϵ_s. The point of intersection of

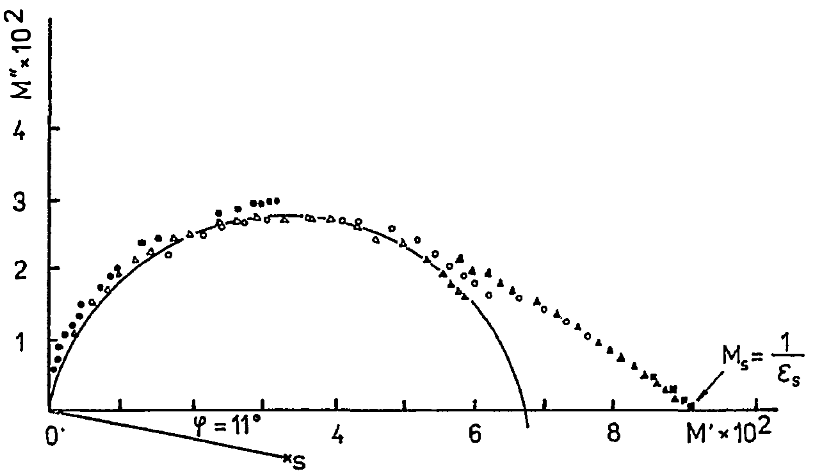

Fig. 10. The dependence of real and imaginary parts of complex electrical modules of the glass No. 3.; ■ 20° C; ▲ 60° C; o 90° C; ● 162° C.

M'' with the axis M' gives the value $M_s = 1/\epsilon_s$ (see Fig. 10), that is important material characteristic of the measured glasses.

DISCUSSION

When the fluoride glass does not contain alkaline ions, the electrical conductivity is caused by fluorine anions F^- moving by "interstices" of a glass structural grid. The conductivity losses together with dipole relaxation are generally known as a migration losses, whose model was developed for the oxide glasses [12, 13] and it is also valid for these investigated materials. According to this model, there is always much more free sites in glasses for each moving ion than the number of migrating ions, while the concentration of these free places is kept constant in the large temperature interval. Only one charge transport mechanism exists within the measured range of 20–250°C, what is also confirmed by the single activation energy value ($W_{dc} = 0.76$ eV) of the charge transport obtained from the d.c. conductivity measurements for the whole interval. The relatively low value of this activation energy confirms, that the glass structure is relatively free, not close, although aluminium ions causing the improvement of the grid continuity are present in the glass. The measured activation energy represents the average value of the distribution on the potential barriers that must be overcome by a migrating ion.

From the a.c. conductivity measurements it results, that this migration process is identical for the temperatures higher than 100°C.

The activation energies yielded from d.c. and a.c. conductivity and relaxation measurements are approximately the same. This fact is in agreement with the theory of Macedo and others [11], that the process of the charge transport in a disordered grid is proved by the dielectric relaxation. Small differences between behaviour in d.c. and a.c. fields are caused by the presence of the polarization effects.

The course of the modular spectra M^* (see Fig. 10) enables better understanding of the process differences performed in the temperature region below 100°C and above 100°C. The modular spectra showed, that the conductivity relaxation is the dominant process in the whole temperature interval and is characterized by the relaxation time distribution. The creation of the "arm" elongated to the area of high frequencies region (at the temperatures higher than 100°C) confirms the occurrence of the relaxation with the relaxation times corresponding to larger groups of ions, which do not reach the adjustment to the a.c. electric field changes. At the temperatures higher than 100°C these groups decompose being completely dissociated. The relaxation time spectrum with the different distribution (corresponding to other relaxation groups) also exists at the temperatures higher than 100°C. The influence of adsorbed moisture of the sample surfaces was eliminated by the fact, that for the repeated measurements in a vacuum the same results were obtained.

CONCLUSIONS

The course of temperature dependence of the electrical conductivity of ZrF_4-BaF_2-LaF_3-AlF_3 glasses in d.c. electrical field showed, that only single conductivity mechanism appeared in the glass in the temperature range from 20 to 250°C, the dependence has the form of the Arrhenius relationship with the activation energy of 0.76 eV. This value corresponds to relatively open glass structure.

From the measurements of the electrical conductivity in a.c. electrical field results that larger groups of ions with the longer relaxation times strongly influencing the dielectric relaxation at lower temperatures are decomposed at the temperatures around 100°C. The activation energies obtained from the electrical conductivity measurements in d.c. and a.c. electric fields similar as the values obtained from the relaxation measurements are in good harmony.

All observed values are reversible, because for the repeated measurements the same courses were yielded. This fact confirms, that the studied glasses are very stable at temperatures lower than 250°C.

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ELEKTRICKÉ TRANSPORTNÍ JEVY V ZrF_4-BaF_2-LaF_3-AlF_3 SKLECH

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Byla studována elektrická vodivost skel složení ZrF_4-BaF_2-LaF_3-AlF_3 ve stejnosměrném i střídavém elektrickém poli při teplotách v intervalu 20 až 250°C.

Průběh teplotní závislosti stejnosměrné elektrické vodivosti prokázal, že ve sledovaném teplotním intervalu se ve skle uplatňuje jediný vodivostní mechanizmus. Závislost má charakter Arrheniova vztahu s aktivační energií přibližně 0,76 eV.

Z měření střídavé elektrické vodivosti (frekvenční interval 0,5 až 100 kHz) vyplývá, že při teplotě přibližně 100°C dochází k rozpadu větších skupin iontů s delšími relaxačními časy. Aktivační energie získané z měření elektrické vodivosti ve stejnosměrném i střídavém elektrickém poli stejně jako z měření relaxačních jsou v dobrém souladu.

Všechny sledované procesy jsou v uvedeném teplotním intervalu vratné, neboť při opakovaných měřeních byly získány shodné průběhy. Tato skutečnost potvrzuje vysokou stabilitu skel ZrF_4-BaF_2-LaF_3-AlF_3 při teplotách nižších než 250°C.

Obr. 1. Teplotní závislost stejnosměrné vodivosti. □ *Sklo č. 1;* ○ *Sklo č. 2;* △ *Sklo č. 3;* ● *Sklo č. 4.*

Obr. 2. Teplotní závislost střídavé vodivosti (f = 1,6 kHz). □ *Sklo č. 1;* ○ *Sklo č. 2;* △ *Sklo č. 3;* ● *Sklo č. 4.*

Obr. 3. Frekvenční závislost vodivosti skla č. 2.

Obr. 4. Teplotní závislost koeficientu náboje S. ○ *Sklo č. 2;* △ *Sklo č. 3.*

Obr. 5. Teplotní závislost reálné části permitivity. □ *Sklo č. 1;* ○ *Sklo č. 2;* △ *Sklo č. 3;* ● *Sklo č. 4.*

Obr. 6. Frekvenční závislost reálné části permitivity skla č. 2. × *20°C;* □ *88°C;* ▲ *105°C;* △ *118°C;* ○ *136°C;* ● *150°C.*

Obr. 7. Frekvenční závislost reálné části elektrického modulu skla č. 2. □ *88°C;* ▲ *105°C;* △ *118°C;* ○ *136°C;* ● *150°C.*

Obr. 8. Frekvenční závislost komplexní části elektrického modulu skla č. 2. □ *88°C;* ▲ *105°C;* △ *118°C;* ○ *136°C;* ● *150°C.*

Obr. 9. Teplotní závislost posunu maxima frekvenční závislosti komplexního elektrického modulu.

Obr. 10. Závislost reálné a komplexní části komplexního elektrického modulu skla č. 3. ■ *20°C;* ▲ *60°C;* ○ *90°C;* ● *162°C.*