ELECTRICAL AND DIELECTRIC PROPERTIES OF TeO_2 - ZnO GLASSES

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Submitted January 2002, accepted March 29, 2002

Keywords: Complex electrical modulus, Direct electrical conductivity

The paper shows the advantages of the exploiting of both electrical and dielectric properties of TeO_2 - ZnO glasses without and with admixtures for finding structural changes caused by chemical composition. Moreover these measurements make it possible to determine the boundaries of temperature and structural stability and to find very quickly the optimal conditions of the glass preparation with reproducible optical properties.

INTRODUCTION

System of binary glass TeO_2 - ZnO prepared on the base of the heavy metal oxide can be considered as very perspective material not only for the production of the passive optical fibres but for active ones with the high transparency in infrared range with wavelength above 2.5 µm [1-3], too. They are suitable for the guiding of the high power laser radiation. Therefore they have possibilities of utilisation not only as chemical sensors but also in medical applications, too [4,5]. Quantum efficiency of fluorescence depends on the high purity of used chemicals and on the solubility of rare-earth ions. Prepared glasses need to have the low concentration of OH groups because they cause decreasing of the solubility of rare-earth ions and develop also the creation of clusters. As a consequence of the decreasing solubility of rare-earth ions is the decreasing of glass fluorescence. Clusters created by the rare-earth compounds cause the radiation scattering what can be detected by the increasing of optical losses.

The technological preparation of these glasses is quite complicated but in spite of this it is performed satisfactory [6-8]. The final properties of the prepared preforms for optical fibres depend considerably on the fair keeping of technology, the material of the crucible where the glass is prepared and the chemical form of added admixtures [9], as well.

We may learn about the final properties of produced glasses only after time-consuming measurements of their physical and chemical properties. We want to show the advantages of the measurements of electric and dielectric properties. These make it possible to find out not only the influence of the preparation of the glass material on the final fibre properties but they explain the influence of the admixtures, mainly the chemical form of addition. Moreover they explain the influence of impurities and both time and temperature stability. Thus we can determine rules which connect physical properties of glasses with their structure, failures, etc.

EXPERIMENTAL

The glasses under investigation were prepared by melting the homogeneous mixtures of very pure oxide in chloride atmosphere and the following very fast cooling. Homogenisation and melting temperature were in the interval 850-1000 °C depending on their composition [4-6]. Samples for the measurements of electric and dielectric properties (diameter ~ 8 mm and the thickness ~ 1 mm) were coated by the conductive layer on the contact surfaces. Direct electrical conductivity *dc* was measured by means of the vibration electrometer. The measurements of the temperature and the frequency dependencies were performed by means of Schering bridge in the frequency interval of 0.2-100 kHz [7,8].

The measurements of *dc*, both temperature and frequency dependencies of complex permitivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) and complex electric modulus [9] ($M^* = 1/\varepsilon^* = M' + i M''$) make possible to find out the information about the influence of the changes caused by technology processes very quickly, but they also show on the breaking of the prescribed conditions of the preparation of their final properties.

Having the performed measurements of the electric and dielectric properties of the samples of required optical properties (standards) and comparing them with the results of the investigated samples, we can exclude before the next processing pre-forms, whose results differ from the "standards".

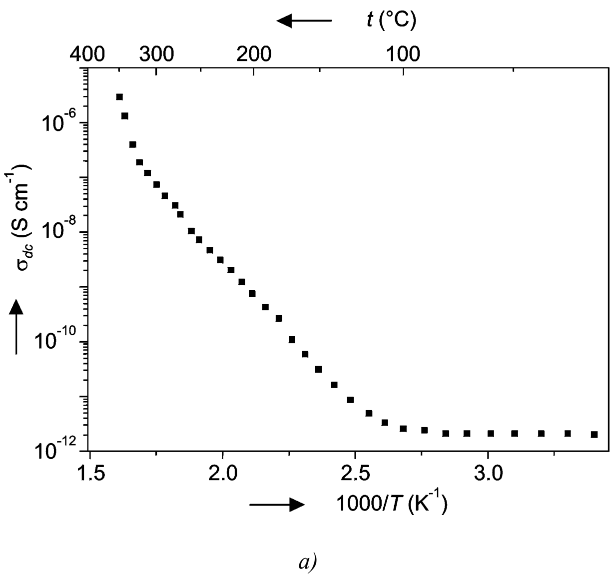
RESULTS

Temperature stability

The measurements of *dc* temperature dependencies of glasses show clearly that glasses 70 mol % TeO_2 - 30 mol.% ZnO both with and without the admixtures (Ca, Pr, Dy) are stable nearly to temperature of 290 °C (figure 1). The glasses start to soften above temperature of 300 °C and change also their structural and mechanical properties.

dc temperature dependencies are sensitive not only to the sort of the added admixture, but also to its chemical form in which it was added to the started material (figure 1). Plotted dependencies do not show any breaks it means that activation energy U_l = 1,1 ± 0.05 eV was constant. It is the evidence that the transport mechanism is not dependent on the sort and the form of admixture in temperature interval of 130-270 °C. The charge carriers also are not changed, but the concentration of charge carriers is slightly changed what may be caused by the structural change (the admixture influence). The low activation energy shows on the relative free structural ordering. Temperature of 270 °C was not overcome in order to exclude the influence of the weak bindings. Measurements show that these glasses are sensible on OH groups, which remain in the glass material when the admixture of the rare earth (RE^{3+}) was added. The glass sensibility on humidity increased. The evidence of this is the fact that conductivity increased to the temperature of 120 °C. The similar property also shows glass $PbCl_2$ [10].

The measured frequency dependencies of complex electric modulus ($M^*=1/\varepsilon^*$) confirm the results earned from *dc* measurements. The first changes in the glass structure are detected at temperature of $T > 270$ °C. The temperature increasing on 10° C caused the large changes in measured dependencies (figures 2, 3). These changes are caused by the disturbing of the weakest bindings. The measured changes are reversible because the measured dependencies for the repeated measurements from the laboratory temperature and when temperature was decreased to 270 °C were the same as during the first measurement.



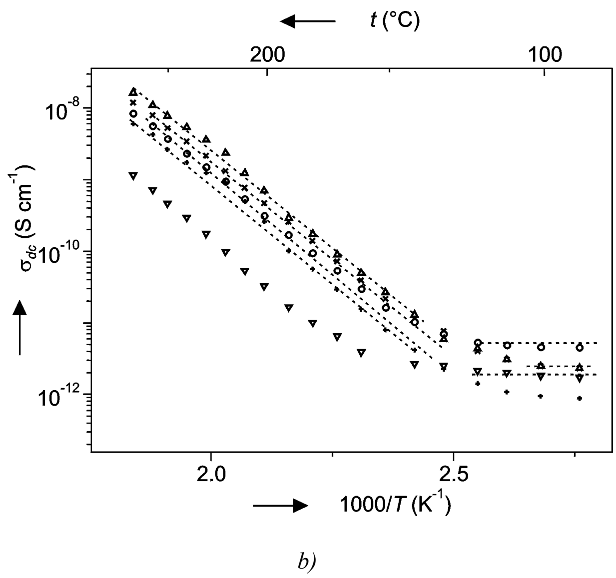


Figure 1. The temperature dependencies of *dc* measured for glass 70 mol.% TeO_2 - 30 mol.% ZnO. *a)* ■ - without admixtures; *b)* + - without admixtures, ▽ - 0.8 wt.% Ca, △ - 0.1 wt.% Pr^{3+} - metal, ○ - 0.1 wt.% Pr^{3+} in the form of Pr_2O_3, + - 0.1 wt.% Dy^{3+} in the form of Dy_2O_3.

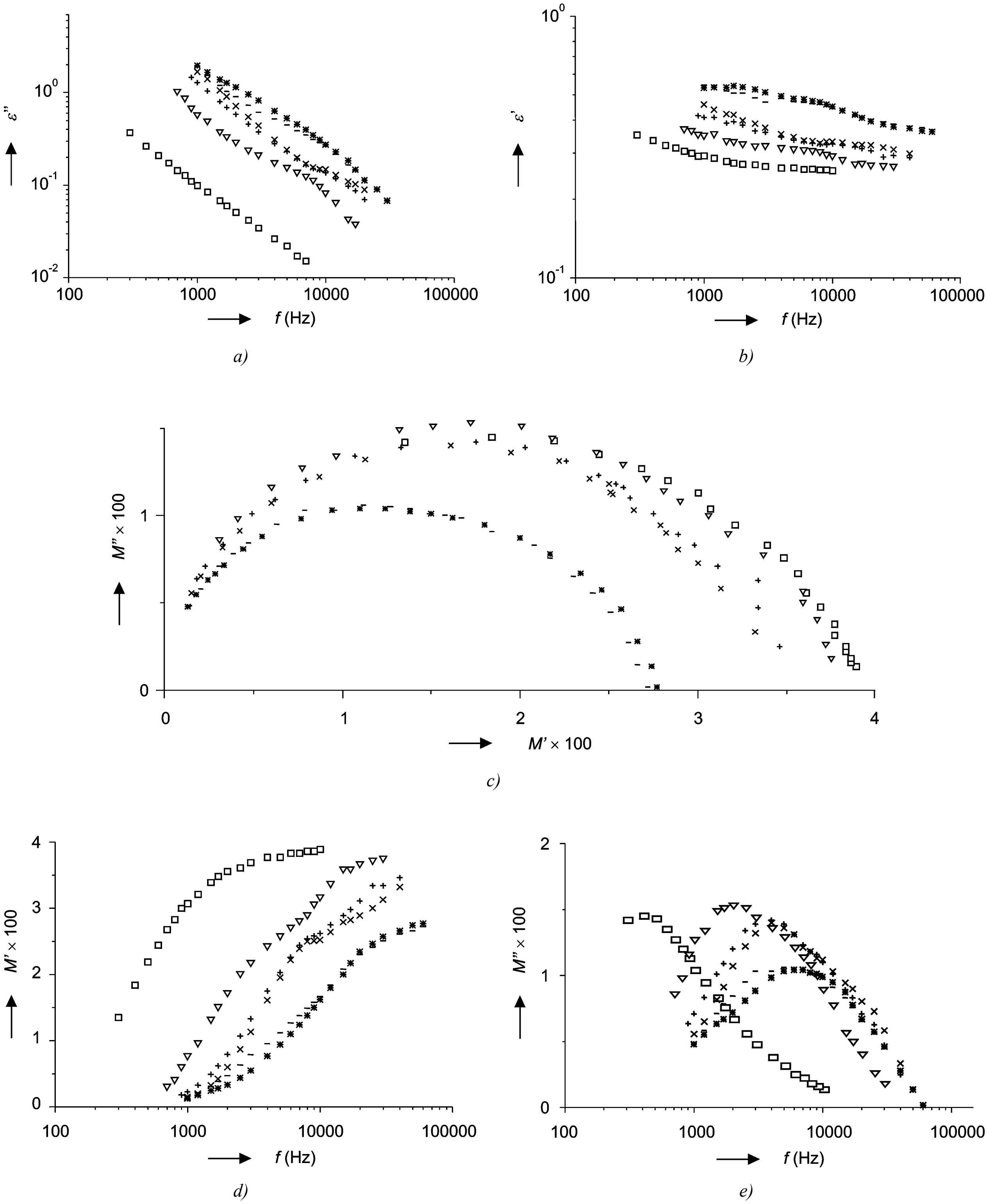
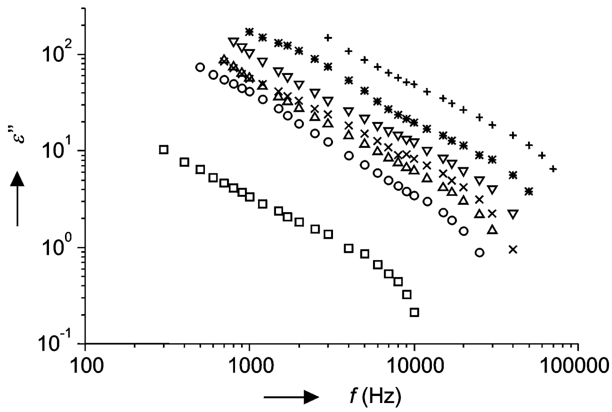


Figure 2. The dependencies for glass 70 mol.% TeO_2 - 30 mol.% ZnO melting in the crucible of Pt measured for the increasing temperature: □ - 270 °C original sample, ▽ - 280 °C, * - 290 °C, + - 290 °C measured the second time, × - 300 °C, – - measured at 300 °C after heating to 310 °C; *a)* The frequency dependencies of the imaginary compound of complex permitivity (ε'' vs. f); *b)* The frequency dependencies of the real compound of complex permitivity (ε' vs. f); *c)* Complex electric modulus (M'' vs. M'); *d)* The frequency dependencies of the real compound of complex electric modulus (M' vs . f); *e)* The frequency dependencies of the imaginary compound of complex electric modulus (M'' vs. f).



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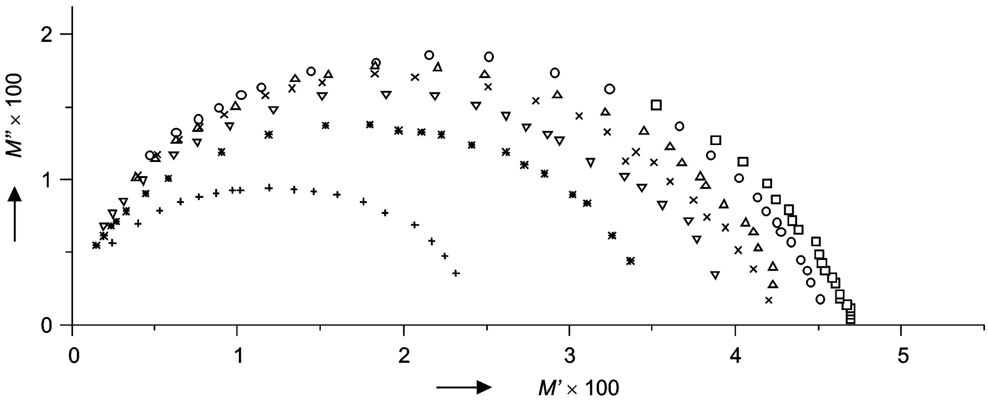

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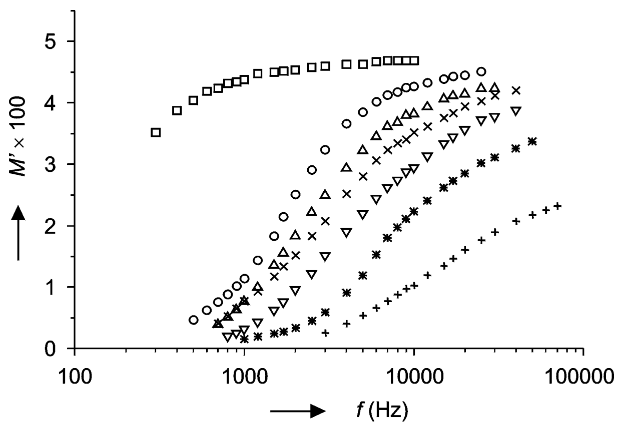

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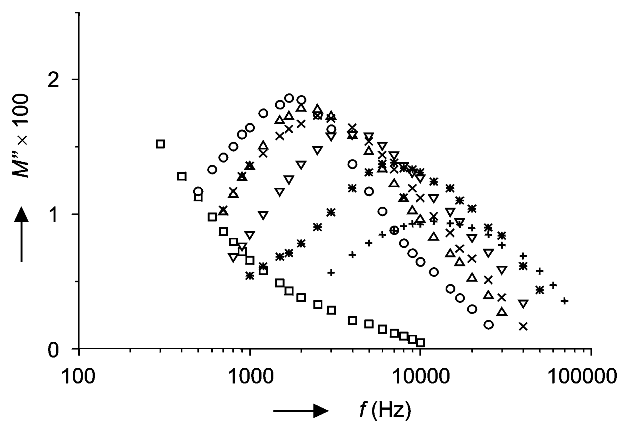

d)

Figure 3. The dependencies for glass 70 mol.% TeO_2 - 30 mol.% ZnO melting in the crucible of Al_2O_3 measured for temperature: □ - 270 °C, ○ - 290 °C, △ - 300 °C, ▽ - 310 °C, * - 320 °C, + - 330°C, × - 300 °C measured the second time after heating to 330 °C; *a)* ε'' vs. *f*; *b)* M'' vs. M'; *c)* M' vs. *f*; *d)* M'' vs. *f*.

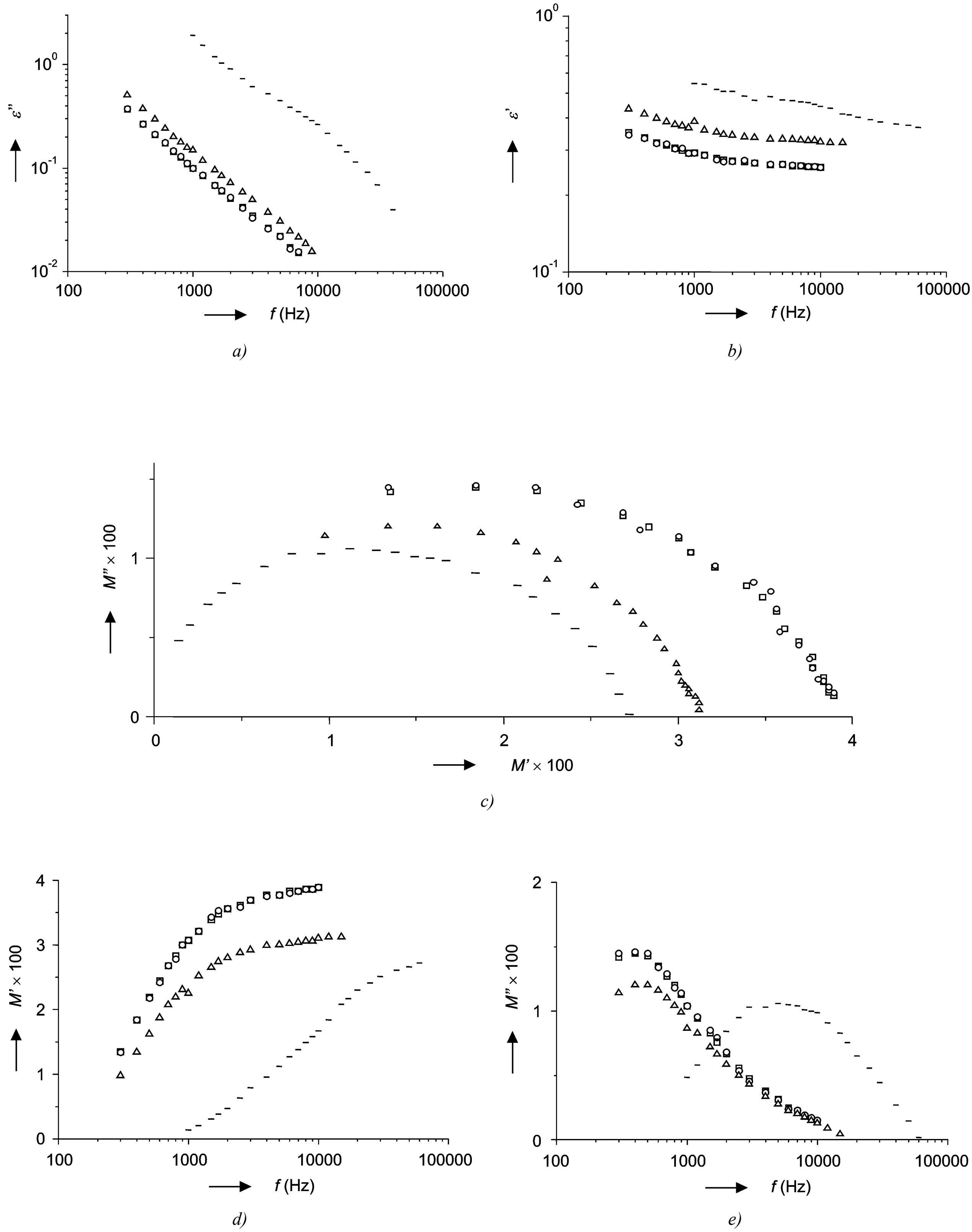

Figure 4. The measurements of glass 70 mol.% TeO_2 - 30 mol.% ZnO melting in Pt crucible: □ - original sample measured at temperature of 270 °C, ○ - measured at temperature of 270 °C after heating to 290 °C, △ - measured at temperature of 270 °C after heating to 310 °C, – - measured at temperature of 300 °C after heating to 310 °C; *a)* ε'' vs. *f* ; *b)* ε' vs. *f* ; *c)* M'' vs. M'; *d)* M' vs. *f* ; *e)* M'' vs. *f*.

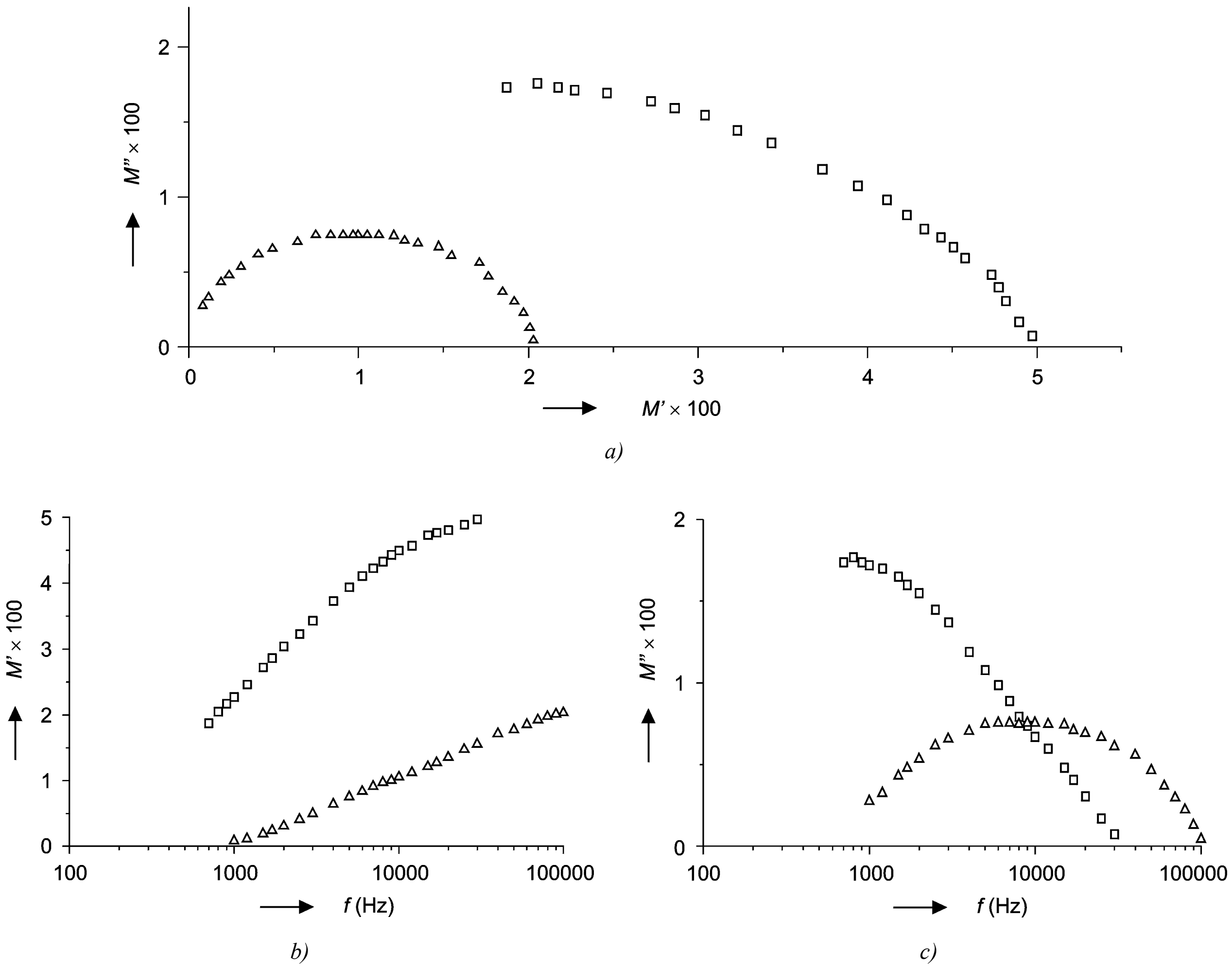

Figure 5. The measurements for glass 70 mol % TeO_2 - 30 mol % ZnO with the admixture 0.8 wt.% Ca at temperature: □ - 300 °C, △ - 330 °C; *a) M″* vs. *M′*; *b) M′* vs. *f* ; c) *M″* vs. *f*.

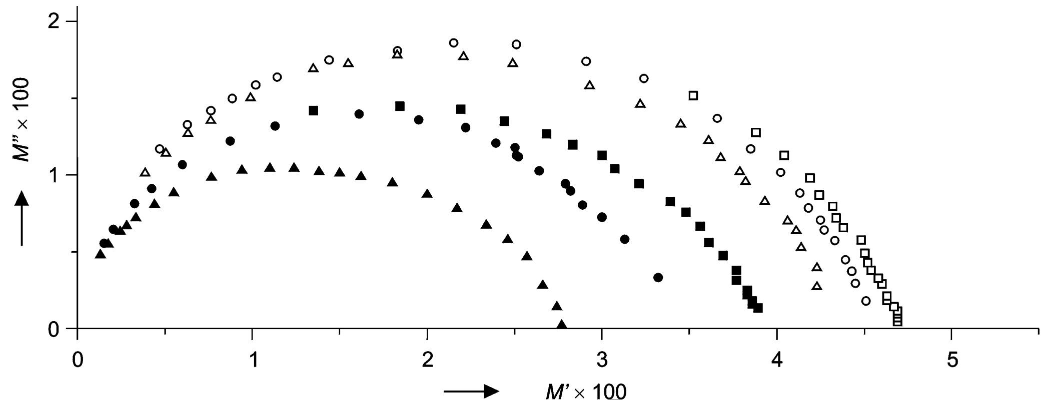

Figure 6. Dependencies of *M″* vs *M′* for glasses 70 mol.% TeO_2 - 30 mol.% ZnO melted in Al_2O_3 crucible measured at temperature of □ - 270 °C, ○ - 290 °C, △ - 300 °C and in Pt crucible measured at temperature of ■ - 270 °C, ● - 290 °C, ▲ - 300 °C.

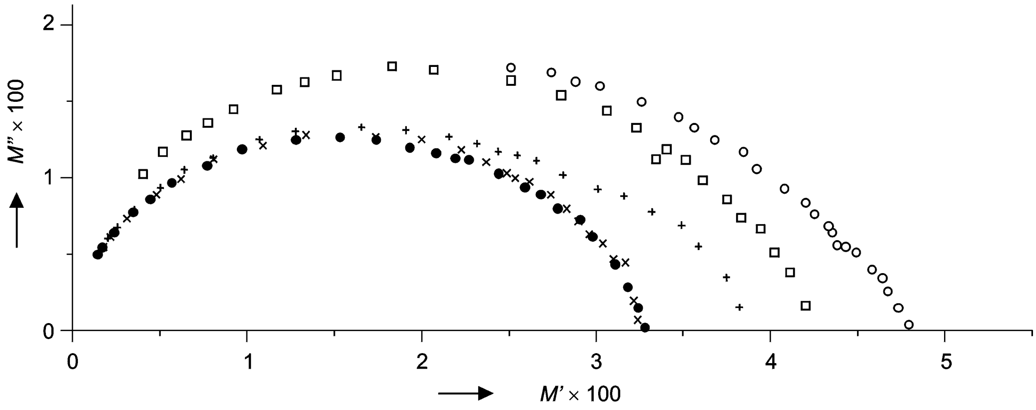

Figure 7. Dependencies of *M″* vs *M′* for glasses 70 mol.% TeO_2 - 30 mol.% ZnO prepared with various admixtures measured at temperature of 300 °C. □ - without of the admixture, ○ - 0.8 wt.% CaO, + - 0.1 wt.% Pr - metal, × - 0.1 wt.% Pr^{3+} as oxide Pr_2O_3, ● - 0.1 wt.% Dy^{3+} as a oxide Dy_2O_3.

The bindings breaking continues with increasing temperature. After the temperature of 300 °C is reached there starts to appear only the small but irreversible changes in the glass structure. One can see it clearly on the dependencies *M″* vs. *f* when the values of maximum start to decrease (figures 2e, 3d, 5). To find temperature when the irreversible changes in the structure start we performed the measurements for each sample at the temperature of 270 °C, it means at temperature when the breaking of the weak bindings in the glass does not appear. The next measurements were performed after heating to temperature of the 310 °C and 330 °C, followed by cooling to the previous temperature (figure 4). The measurements confirmed that the irreversible changes appear in glass structure at temperature of 310 °C. We could not perform measurements at temperature above 330 °C because glass started to soften as one can see on the measurements of *dc* (figure 1a). Glasses with content of 0.1 wt.% CaO (0.8 wt.% Ca) had the similar behaviour (figure 5).

One can very clearly see the influence of the crucible (Pt, Al_2O_3) used for melting of glass raw material from the measurements of both temperature and frequency dependencies of complex modulus *(M″* vs *M′*). It is obvious by comparing the results of the glass samples of the same composition prepared from the same basic material (figures 3, 6). It is shown that the results of the glass prepared in Pt crucible have lower dispersion. Similar result was found out for system of glasses TeO_2 - $PbCl_2$ [10]. Glasses are homogeneous, one phase composition and do not contain large concentration of disturbances (grains, phases, great inhomogeneities). The dependencies of *M″* vs *M′* show the non-significant deviations in the high frequency part and the centres of half circles are only a little shifted under the axis M´ what is the evidence of the mentioned.

The influence of the admixtures

To find out mainly the influence of admixtures on the optical properties, we added to the glass raw material the admixtures Pr (0.1 wt.%) as a metal, Pr_2O_3, Dy_2O_3 and CaO (0.8 wt.%). While the rare earth (RE^{3+}) are added to glass in order to increase luminescence we tried to decrease concentration of OH groups by adding of CaO. Measured results were compared with the results of the glasses without the admixtures. The influence of the individual admixtures was various. CaO adding affected mostly the properties and thus also the structure of glasses. The influence was significant both for electric and dielectric properties, but the content of OH groups did not decrease as we expected (figures 1b, 7). The various chemical forms of the added admixture (Pr as a metal or in the form of oxide Pr_2O_3) influenced also shown on the measured dependencies and it proved its affect on the structure of prepared glass. Glasses which contained rare earth admixtures of the same concentration and the same chemical composition (Pr_2O_3 a Dy_2O_3) had the same electric and dielectric properties.

DISCUSION

It is very important to know the structure and the temperature stability of the new searched glasses, which are related with their technical possibilities of the exploitation but with their long time utilisation, too. As we showed, the measurements of both temperature and frequency dependencies of electrical conductivity and complex permitivity enable very quickly to find out important information about the glass preparation as is the influence of the used crucibles, various chemical forms of the added admixture to glass material etc.

We can state from the measurements of the temperature dependencies of both electric and dielectric properties of the searched glasses that 290 °C is the temperature limit to the extent that all observed changes in their structure are reversible. This temperature is the limit also for optical fibres and optical elements what is significant for example at the power laser radiation transmission that may be influenced by their properties degradation due to structural changes.

The measurements of the temperature dependencies of direct conductivity showed that glasses are very sensitive on the OH groups content. The evidence of this is that the measured dependencies start to increase above the temperature of 100 °C. The dependencies found out by measuring both temperature and frequency dependencies of electric and dielectric properties prove that these methods are very sensitive to finding all changes caused by the technology procedure of preparation which should make the structure change of prepared glass. They able the quick determination of the optimal conditions of their preparation as well as the assessment of the properties reproducibility of glasses. Most of the changes of the glass properties are connected with the changes of their structure. The finding out of these changes is connected with the changes of dependencies of ε'' vs f, M'' vs M', M'' vs f.

CONCLUSION

When analysing the performed measurements, it can be concluded, that increasing temperature brings changes in the structure of studied glasses, which are reversible up to the temperature of 290 °C. In addition, the temperature increase results in changes electrical and dielectrical properties affected by the different concentration of the OH group. The used methods are suitable to optimise the glass processing technology and evaluate the properties reproducibility.

Acknowledgement

This work was supported by Grant Agency of Czech republic, Grant number 104/99/0342 and Project of the Slovak Grant Agency No/4338/97.

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ELEKTRICKÉ A DIELEKTRICKÉ VLASTNOSTI TeO_2 - ZnO SKIEL

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Článok ukazuje výhody použitia meraní elektrických a dielektrických vlastností skiel TeO_2 - ZnO bez prímesí ako aj s prímesami na zistenie zmien v štruktúre skla spôsobených zmenou chemického zloženia prímesí. Okrem toho tieto merania umožňujú určiť hranice teplotnej a štruktúrnej stability, rýchle nájsť optimálne podmienky prípravy skiel s reprodukovateľnými, najmä optickými vlastnosťami.