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Measurements of TSC in the UV-irradiated silicate glasses

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In the paper the results of TSC (Thermally Stimulated Conductivity) measurements for borosilicate glasses containing alkaline ions are presented. The measurements of TSC were performed for UV-irradiated samples in the range of 300–680 K. The presence of peaks in the TSC-curves is believed to reflect defects of the glass structure. Additionally, TSP (Thermally Stimulated Polarization) was made in the temperature range of 300–680 K for identical samples.

1. Introduction

The electrical measurements [1], [2] of alkali-borosilicate glasses have shown that electrical conductivity in these glasses is in principle ionic. The ionic conductivity is a thermally activated process. The activation energy ranges within 0.6–1.2 eV. But there is some electronic transport present in these glasses. An important electronic transport mechanism is the hopping through localized states. These localized states consist of band tail states and gap states. The tail states are due to the disorder of the glass network, while the gap states result from structural defects.

Up to now, the measurement techniques of thermally stimulated current have been applied to the investigation of the alkaline ion motion in glasses [3–6].

In present paper the TSC method was applied to the study of structural defects in glasses. In order to distinguish between the effects related to trapping light-induced carriers and dipole relaxation, the measurements of the TSP were performed. In the TSC method the sample is preliminary irradiated (by UV-, X-, γ-rays). Next, the sample is heated linearly and its conductivity is measured. During heating the light-induced carriers are detrapped and there appear peaks in the corresponding TSC curves. The TSP technique involves measurements of the current from a glass subject to a steady electrical field. The sample is heated at a constant rate starting with a low temperature. Measured current is a charging current induced either by orientation or by charge migration [7].

So far, thermally stimulated current technique has been applied to the study of structural defects of nonirradiated glasses [8]. This paper shows the results obtained for irradiated glasses and for glasses the compositions of which were different from these described in paper [8]. The results presented here are original and were obtained for the first time.

2. Experiment

The objects under investigation were two types of alkali-borosilicate glasses of the following compositions (percentage by weight):

– A-glass: 20% Na_2O, 40% B_2O_3, 40% SiO_2,

– B-glass: 11% Na_2O, 6% K_2O, 2.4% BaO, 1% As_2O_3, 11% B_2O_3, 68% SiO_2.

The measurements of TSC and TSP were performed in the device consisting of: measurement chamber placed in a furnace, nanoammeter and voltage power supply. The sample temperature was measured using Ni–Cr Ni thermocouple. The samples were of disc shape with diameter of 28 mm and thickness of 1 mm, polished on both sides. Aquadag electrodes were used in the experiment (aquadag is a suspension of graphite in water). The measurements of TSC/TSP were performed in the temperature range of 300–680 K. Samples were biased by voltage (E_p) of 10 V. They were heated with the rate $\Delta T/\Delta t = \beta = 0.2$ K/s. In the TSC experiment glass-samples were UV-irradiated before the current measurements. Because of the reconnaissance type of the measurements, the lamp of possible heigh power and with the whole range of UV spectrum was used. No filter was applied in this range of wavelength. (The filter was used only for visible light). The Xenon lamp "Helios" used in the experiment has discontinuous spectrum in the 240–550 nm wavelength interval. For A-glass the absorption edge is for $\lambda = 250$–300 nm. The aquadag electrodes were prepared after irradiation of sample. During irradiation the voltage has not been applied to the sample.

3. Results

Figure 1 shows the TSC-curves (2, 3, 4) and TSP-curve (1) for A-glass. For non-irradiated samples (curve 1) there are two peaks, one in the temperature range 300–320 K and the second in high temperature between 560–580 K. For irradiated samples there appears an additional peak between 360–400 K. This maximum occurs for the samples with external field (curves 2, 3) as well as without it (curve 4). The height of this peak rises with the irradiation time (curves 2 and 3). The partial discharge technique [8] was used to determine the activation energy. Figure 2 shows results for partial discharge measurements, when an irradiated sample was heated to some temperature lower than T_{max} (curve I), cooled and reheated to a slightly higher temperature (curve II); this procedure was repeated (III–IV–V–VI) until TSC peak was fully discharged. The activation energies as determined from slopes of the lines for the subsequent cycles are: 0.31, 0.24, 0.24, 0.16, 0.18 and 0.17 eV. The heigh-temperature peak for irradiated samples if compared to non-irradiated sample is shifted toward a higher temperature (600–630 K).

The TSC-curve (2) and TSP-curve (1) for B-glass are shown in Fig. 3. In both the TSC and TSP curves there are two peaks: first appears in the temperature

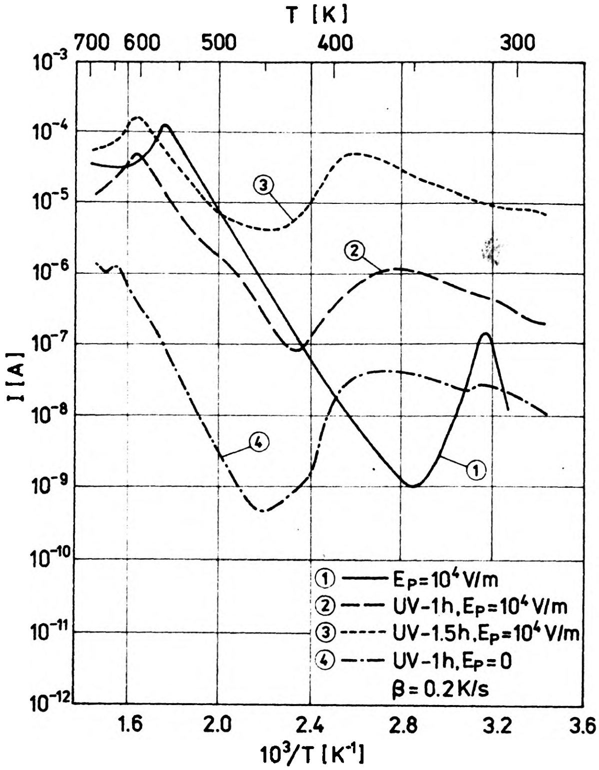

Fig. 1. TSC (2, 3, 4) and TSP (1) curves for A-glass

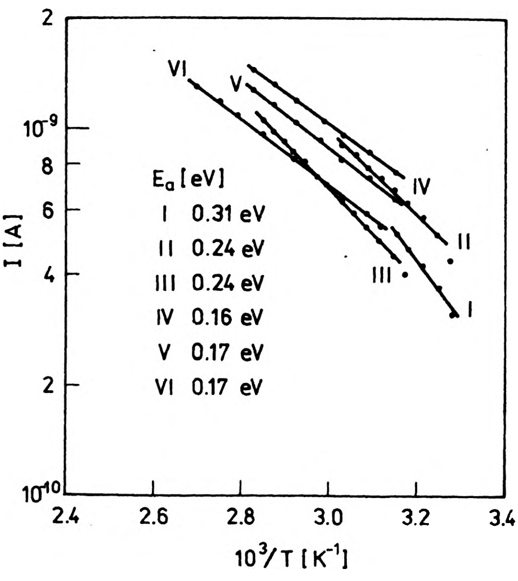

Fig. 2. Partial discharge curves used to determine activation energy for TSC peak

interval 300–330 K, while the second appears within 600–620 K for the TSP curve, and within 650–670 K for the TSC-curve.

In order to identify the type of carriers (positive or negative) generated during UV irradiation, the measurement of current in the A-glass was performed in the time of lighting. On the irradiated side of sample two electrodes were made, one of

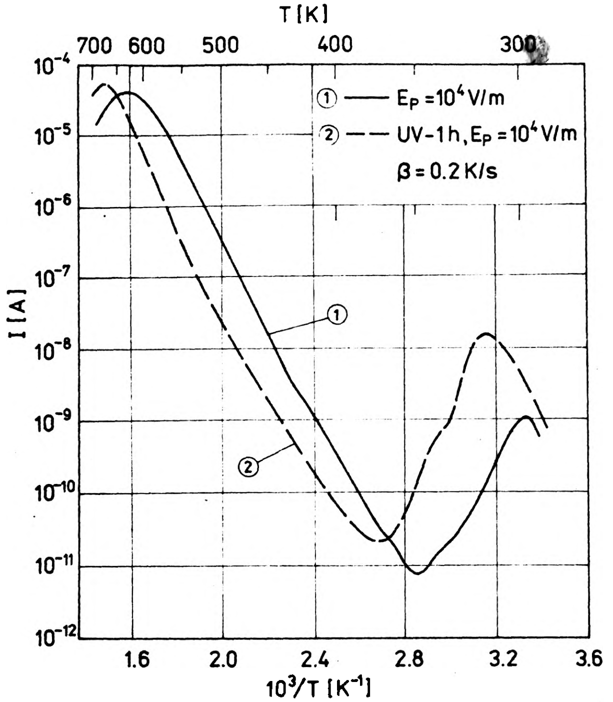

Fig. 3. TSC (2) and TSP (1) curves for B-glass

the "comb" shape, and a protecting one from aquadag. The other side of sample was also covered by aquadag. The measurements showed the negative charge on the irradiated side of sample.

Moreover, the TSC measurements for A-glass with the changed voltage polarity (−10 V) were done. It has been found out that the direction of current in the sample is opposite to the direction of current in the sample with polarity +10 V. The maximum value of the TSC peak appears at the same temperature (360–400 K) and attains the values of one order of magnitude less than the values obtained with $E_p = +10$ V. The maximum of high temperature peak (560–590 K), for both polarities, is placed in the same range of temperatures and reaches the same order of magnitude.

4. Discussion

In the alkali-borosilicate glasses mainly alkaline ions are responsible for electrical conductivity. The increase of temperature gives rise to the mobility of ions and consequently electrical conductivity increases. It is known [3–5] that from the slope of TSP curve (I vs. $1/T$) it is possible to calculate the activation energy of the ions participating in the conductivity. Electronic conductivity can also contribute to the electrical conductivity evoken by mobility of ions. As a result the decrease of conductivity is observed.

4.1. Peak 300–340 K

The TSC and TSP curves for both A- and B-glasses shown their maxima in the temperature interval 300–340 K. In our experiments we have noticed that the value of this maximum increases with the increasing air humidity. We suggest that the presence of water in the glasses-samples is responsible for the behaviour of this peak. It is likely that the absorption of water on the surface of sample takes place during preparation of samples.

4.2. TSC peak 360–400 K

In the TSC curve of irradiated A-glasses sample, the maximum appears in the temperature range of 360–400 K. In the experiment of the partial discharge the calculated values of activation energies suggest that those obtained in the first three cycles come out of the "water" peak, the activation energy of this peak being given only by the values 0.16, 0.18, 0.17 eV, obtained in IV, V and VI cycles.

Electrical current measured in the irradiated sample can be caused either by depolarization or polarization or conductivity processes. The height of the maximum in the curve $I = f(T)$ for irradiated sample, studied without external electric field (curve 4), is much lower than that of the TSC curve obtained for the sample measured in the presence of electrical field (curve 2). The value of the maximum of TSC curve measured with $E_p = -10$ V is much lower than that of TSC curve measured in external electrical field with opposite polarization. These results prove that the current in the irradiated sample placed in external field ($E_p = +10$ V) is neither depolarization nor conductivity, but the polarization current. Polarization is caused by charges accumulated in the glass layer close to the sample surface. The measurements of the current performed for the sample during irradiation have shown that the negative free charges are accumulated in that layer. Because of the low energy photons of the used light it can be concluded that the generated charges are electrons (but not negative ions). The electrons generated during irradiations are trapped by glass structure defects. It is quite likely that oxygen vacancies are the traps for electrons. A-glass containing solely sodium ions and the ratio of alkali oxide to boron oxide less than unity differs from B-glass. The structural studies [10] of the sodium borosilicate glasses show that when the ratio of Na_2O to B_2O_3 ranges between 0.5 and 1, then nonbridging oxygens in the glass should be present, not in the silicon sites but in the borosilicate groups. It is stated that the high temperature maximum appears in the thermoluminescence curves for irradiated samples [11]. The presence of this maximum is correlated with the existence of glass structure defects. The investigations mentioned above as well as our measurements of TSD (Thermally Stimulated Depolarization) for such sort of glass [12] suggest that structure defects of oxygen vacancies type might be responsible for the presence of the peak in the A-glass at 360–400 K. The trapped electrons are released in the temperature ranges of 360–400 K.

4.3. High-temperature peak

The high-temperature peak is present in both types of glasses for all TSC/TSP measurements. Up to now, the origin of the high temperature peak is not known. It might be related to ohmic conductivity of the sample (so-called ϱ-peak [7]). This statement is supported by identical values of the height of the peaks regardless of the sign of polarity.

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Измерения TSC в UV-освещённом силикатном стекле

В работе представлены результаты измерений TSC для боросиликатного стекла содержащего щелочные ионы. Измерения TSC проведены были для UV-освещённого стекла в пределах температуры 300–680 K. Присутсвие пика на кривой TSC связано с существующими в стекле дефектами структуры. Добавочно для этих же образцов совершены измерения TSP.