INVESTIGATION OF IONIC MOTIONS IN Ag-DOPED $LiPO_3$—$Al(PO_3)_3$ GLASSES BY THERMALLY STIMULATED DEPOLARIZATION

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Influence of Ag doping on the mobility of the charge carriers (Li ions) in $LiPO_3$-$Al(PO_3)_3$ glasses has been investigated by the thermally stimulated depolarization (TSD) method. The mobility decreases with an increasing Ag content, the Ag ions probably occupy some sites available for Li ions. Analysing the dielectric behaviour in terms of the theory of Boksay and Lengyel (1974), the relative concentration of vacancies as well as the contribution of ionic motions to the low frequency permittivity $\varepsilon_s - \varepsilon_\infty$ are estimated. d.c. conductivity data corresponding to the temperature region of the TSD are presented, too. The protons, which are present as a product of hydrolysis of the glasses, influence the Li ions mobility in a similar manner as do Ag ions.

ИССЛЕДОВАНИЕ ПОДВИЖНОСТИ ИОНОВ В СТЁКЛАХ $Li\ PO_3$-$Al(PO_3)_3$ С ПРИМЕСЬЮ СЕРЕБРА ПРИ ПОМОЩИ ТЕРМИЧЕСКИ СТИМУЛИРОВАННОЙ ДЕПОЛЯРИЗАЦИИ

В работе исследуется влияние примеси серебра на подвижность носителей заряда (ионы лития) в стёклах $LiPO_3$-$Al(PO_3)_3$ с помощью метода термически стимулированной деполяризации. С увеличением содержания серебра подвижность носителей заряда уменьшается, так как, по всей вероятности, ионы серебра занимают некоторые из мест, которые могут занимать ионы лития. На основе анализа диэлектрических свойств, исходящего из теории Боксея и Ленгьеля (1974), вычислена относительная концентрация вакансий, а также воздействие подвижности ионов на диэлектрическую постоянную $\varepsilon_s - \varepsilon_\infty$ при низких частотах. Приведены также данные об удельной проводимости при постоянном напряжении, соответствующей области температур, в которой применён метод термически стимулированной деполяризации. Протоны, являющиеся продуктом гидролиза стёкол, влияют на подвижность ионов лития подобно тому, как и на ионы серебра.

I. INTRODUCTION

The nature of the most mobile ionic species (Li^+) in lithium metaphosphate glasses has been established by van Ass and Stevels [1] on the basis of both internal friction and dielectric losses measurements. A pronouced effect of dissolved water on the mobility of Li ions has been found by the above cited authors [1].

The present investigation is devoted primarily to the dielectric behaviour in $LiPO_3$-$(PO_3)_3$ glasses doped with Ag. The thermally stimulated depolarization method (TSD) [2] is used instead of the conventional a.c. bridge methods. The former is more advantageous when several relaxations due to various mobile species are to be distinguished, this being certainly the case for Ag-doped and hydrolysed lithium metaphosphate glasses. The TSD method was used earlier by the present author and Bohun for proving protonic effects in alkali-free aluminophosphate glasses [3].

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II. EXPERIMENTAL METHOD

The TSD experimental procedure is completely identical with that of ionic thermocurrents (ITC), developed by Bucci et al. [4] to study the reorientation of "impurity-vacancy" complexes in ionic crystals. A glass sample ($\Phi = 8$ mm, $L = 1$ mm) with dag electrodes is polarized at a properly chosen temperature T_p for a time t_p and then cooled under bias down to 90 K. At this temperature the bias is reduced to zero and the electrodes are shortcircuited by a resistor 10^{11} Ω connected in parallel with the electrometer input. When heating the sample at a uniform heating rate $v = 0.12$ Ks^{-1}, pronounced maxima of the depolarization current are detected.

d. c. conductivity measurements were performed in the same experimental set-up applying a d. c. bias of 60 V. Dag dispersion in alcohol was used for the preparation of the contacts.

The compositions (in w. %) of the glasses investigated in the present study are summarized in Table 1.

III. EXPERIMENTAL RESULTS

The j-T thermograms which are characteristic of Ag-doped $LiPO_3$-$Al(PO_3)_3$ glasses, are plotted in Fig. 1. The peaks represent spectra of relaxations rather than

Table 1

Sample No.	$LiPO_3$	$Al(PO_3)_3$	$AgPO_3$	$Mn(PO_3)_2$
5	49.50	49.50	0.5	0.5
6	49.25	49.25	1.0	0.5
7	48.75	48.75	2.0	0.5
8	47.75	47.75	4.0	0.5
9	45.75	45.75	8.0	0.5

discrete peaks. This becomes evident from an inspectiion of Fig. 2, where the temperature T_{max} at the maximum of the current shifts with polarization temperature T_p. For sufficiently high T_p another TSD extreme is observed, which will be later shown to result from a polarization of the electrodes. Each of the thermograms in Fig. 2 corresponds to a T_p, at which temperature the electrode polarization is slow enough not to affect the TSD peak from the uniform polarization.

One widely used approach when analysing TSD peaks from distributed polarizations is the multistage depolarization procedure, recommended by van Turnhout

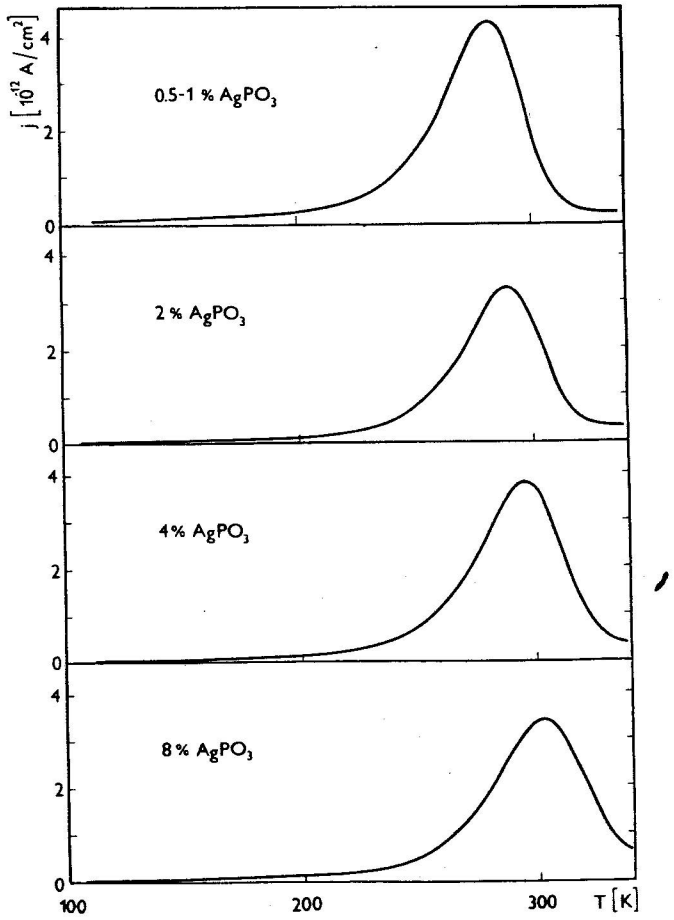

Fig. 1. TSD thermograms of Ag-doped $LiPO_3$-$Al(PO_3)_3$ glasses for electric field intensity $E_p = 3 \times 10^3$ V/cm.

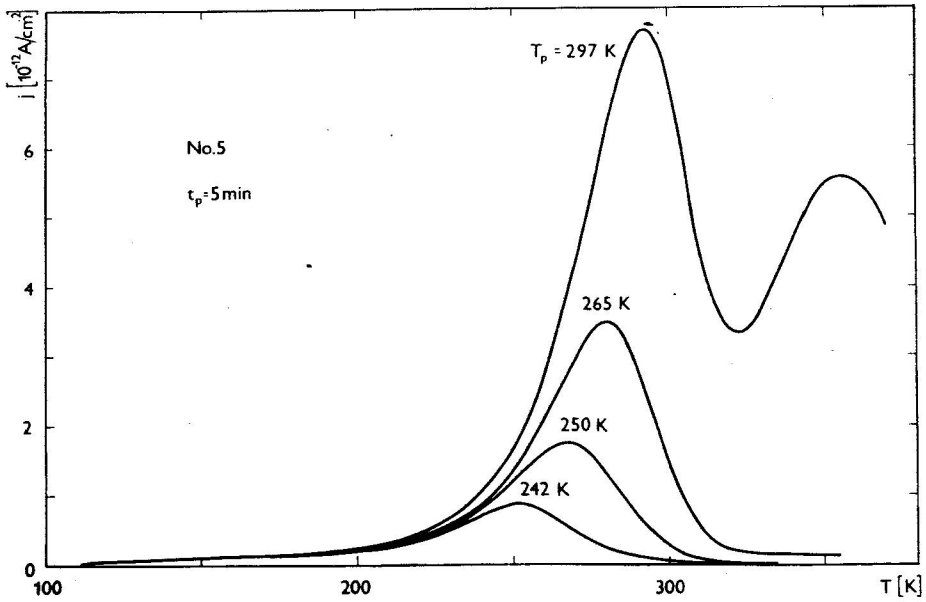

Fig. 2. Development of the TSD spectrum with increasing T_p.

[5]. Namely, in the case of a distribution of relaxation times the depolarization current is expressed by the relation [6]

$$dj(T) = \frac{p_0}{\tau_r \exp(A'/kT)} \exp -\left[\frac{1}{\tau_r}\int_{T_s}^{T} \frac{dT'}{v \exp(A'/kT')}\right] G(\tau_r)\, d\tau_r ,$$

in which case the method of evaluating the activation energy A' from the initial rise does not apply [5]. The Arrhenius plot of individual partial heatings of all the glasses listed in Table 1 yielded a unique slope at the temperature region of T_{max}, as illustrated, e.g., for a glass No. 9 in Fig. 3. Activation energies A' obtained from such slopes for glasses NO. 5—9 are given in Table 2. It is well known that the dielectric dispersion connected with long range ionic motions in glasses is characterized by the "conductivity" relaxation time [7, 8]

$$\tau = \frac{\varepsilon_0 \varepsilon_\infty}{\sigma(0)} ,$$

$\sigma(0)$ being the conductivity of the glass in the limit $\omega \to 0$. Then, the activation energy of ionic jumps can be readily obtained also from d.c. conductivity measurements.

To avoid electrode polarization in the course of the d.c. conductivity measurements with irreversible dag electrodes, the measumerements were restricted to the

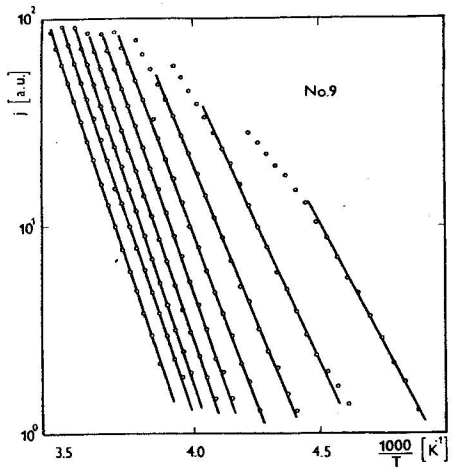

Fig. 3. An Arrhenius plot of multistage depolarization

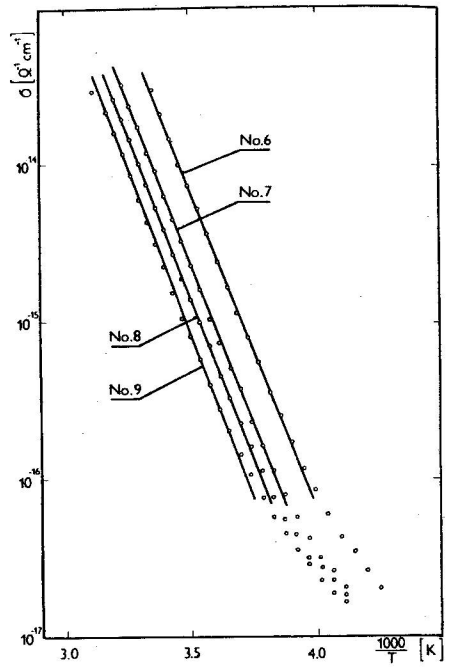

Fig. 4. d.c. conductivities of the investigated glasses.

low-temperature region. The d.c. bias was applied at the temparature T_p (as in the case of TSD) to establish completely the uniform polarization analysed above. The samples were then cooled down under the applied bias. Neglecting the change in the dielectric polarization due to a finite cooling rate, only a pure d.c. conductivity current is flowing in the circuit when raising the temperature of the sample. d.c. conductivity data for the samples No. 6—9 obtained in this way are shown in Fig. 4. Strictly speaking, an approximation of the measured conductivities as $\sigma = \sigma_0 \exp(-A/kT)$ holds only at elevated temperatures. From an inspection of Table 2 a discrepancy between A and A' as determined from d.c. conductivity and TSD, respectively, is evident. No conclusive explanation of the discrepancy is available at present. It may be that we deal with a distribution of both τ_r and A', which

Table 2

Sample No.	$\sigma_0(\Omega^{-1}\mathrm{cm}^{-1})$	A(eV)	A'(ev)	$\varepsilon_s - \varepsilon_\infty$
5, 6	0.9	0.80	0.69	7.0
7	0.5	0.81	0.71	5.5
8	0.4	0.815	0.74	6.0
9	0.4	0.83	0.74	5.5

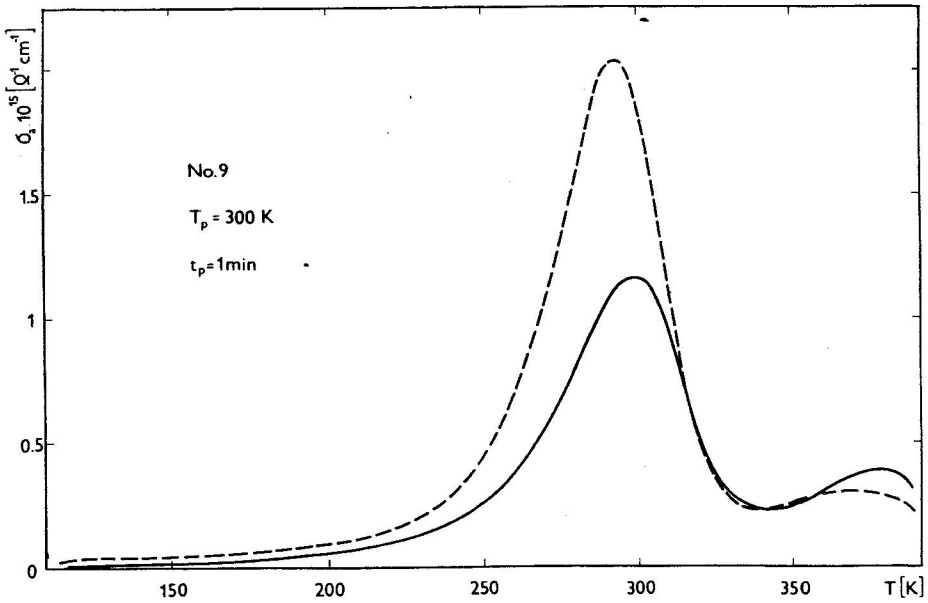

Fig. 5. TSD of both "dry" (broken line) and standard glass (solid line). $\sigma_a = j/E_p$.

situation has not been treated quantitatively as yet. Nevertheless, the A values agree fairly with the activation energies of the dielectric losses in lithium metaphosphate glasses [1].

Let us note that the contribution of Li ions to the low-frequency permittivity in $LiPO_3$-$Al(PO_3)_3$ glasses (see Table 2) was estimated taking the data from Fig. 1 and applying the relation

$$\varepsilon_s - \varepsilon_\infty = \frac{1}{\varepsilon_0 v E_p} \int_0^\infty j(T)\,\mathrm{d}T\,.$$

To establish the influence of dissolved water on the dielectric behaviour, a glass with a composition almost identical with No. 9 was prepared from a melt bubbled with dry oxygen. TSD of the "dry" glass is represented in Fig. 5 by the broken line, the solid line corresponds to the standard glass No. 9. The relative intensity of the *IR* absorption between 1400 and 3500 cm^{-1} in Fig. 6 may be regarded as a measure of the water content of the respective glasses. Evidently, both the observed shift and the height reduction of the relaxation peak[1] from Fig. 5 with increasing water content are in accordance with the behaviour of the Li mechanical peak [1].

[1] $T_{max} \approx 300$ K.

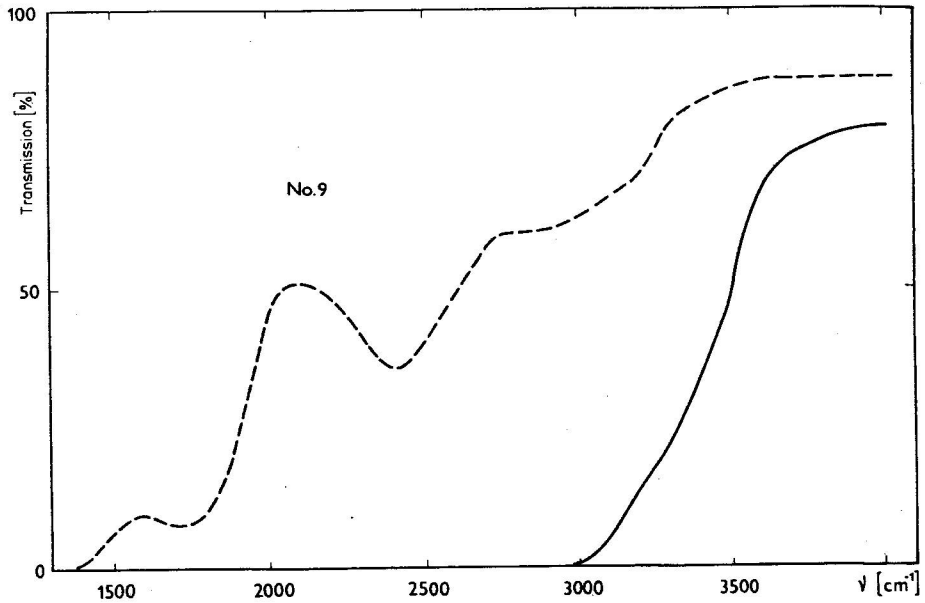

Fig. 6. IR absorption spectra of the glasses from Fig. 5.

Next, we return once more to Fig. 2, where the two distinct relaxation peaks are shown for the glass polarized close to 300 K. The internal friction peaks observed by van Ass and Stevels [1] strongly resemble the TSD spectrum from Fig. 2 (the curve corresponding to $T_p = 297$ K). At first sight the high-temperature TSD peaks might correspond to the intermediate lithium-proton peak evidenced by the internal friction in pure lithium metaphosphate glass. However, such an analogy is misleading, as will be proved further. The solid line in Fig. 7 is the standard TSD measured after the glass had been polarized above 300 K. Recently, a modified TSD method has been suggested to distinguish directly between uniform and space charge polarizations in high-resistivity glasses [2]. Applying the latter, the high temperature TSD peak is easily identified with space charge relaxation as follow. When the polarized sample was stored shortcircuited for 20 min. at ambient temperature, the corresponding TSD record (broken line in Fig. 7) consisted of the high-temperature peak only. The TSD denoted by circles was obtained, when prior to the depolarization dag electrodes were removed and replaced by virgin ones during the storage time (20 min.). Clearly, the discussed peak arises from a space charge relaxation, the discharged ions being located predominantly on the electrode.

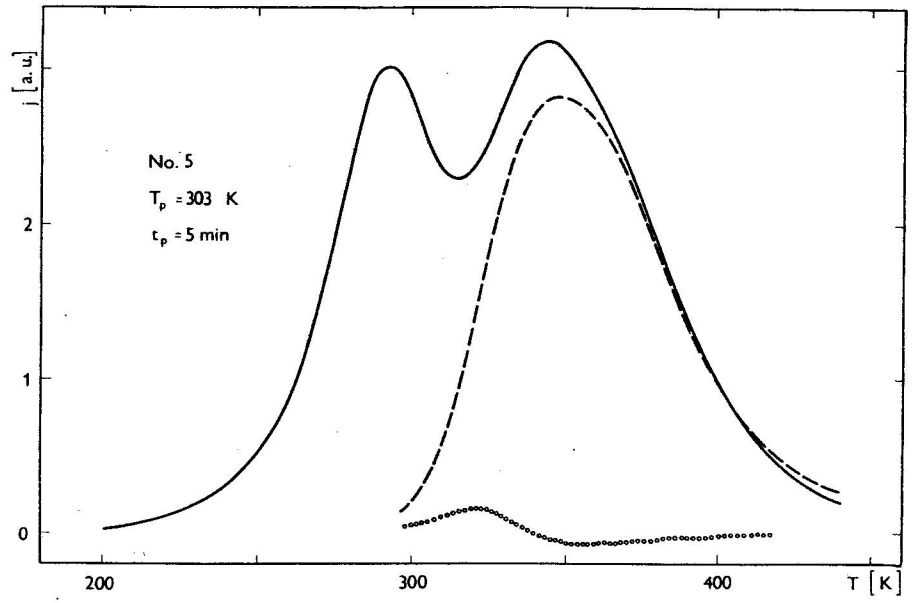

Fig. 7. Evidence for high-temperature space charge relaxation — for details see text.

IV. DISCUSSION

A comparison between the activation energy of ionic motions in $LiPO_3$-$Al(PO_3)_3$ glasses 0.80—0.83 eV (18.4—19.1 kcal/mole) and that of the pure lithium metaphosphate glass [1] leaves little doubt that Li ions are the most mobile species in both types of glass in spite of considerable hydrolysis. Boksay and Lengyel [9] suggested a model for the electrical relaxation processes in glasses in which a vacancy mechanism prevails. The present discussion will proceed on the lines of their model devoted to glasses with one type of alkali ion only. We feel, of course, that accomodation of the model for phosphate glasses requires to ignore the role of protons present as a consequence of hydrolysis, any dependendce of the Li mobility on the Al content is ignored as well. The analysis presented further should be, therefore, accepted with caution.

The main consequence of the model suggested by Boksay and Lengyel [9] is that the relative vacancy concentration is given by the relation

$$\frac{c_v}{c + c_v} = \frac{3T(\varepsilon_s - \varepsilon_\infty)}{7N} \frac{3\varepsilon_0 R}{e\delta^2 F},$$

cf. [9]. Then, e.g., for the glass No. 5 and T = 280 K, $\varepsilon_s - \varepsilon_\infty = 7$, density of 3 g/cm^3,

$N = 6 \times 10^{20}$ cm^{-3}, $\delta = 12$ Å[2], one obtains $c_v/(c + c_v) \sim 0.014$, which value is of the same order of magnitude as that in a sodium silicate glass [9].

Addition of Ag in amounts greater that 1 % $AgPO_3$ leads to a decrease in mobility of Li ions manifested by the change in the activation energy of mobility ($c_v = \text{const.}$). We suggest that the Ag ions substitute some Li ions sites with a subsequent lowering of the mobility of the latter ions. Such a behaviour is similar to the effect of silver on the mobility of Na ions in silver borate glasses [10].

In contrast to the internal friction measurements [1] the relaxation due to the lithium proton interaction could not be enviasaged by means of the TSD. An electrical activity of protons cannot be excluded definitely as long as dielectric measurements with nonpolarizable electrodes are missing. The role the protons play in electrical phenomena is deduced indirectly from the shift of the TSD peak to higher temperatures with an increasing water content. This finding is in qualitative agreement with the behaviour of the mechanical lithium peak in lithium metaphosphate glasses [1]. The observed Li-H interaction implies a mechanism like the well-known mixed alkali effect.

V. CONCLUSIONS

The mobility of Li ions in the $LiPO_3$-$Al(PO_3)_3$ glasses is found to be thermally activated by activation energies 0.80—0.83 eV, dependent on the Ag content. The effect of dissolved water on the mobilty of Li ions is the same as in the case of pure lithium metaphosphate glass [1]. The TSD peak due to Li ions long range diffusion is located near 280 K ($v = 0.12$ Ks^{-1}) and shifts to higher temperatures with increasing water content. Another TSD peak with T_{max} above 300 K is shown to result from an electrode polarization. The latter prevented us from observing the intermediate Li-H peak envisaged by the internal friction measurements, if the corresponding electrical relaxation should exist.

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[2] $\delta \sim 1/\sqrt[3]{N}$, N being the concentration of Li ions distributed uniformly.

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