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IONICALLY CONDUCTIVE GLASSES IN THE SYSTEM Li_2Cl_2—Li_2O—B_2O_3

Part III. Electrical Conductivity

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Electrical conductivity of glasses in the system Li_2Cl_2-Li_2O-B_2O_3 was measured by the complex impedance method over the frequency range of 100 to 20,000 Hz using three-electrode connection of the specimen in the circuit. The results showed a distinct increase in conductivity and decrease of the activation energy with increasing content of Li_2 Cl_2, while an increase in the content of Li_2 O brought about a mild increase in conductivity and a mild decrease of activation energy. The effects of Li_2Cl_2 and Li_2O on conductivity are discussed with respect to their function in the structure of the glasses.

INTRODUCTION

There are several glassy systems with a high concentration of alkali ions which exhibit high ionic conductivity. This, jointly with the possibility of changing the composition in a continuous way and the simple preparation of complex and thin-walled shapes (films and capillaries) make the materials advantageous for special applications in electrochemical apparatus [1]. This group of glasses also includes lithium-boron glasses.

The ionic conductivity of pure B_2O_3 is very small ownig to the absence of mobile charge carriers. Addition of Li_2O_3 causes the conductivity to increase. The conductivity of two-component glasses results from the mobility of the Li^+ ions [2]. The activation energy of the conductivity process decreases with increasing Li_2O content [3].

Considerable attention has been recently paid to three-component glasses based on Li_2Cl_2—Li_2O—B_2O_3 [2, 4—6]. The presence of Li_2Cl_2 in lithium-boron glasses has a considerable effect on increasing the ionic conductivity. It also reduces the activation energy of the conductivity process [5]. On assessing the effect of Li_2O and Li_2Cl_2 on the conductivity level one should take into account, apart from changes in the concentration of conductive ions, also other factors such as the structure, molar volume, and others [7].

EXPERIMENTAL

The chemical composition of the glasses being studied can be expressed by the formula X Li_2Cl_2—Y Li_2O—7 B_2O_3 (by mol), X—Y—7 in the abbreviated form. The investigation was concerned with a series of glasses with varied Li_2Cl_2 content,

$$X—3—7, X = \langle 0; 3.0 \rangle$$

and three series of glasses with varied Li_2O content, 2—Y—7; 2.5—Y—7; 3—Y—7; $Y = \langle 3.0; 4.5 \rangle$.

The electrical conductivity of the glasses was measured by the complex impedance method [8—11] using three-electrode connection of the specimen in the measuring circuit. The arrangement of electrodes on the specimen is shown schematically in Fig. 1. The size of the electorde, that of the annulus and the specimen thickness were chosen according to the recommendation of Czechoslovak Standard ČSN 72 5042. The specimens were 2.0—2.2 mm in thickness. Platinum electrodes were applied on to the smooth and glossy surface of the specimens by the method of high-frequency cathodic deposition.

The measuring apparatus consisted of the following main components: a resistance furnace with a chamber for placing the specimen, an autotransformer for controlling the heating rate, a digital thermometer, and the TESLA BM 595 RLCG bridge.

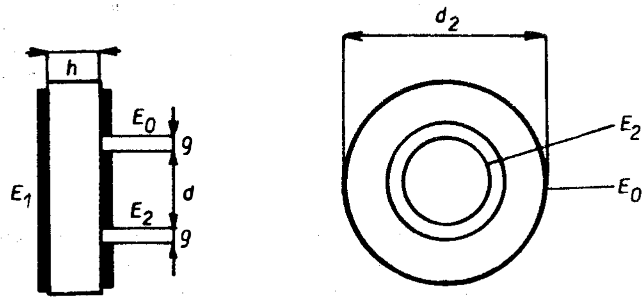

Fig. 1. Schematic diagram of the arrangement of electrodes on the specimen for measuring the electrical conductivity by the three-point method.

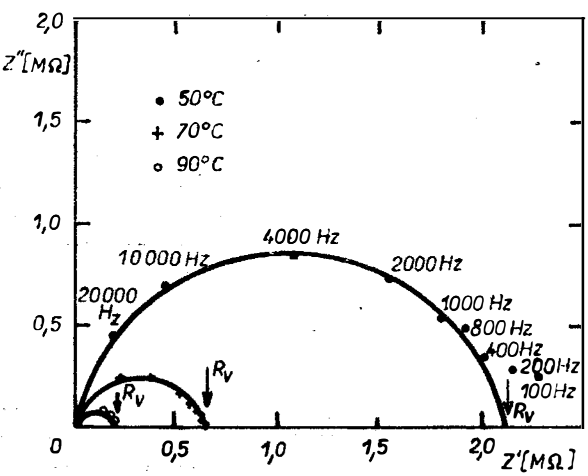

Fig. 2. Typical impedance spectrum of glasses in the system Li_2Cl_2—Li_2O—B_2O_3.

The connecting wires and the contacts were all of platinum, so that there were no undesirable contact resistances. The specimen was fitted in a teflon holder and placed in the furnace chamber. The automatic digital RLCG bridge indicated automatically the value and the dimension of the quantity being measured, i.e. impedance (its absolute value) $|Z|$ and angle φ in polar ordinates. The masurements were carried out at 150°, 130°, 110°, 90°, 70° and 50°C. At each temperature the impedance was measured at frequencies of 100, 200, 400, 800, 1 000, 2 000, 4 000, 10 000 and 20 000 Hz.

The values of impedance $/Z/$ and angles φ in polar ordinates were recalculated to rectangular coordinates, thus obtaining the values of real Z' and imaginary Z'' components of the impedance. These were plotted in a complex plane (negative imaginary component vs. the real one). Joining of the measuring points yielded curves characteristic of this type of materials (Fig. 2), and their evaluation provided the resistance of the material R [Ohm]. The resistivity ϱ_v [Ωcm] of the specimen being investigated was determined from the equation

$$\varrho = \frac{(d + g)^2}{4h} R \tag{1}$$

EXPERIMENTAL RESULTS AND DISCUSSION

The values of $\sigma(\sigma = 1/\varrho[\Omega^{-1}cm^{-1}])$, obtained by evaluation of the impedance spectra, were plotted as log σ vs. $1/T$. All of the realtionships fit well the Rasch -Hinrichsen equation for electrical conductivity of glasses (log $\sigma = A—B/T$) (Fig. 3). On the basis of the experimental data, the value of electric conductance at 25 °C, σ_{25}, was calculated by extrapolation for each specimen. The temperature dependence of conductivity was utilized for determining the activation energy E_σ of the conductivity process, using the equation $\sigma = \sigma_0$ exp $(—E/RT)$.

Evaluation of the dependence of conductivity and activation energy on chemical composition was based on chemical analyses of the glasses prepared [12].

The effect of chemical composition of the glasses on the value of their electrical conductivity at 25 °C can be assessed from the relationships plotted in Figs. 4 and 5. Li_2Cl_2 has obviously a greater effect on conductivity than Li_2O. Wheras an increase in Li_2Cl_2 content by 1.5 mol brought about an increase in conductivity by one and half order of magnitude, the same increase in Li_2O content by 1.5 mol at the same Li_2Z content ($Li_2Z = Li_2Cl_2 + Li_2O$) resulted in an increase in conductivity by only a half order of magnitude.

The increase in conductivity with increasing Li_2Cl_2 content is due to several factors. First of all, one has to consider the higher concentration of condutive ions in the system. An important role is played by facilitated jumps of Li^+ ions in the proximity of Cl^- ions [7]. It is also necessary to take into account the structural aspects associated with the Li_2Cl_2 additions. It is assumed that an addition of voluminous Cl^- ions stabilizes the [BO_4] groups by creating larger structrual aggregations (diborates) [13]. This phenomenon likewise affects favourably the conductivity. A comparison of the dependence of molar volume (Fig. 2 in Part II [14]) and conductivity (Fig. 4) on the chemical composition of the glasses indicates a clear correspondence of the two relationships. An increase in molar volume thus facilitates the migration of Li^+ ions.

An increase in the content of Li_2O likewise brings about an increase in conductivity, although a smaller one than in the case of Li_2Cl_2. This fact follows from the different role played by Li_2O in the structure of glass. An addition of Li_2O is responsible for changes in the structure of the *B—O′* skeleton; at first it is the conversion of [BO_3] groups to [BO_4] and at still higher content, the formation of non-bridging oxygen [15]. A rising Li_2O content (a growing *O/B* ratio) also reduces the molar volume (Fig. 3 in Part II [14]), i.e. the structure of glass is densified, thus to a certain degree exerting resistance to the movement of Li^+ atoms.

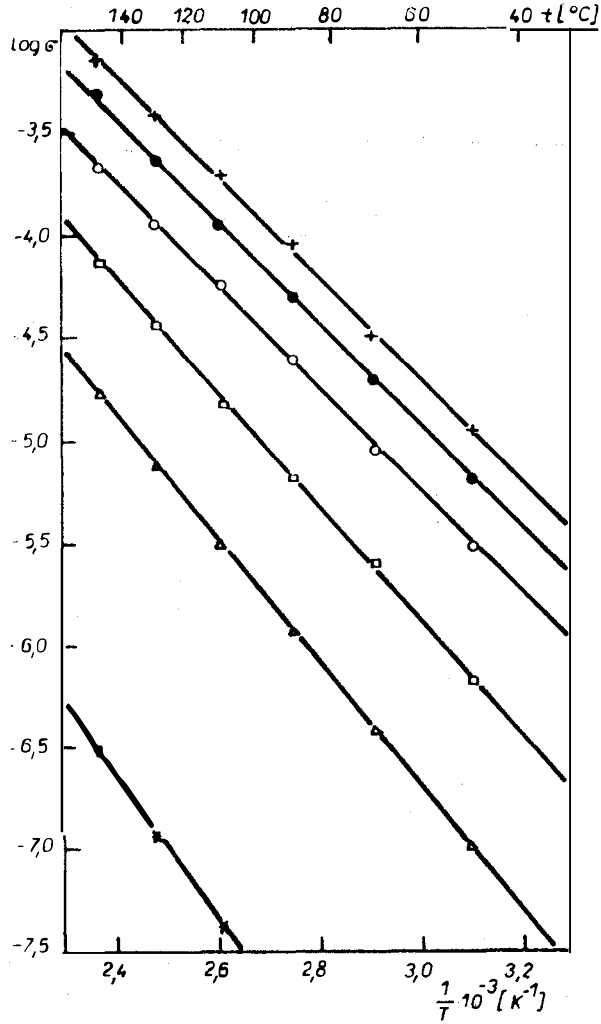

Fig. 3. Temeprature dependence of electrical conductivity of glasses having the composition
X Li_2Cl_2—3 Li_2O—7 B_2O_0

* — *X = 0* △ *X = 1* □ *X = 1.5*
0 — X = 2 • — *X = 2.5* + — *X 3*

The effect of the individual components on conductivity is also reflected by the changes in activation energy due to changes in the content of Li_2Cl_2 and Li_2O (Figs. 6 and 7). It may be pointed out that the relationships of activation energy and chemical composition correspond to the conductivity relationships. An increase in Li_2Cl_2 content is responsible for a rapid decrease of activation energy, which is only mildly reduced by an addition of Li_2O. The activation energy is determined by dissociation energy and the energy of jumps in the structure of glass. The dissociation energy increases in the sequence Li—Cl ⟨Li—non-bridging oxygen⟨Li

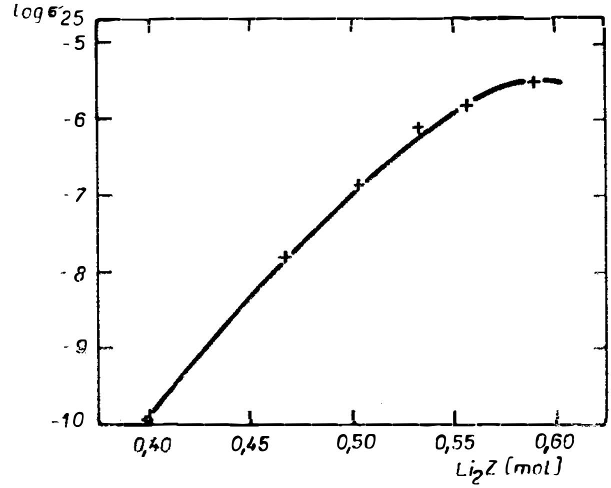

Fig. 4. Log σ_{25} vs. Li_2Z *content in glasses having the composition X* Li_2Cl_2—3 Li_2O—7 B_2O_3.

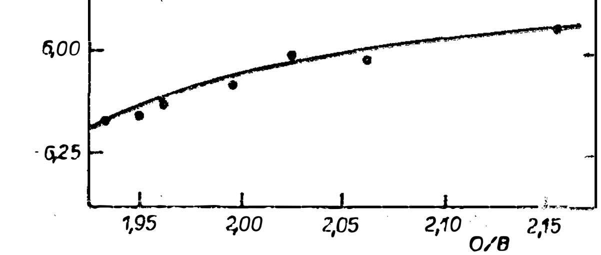

Fig. 5. Log σ_{25} vs. the O/B ratio in glasses having the composition X Li_2Cl_2—*Y* Li_2O—7 B_2O_3 (• — *X* = *2*; + — *X 2.5*; *0* — *X* = *3*).

— $[BO_4]$ [16]. A decrease of the jump energy is affected by the presence of Cl^- ions. The voluminous Cl^{-1} ions expand the structure of three-component glasses, thus creating the conductive paths favourable for the jumps of Li^+ ions [7].

The maximum conductivity of $3.13 \cdot 10^{-3}\Omega^{-1}cm^{-1}$ was achieved with the basic glass having the composition 3 Li_2Cl_2 — 3.1 Li_2O — 7 B_2O_3, which is in satisfactory agreement with the highest conductivities specified by other authors ($3.2 \cdot 10^{-3}\ \Omega^{-1}cm^{-1}$ [17]).

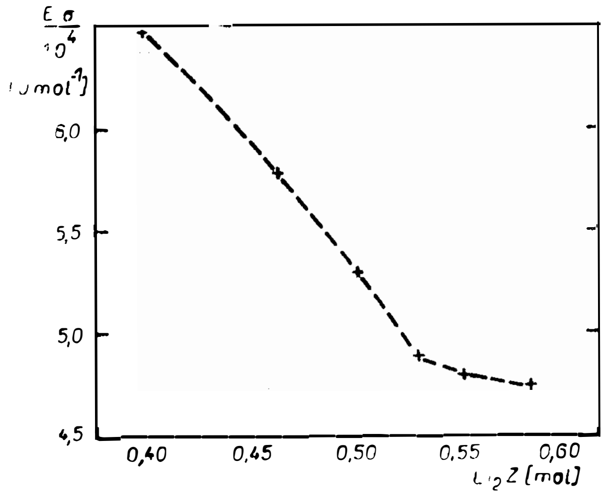

Fig. 6. E_σ vs. Li_2Z content in glasses having the composition X Li_2Cl_2—3 Li_2O 7—B_2O_3.

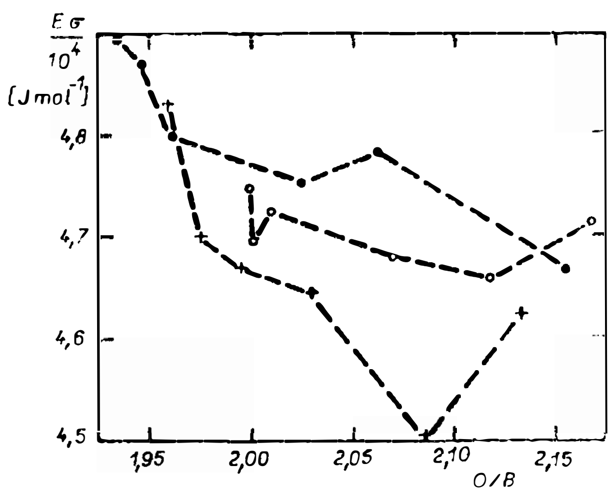

Fig. 7. E_σ vs. the O/B ratio in glasses having the composition X Li_2Cl_2—Y Li_2O—7 B_2O_3 (● — X = 2; + — X = 2.5; ○ — X = 3).

The share of electron conductivity in the total conductivity of the glasses in question is a criterion for assessing the applicability of these materials as glass electrolytes. The electron conductivity of boric glasses is lower than 10^{-12} $\Omega^{-1}cm^{-1}$ [2]. The electron conversion numbers thus attain an order of 10^{-3} which is indicative of excellent electrolytical properties of boric glasses.

CONCLUSION

A study of the electrical conductivity of glasses in the system Li_2Cl_2—Li_2O—B_2O_3 has borne out a strong dependence of conductivity on Li_2Cl_2 content. The increase in conductivity anociated with growing content of Li_2Cl_2 involves a decrease of activation energy. The effect of Li_2O on the level of conductivity is not so substantial; its increased content raises the conductivity mildly, also mildly reducing the activation energy. The different effect of Li_2Cl_2 and Li_2O on conductivity is given by their functions in the structure of glass; also the molar volume of the glasses plays a significant part, together with the factors influencing the value of activation energy.

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IÓNOVO VODIVÉ SKLÁ V SÚSTAVE Li_2Cl_2—Li_2O—B_2O_3

Časť III. Elekrická vodivosť

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Na meranie elekrickej vodivosti skiel v sústave Li_2Cl_2—Li_2O—B_2O_3 sa použila metóda merania komplexnej impedance vo frekvenčnom rozsahu 100—20 000 Hz pri trojelektródovom zapojeni vzorku v obvode. Merania potvrdili silnú závislosť vodivosti od obsahu Li_2Cl_2. Zvýšenie vodivosti s rastúcim obsahom Li_2Cl_2 je sprevádzané znižením aktivačnej energie. Vplyv Li_2O na úroveň vodivosti nie je taký výrazný, zvyšujíci sa obsah Li_2O zvyšuje vodivosť mierne, čomu zodpovedá i mierny pokles aktivačnej energie. Odlišný vplyv Li_2Cl_2 a Li_2O na vodivosť je určený ich odlišnou funkciou v štruktúre skiel. Významne sa uplatňuje i mólový objem pripravených skiel a faktory ovplyvňujúce výšši aktivačnej energie vodivostného procesu.

Obr. 1. Náčrt usporiadania elektród na vzorke pre meranie elektrickej vodivosti trojbodovou metódou.

Obr. 2. Typické impedančné spektrum skiel v sústave Li_2Cl_2—Li_2O—B_2O_3.;

Obr. 3. Teplotná závislosť elektrickej vodivosti skiel zloženia X Li_2Cl_2—3 Li_2O—7 B_2O_3
*—$X = 0$ △—$X = 1$ □—$X = 1,5$
0—$X = 2$ ●—$X = 2.5$ +—$X = 3$.

Obr. 4. Závislosť log σ_{25} od obsahu Li_2Z *v sklách zloženia* X Li_2Cl_2—3 Li_2O—7 B_2O_2.

Obr. 5. Závislosť log σ_{25} od pomeru O/B v sklách zloženia X Li_2Cl_2—3 Li_2O—7 B_2O_3 (●—X = 2; +—X = 2,5; ○—X = 3).

Obr. 6. Závislosť E_σ od obsahu Li_2Z *v sklách zloženia* X Li_2O—3 Li_2Cl_2—7 B_2O_3.

Obr. 7. Závislosť Ee *od pomeru O/B v sklách zloženia* X Li_2Cl_2—Y -K_2O—7 B_2O_3 (●—$2 = 2$; +—$X = 2,5$; ○—$X = 3$).

ИОННОПРОВОДЯЩИЕ СТЕКЛА В СИСТЕМЕ Li_2Cl_2—Li_2O—B_2O_3 III.

Электропроводность

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Для измерения электропроводности стекол в системе Li_2Cl_2—Li_2O—B_2O_3 использовали метод измерения комплексного импеданса в пределах частотности 100—20 000 Гц при трехэлектродном подключении в цепи. Измерения доказали сильную зависимость проводимости от содержания Li_2Cl_2. Повышение проводимости с растущим содержанием Li_2Cl_2 сопровождается понижением энергии активации. Влияние Li_2O на уровень проводимости не оказывается настолько резким, повышающееся содержание Li_2O повышает проводимость умеренно и тому соответсвует даже умеренное понижение энергии активации. Отличительное влияние Li_2Cl_2 и Li_2O на проводимость определяется их отличительной функцией в структуре стекол. Резкое влияние оказывает также мольный объем приготовленных стекол и факторы, влияющие на величину энергии активации проводимого процесса.

Рис. 1. *Схема упорядочения электродов на пробе, предназначенной для измерения электропроводности трехточечным методом,*

Рис. 2. *Типичный спектр импеданса стекол в системе* Li_2Cl_2—Li_2O—B_2O_3.

Рис. 3. *Температурная зависимость электропроводности стекол составом* X Li_2Cl_2—3 Li_2O—7 B_2O_3:

* — $x = 0$	△ — $x = 1$	□ — $x = 1{,}5$
0 — $x = 2$	● — $x = 2{,}5$	+ — $x = 3$.

Рис. 4. *Зависимость* log σ_{25} *от содержания* Li_2Z *в стеклах составом* X Li_2Cl_2—3 Li_2O—7 B_2O_3.

Рис. 5. *Зависимость* log σ_{25} *от соотношения O/B в стеклах составом* X Li_2Cl_2—$Y$$Li_2O$—7 B_2O_3 (● — $x = 2$; + — $x = 2{,}5$; ○ — $x = 3$).

Рис. 6. *Зависимость* E_σ *от содержания* Li_2Z *в стеклах составом* X Li_2Cl_2—3 Li_2O—7 B_2O_3

Рис. 7. *Зависимость* E_σ *от соотношения* O/B *в стеклах составом* X Li_2Cl_2—Y_4 Li_2O—7 B_2O_3 (● — $x = 2$; + — $x = 2{,}5$; ○ — $x = 3$).1