CERAMICS — Silikáty 34, s. 335—341 (1990)

IONICALLY CONDUCTIVE GLASSES IN THE SYSTEM Li_2Cl_2—Li_2O—B_2O_3

Part II. Properties and structure

PETER ZNÁŠIK*, LADISLAV ŠAŠEK

Institute of Chemical Technology, Department of Silicate Technology, Suchbátarova 5, 166 28 Prague 6

Received 15. 1. 1990

IR spectroscopy, measurement of T_g and calculation of the molar volume were used as a basis for assessing the structural conditions in glasses of the system Li_2Cl_2—Li_2O—B_2O_3. Li_2O and Li_2Cl_2 have different functions in the structure of glasses. Li_2O enters the structure of the B—O skeleton as a modifier, whereas Li_2Cl_2 does not take part in modification of the basic skeleton of glasses. Observation of the fracture areas by a scanning electron microscope revealed the presence of metastable separation in the glasses in question.

INTRODUCTION

Glasses in the system Li_2Cl_2—Li_2O—B_2O_3 are studied in particular with respect to their electrical properties. To understand better the rules of ionic conductivity, however, it is necessary to obtain detailed information on the structure of these glasses. The structure of boric glasses was discussed by numerous authors on the basis of results obtained by various experimental techniques, such as NMR, Raman's and IR spectroscopy, X-ray diffraction, and others. The basic structure of boric glasses was described by Krogh-Moe [1]. In this model, the changes in the structure of glass are discussed as an effect of a network modifier. Griscom [2] discussed this model in detail: he assumed the structure to be formed by a system of certain different local structures: boroxol rings, pentaborate, triborate, diborate, metaborate, pyroborate, orthoborate and free BO_4 groups. These conclusions concern two-component glasses Li_2O—B_2O_3. Introduction of a third component, Li_2Cl_2, brings about changes of some properties, such as density, T_g and the molar volume, indicating the function of Li_2Cl_2 in the structure of glass. Soppe [3] studied three-component glasses containing alkalies ($Li_2O + Li_2Cl_2$) up to 40 mol. % and came to the conclusion that the structure of the basic skeleton of three-component glasses does not differ from that of the corresponding binary glasses.

The chemical composition of the glasses in question can be expressed in the form:

X Li_2Cl_2—Y Li_2O—7 B_2O_3 (mol) — abbreviated record X—Y—7. The following series of glasses with a changing content of Li_2Cl_2 were studied:

X—3—7 $\quad X = \langle 0; 3.0 \rangle$

and three series of glasses with changing Li_2O content

2—Y—7; 2.5—Y—7; 3—Y—7 $\quad Y = \langle 3.0; 4.5 \rangle$.

*Present address: Slovak Technical University, Faculty of Chemical Technology, Department of the Chemical Technology of Silicates, Radlinského 9, 812 37 Bratislava

EXPERIMENTAL

X-ray diffraction analysis (Geigerflex-Rigaku Denki) was used in the study of all the samples in question. The purpose was to identify the presence of undesirable crystalline phases.

The density of glasses was determined by the pycnometric method described in Czechoslovak Standard ČSN 70 0513.

All the glasses were subjected to DTA analysis (heating rate 10 °C min^{-1}). T_g values were determined from the DTA curves in the way indicated in Fig. 1.

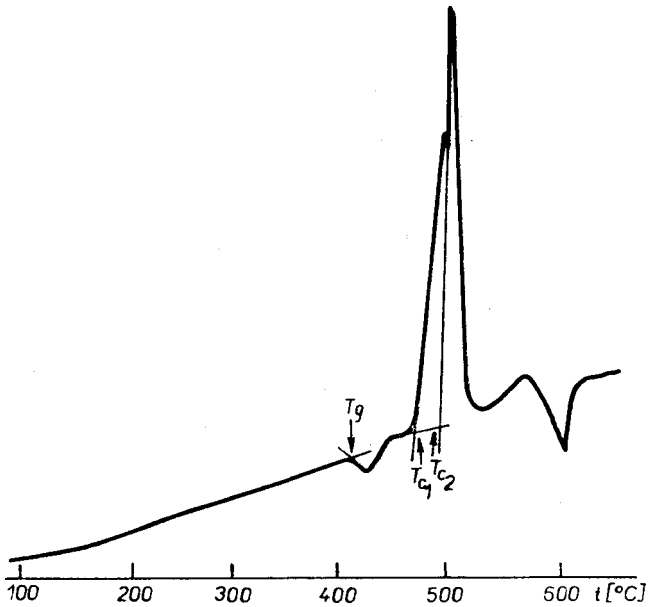

Fig. 1. Typical DTA record of glasses in the system Li_2Cl_2—Li_2O—B_2O_3.

The structural analysis was based on IR spectroscopic measurement of the glasses (Perkin Elmer 325). The measurements were carried out by the method of KBr pellets.

The surface of fracture areas of the glasses was investigated by the scanning electron microscope (Joel/JEM 100 B) in order to reveal possible phase separation. The fracture areas were leached with H_2O and 2% HF to facilitate detection of phase separation.

EXPERIMENTAL RESULTS AND DISCUSSION

All of the samples were subjected to X-ray diffraction analysis. In the following stage, only glasses free of crystalline phases were analyzed.

Assessment of the dependence of properties on chemical composition was based on chemical analyses of the glasses [4].

Determination of density and knowledge of the precise chemical composition allowed the molar volume of the glasses to be calculated. The effect of the individual components on changes in molar volume can be assessed from a graphic plot of molar volume of the glasses vs. their chemical composition (Figs. 2 and 3).

The dependence of transformation temperature T_g on chemical composition of the glasses is plotted in Figs. 4 and 5.

The IR absorption spectra of glasses having the composition Y Li_2Cl_2—3 Li_2O—7 B_2O_3 are shown in Fig. 6.

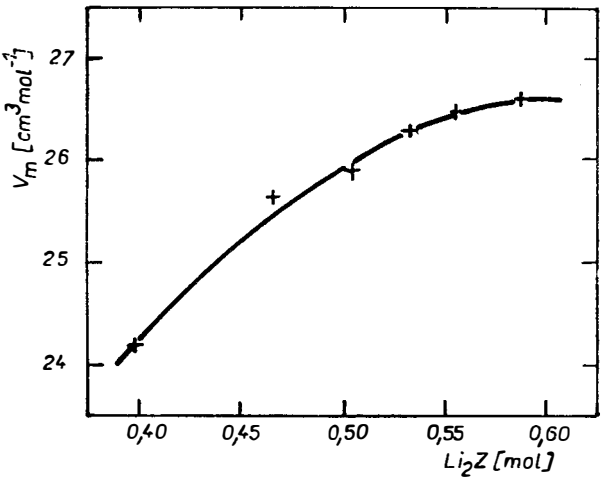

Fig. 2. Molar volume vs. Li_2Z *content at glasses having the composition* X Li_2Cl_2—3 Li_2O—7 B_2O_3 (Li_2Z = Li_2O + Li_2Cl_2).

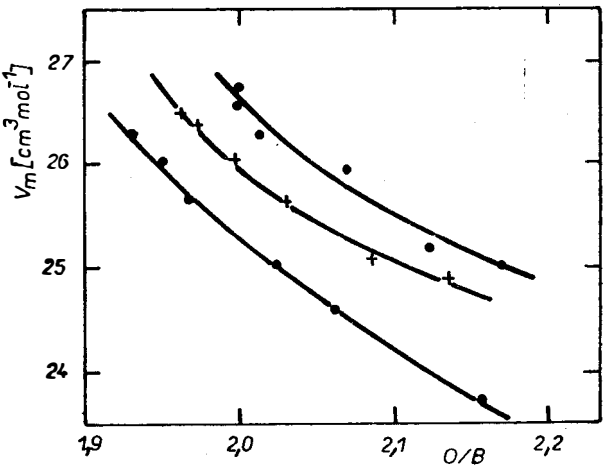

Fig. 3. Molar volume vs. O/B ratio in glasses having the composition X Li_2Cl_2—Y Li_2O—7 B_2O_3 (• — X = 2; + — X = 2.5; o — X = 3).

The presence of $[BO_3]$ and $[BO_4]$ groups was determined according to the absorption spectra. The $[BO_3]$ groups are characterized by absorption bands in the regions of 1360 cm^{-1} and 700 cm^{-1}. The vibrations of $[BO_4]$ groups can be attributed to the absorption peaks in the 970 cm^{-1} and 760 cm^{-1} region [5].

Li_2O performs the function of a modifier of the B—O structure. An addition of Li_2O, built into the B_2O_3 network, causes the $[BO_3]$ triangles to be converted to $[BO_4]$ tetrahedra. At a content higher than 30 mol. % of Li_2O, non-bridging oxygens are formed, and the number of $[BO_4]$ groups decreases [6, 7]. An increase in the content of Li_2O (increasing O/B ratio) was found to result in a decreasing

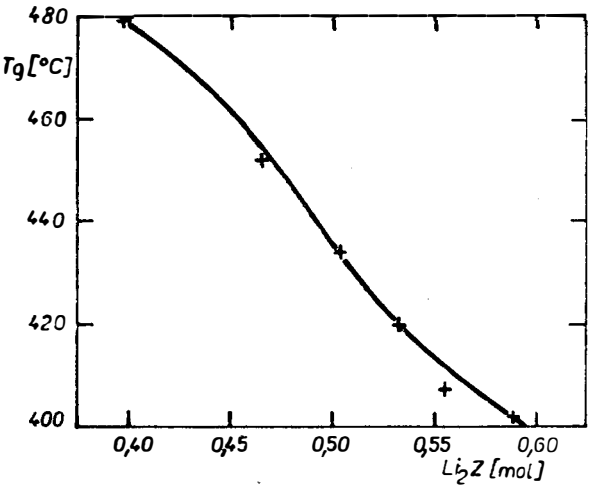

Fig. 4. Transformation temperature (T_g) vs. content of Li_2Z in glasses having the composition X Li_2Cl_2—3 Li_2O—7 B_2O_3.

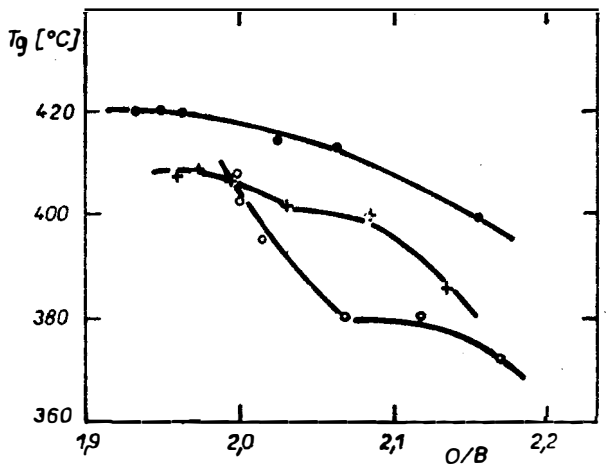

Fig. 5. Transformation temperature T_g vs. the O/B ratio in glasses having the composition X Li_2Cl_2— —Y Li_2O—7 B_2O_3 (• — X = 2; + — X = 2.5; ○ — X = 3).

molar volume (Fig. 3). This densification of the structure of glasses may eventually be reflected to the transport properties of Li^+ ions. As indicated by Fig. 6, changes in the content Li_2Cl_2 do not bring about any significant changes in the IR spectra. No substantial differences were found in the spectra of glasses free of Li_2Cl_2 (0—3—7) and those with the highest content of Li_2Cl_2 (3—3—7). From this it may be concluded that an addition of Li_2Cl_2 does not cause any changes in the skeleton composed of B_2O_3 and Li_2O. The Li_2Cl_2 probably fills the voids in the structure of the B—O skeleton. In view of the large radius of the Cl^- ions, the voids will already be filled at low contents of Li_2Cl_2. Further additions of

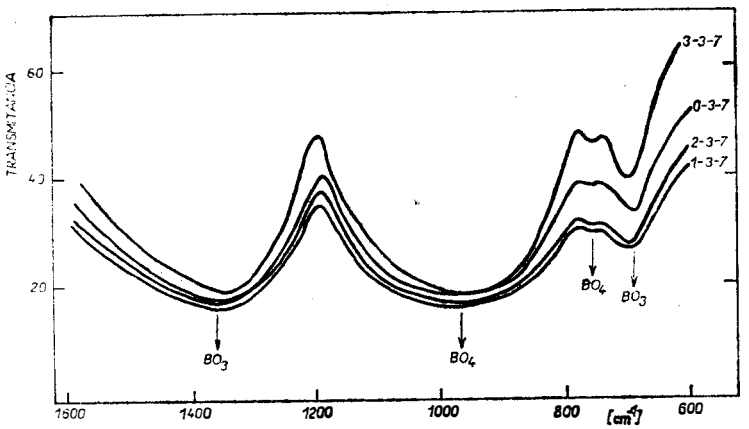

Fig. 6. Infrared (IR) spectra of glasses having the composition, X Li_2Cl_2—3 Li_2O—7 B_2O_3.

Li_2Cl_2 will expand the structure of the glass, as also indicated by the increase in the molar volume of glasses shown in Fig. 2. Simple electrostatic considerations show that the voluminous negatively charged ion Cl^- may place itself in positions more distant from the negatively charged groups [BO_4], thus likewise promoting expansion of the system. The increase in the molar volume may favourably affect the transport properties of Li^+ ions.

The decrease of T_g with increasing O/B ratio (Fig. 5) is a logical consequence of a modification of the B—O skeleton in the glasses. The decrease of T_g resulting from Li_2Cl_2 addition is more marked (Fig. 4). The decrease is due to a considerable expansion of the system, involving general relieving of the bonding relations.

The glasses prepared were visually clear and free of inhomogeneities. However, examinations of the fracture surfaces on the scanning electron microscope revealed the presence of metastable separations of phases, which was emphasised by elutriation in H_2O and 2% HF (Fig. 7). The separated phases were continuous and intergrown. The existence of two phases of different composition was also proved by DTA records of the glasses:

— two exothermic deflections indicating crystallization of the two separated phases appeared on the thermograms over a narrow temperature interval (Fig. 1) [8].

The structure was discussed from the standpoint of a complete homogeneity of the glasses prepared. Because phase separation was found to take place in the specimens, further investigations will be aimed at determining the chemical composition and structure of the separated phases.

CONCLUSION

IR spectroscopy and detailed investigation of T_g and of the molar volume indicated the different functions of Li_2O and Li_2Cl_2 in the structure of glasses having the composition Li_2Cl_2—Li_2O—B_2O_3. Li_2O enters the structure of glass as a modifier taking part in modification of the B—O skeleton. Its addition decreases the molar volume of the glasses. IR spectroscopic measurements showed that the structure of the basic skeleton is not changed by the addition of Li_2Cl_2. The molar volume of glasses increases with the increasing Li_2Cl_2 content.

The structure of the ternary glasses therefore depends mainly on the O/B ratio, and additions of Li_2Cl_2 do not lead to any formation of new elementary units in the structure of the glasses.

References

[1] Krogh-Moe J.: Phys. Chem. Glasses *6*, 46 (1965).
[2] Griscom D. L., in *Borate Glasses Structure, Properties, Applications* (eds. L. D. Pye, V. D. Frechette, N. J. Kreidl), p. 11, Plenum Pres., New York, 1978.
[3] Soppe W.: Structure and Dynamics of Borate Glasses, D.Sc. Thesis, University of Groningen 1989.
[4] Znášik P., Šašek L., Kašparová V.: Silikáty (in press).
[5] Weidlein J., Müller V., Dehnike K.: *Schwingungsfrequenzen* 1. Georg Thieme, Stuttgart—New York 1981.
[6] Button D. P., Tandon R., King C., Veléz M. H., Tuller H. L., Uhlmann, D. R.: J. Non-Cryst. Solids *49*, 129 (1982).
[7] Tuller H. L., Button D. P.: *Proc. of Int. Conf. on Transport-Structure Relations in Fast Ion and Mixed Conductors*, Riso National Lab., 119, Denmark, Sept. 1985.
[8] Znášik P.: Special Classes Based on B_2O_3 and P_2O_5, Candidate's Thesis, VŠCHT Prague, 1989.

IÓNOVÉ SKLÁ V SÚSTAVE Li_2Cl_2—Li_2O—B_2O_3. ČASŤ II: VLASTNOSTI A ŠTRUKTÚRA

Peter Znášik*, Ladislav Šašek

Vysoká škola chemicko-technologická, katedra technologie silikátů, Suchbátarova 1905/5, 166 28 Praha 6

**SVŠT, Chemickotechnologická fakulta, katedra chemickej technologie silikátov, Radlinského 9, 812 39 Bratislava*

Východiskom k posúdeniu štruktúrnych aspektov skiel v sústave Li_2Cl_2—Li_2O—B_2O_3 boli IČ spektroskopia, merania T_g a výpočet mólového objemu skiel. Li_2O vstupuje do štruktúry B—O skeletu ako modifikátor, jeho zvyšujúci sa obsah sposobuje zníženie mólového objemu. Spektroskopické merania skiel v IČ oblasti podali dôkaz o tom, že štruktúra základného skeletu skiel sa prídavkom Li_2Cl_2 nemení. Mólový objem sa pri rastúcom obsahu Li_2Cl_2 zvyšuje. Pozorovania povrchu lomových ploch × rastrovacím elektrónovým mikroskopom odhalili prítomnosť metastalného odmiesenia skiel.

Obr. 1. Typický DTA záznam skiel v systéme Li_2Cl_2—Li_2O—B_2O_3.

Obr. 2. Závislosť mólového objemu od obsahu Li_2Z *v sklách zloženia* X Li_2Cl_2—3 Li_2O—7 B_2O_3 (Li_2Z = Li_2O + Li_2Cl_2).

Obr. 3. Závislosť mólového objemu od pomeru O/B v sklách zloženia X Li_2Cl_2—Y Li_2O—7 B_2O_3 (• — X = 2; + — X = 2,5; ○ — X = 3).

Obr. 4. Závislosť transformačnej teploty (T_g) *od obsahu* Li_2Z *v sklách zloženia* X Li_2Cl_2—3 Li_2O—7 B_2O_3.

Obr. 5. Závislosť transformačnej teploty (T_g) *od pomeru O/B v sklách zloženia* X Li_2Cl_2—Y Li_2O—7 B_2O_3 (• — X = 2; + — X = 2,5; ○ — X = 3).

Obr. 6. Infračervené (IČ) spektrá skiel zloženia X Li_2Cl_2—3 Li_2O—7 B_2O_3.

Obr. 7. Snímka lomovej plochy skla zloženia Li_2Cl_2—Li_2O—B_2O_3 *lúženej 15 min. v* H_2O (*zväčšenie 10 000* ×).

ИОННЫЕ СТЕКЛА В СИСТЕМЕ Li_2Cl_2—Li_2O—B_2O_3 II. СВОЙСТВА И СТРУКТУРА

Петер Знашик*, Ладислав Шашек

Химико-технологический институт, кафедра технологии силикатов, Сухбатарова 5, 166 28 Прага 6

**Словацкий политехнический институт, химико-технологический факультет, кафедра химической технологии силикатов, Радлицкего 9, 812 39 Братислава*

Исходным критерием для рассмотрения структурных аспектов стекол в системе Li_2Cl_2—Li_2O—B_2O_3 являются ИК спектроскопия, измерение T_g и рассчет и мольный объем стекол. Li_2O входит в структуру B—O скелета в виде модификатора, его растущее содержание вызывает понижение мольного объема. Спектроскопические измерения стекол в ИК области являются доказательством того, что структура основного скелета стекол с добавкой Li_2Cl_2 не изменяется, в то время как объем при растущем содержании Li_2Cl_2 повышается. Наблюдения поверхности излома посредством сканирующего микроскопа показали присутствие метастального расслоения стекол.

Рис. 1. Типическая ДТА запись стекол в системе Li_2Cl_2—Li_2O—B_2O_3.

Рис. 2. Зависимость мольного объема от содержания Li_2Z *в стеклах составом* X Li_2Cl_2—3 Li_2O—7 B_2O_3 (Li_2Z = Li_2O + Li_2Cl_2).

Рис. 3. Зависимость мольного объема от отношения O/B в стеклах составом X Li_2Cl_2—Y Li_2O—7 B_2O_3 (• — X = 2; + — X = 2,5; ○ — X = 3).

Рис. 4. Зависимость трансформационной температуры (T_g) *от содержания* Li_2Z *в стеклах составом* X Li_2Cl_2—3 Li_2O—7 B_2O_3.

Рис. 5. Зависимость трансформационной температуры (T_g) *от отношения 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. Инфракрасные (IČ) спектры стекол составом X Li_2Cl_2—3 Li_2O—7 B_2O_3.

Рис. 7. Съемка поверхности излома стекла составом Li_2Cl_2—Li_2O—B_2O_3, *выщелачиваемой 15 мин. в* H_2O.

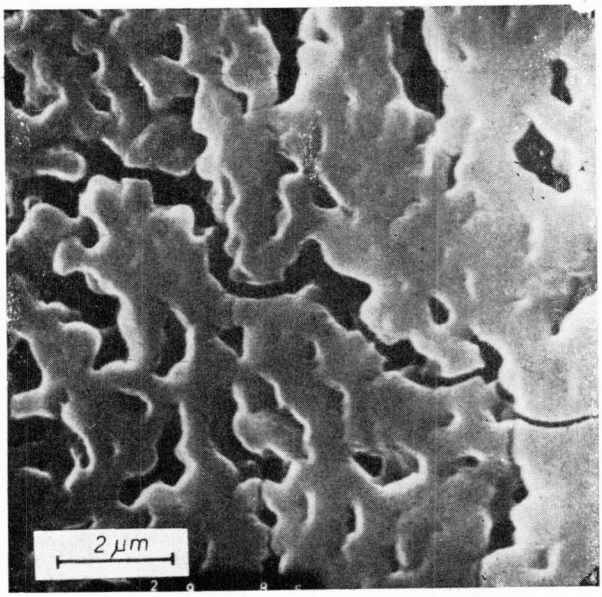

Fig. 7. *Electron micrograph of the fracture surface of glass having the composition* Li_2Cl_2—Li_2O—B_2O_3 *elutriated for 15 minutes in* H_2O *(magn. 10 000×).*