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ELECTRON MICROSCOPIC DETERMINATION OF THE META-
STABLE DISSOCIATION REGION IN THE SYSTEM Li_2SiO_3
$--SiO_2$

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16. Abstract

Seven glasses with an alkali oxide content in the range 9.57 to 29.53 mole percent were investigated. The temperature at which the transition of micro-heterogeneous mixing to the condition of mutual solubility occurs on heating is found. It is found that the altered constituent composition results in the alteration in the percentage amount of the coexisting phases.

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Electron Microscopic Determination of the Metastable Dissociation
Region in the System Li_2SiO_3--SiO_2

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(Presented by Academy Member D. Ivanov on June 21, 1966)

The phase equilibrium in the system Li_2SiO_3 – SiO_2, a particular case of the
Li_2O – SiO_2 diagram, was investigated by Kracek[1] some time ago. However, the
S-shape course of the liquidus curve of this system in the crystallization region
of α-cristobalite (Fig. 1) suggests the possibility of a metastable mixture.[2]

Recently Vogel and Byhan,[3] and shortly thereafter Andrejew, Goganow, Poraj-
Koschitz and Sokolow,[4] succeeded in demonstrating this hypothesis experimentally,
although they determined the boundary of the dissociation region of the liquid
state only on the curve maximum left of the critical point of the mutual solubility
of both coexistent phases. From this result , as well as from our desire to
thoroughly investigate the structural correlation in the same system, there resulted
the necessity of a preliminary determination of the metastable dissociation region
in an additional publication. Thereby our investigations concerning the system
$Li_2O.SiO_2$ -- $Li_2O.Al_2O_3.4SiO_2$ -- SiO_2, the metastable dissociation region of which
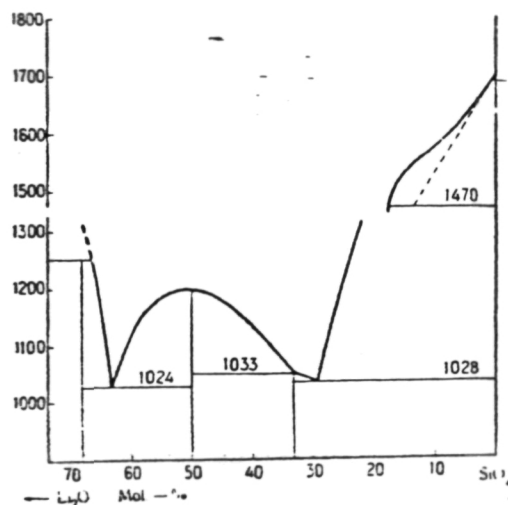still remains univestigated, were also considerably expidited.

Fig. 1

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* Numbers in margin indicate pagination of foreign text.

For this purpose we investigated 7 glasses with an alkali oxide content in the range 9.57 to 29.53 mole percent (Table), in which the samples with up to 23.37 mole percent Li_2O were melted in a platinum crucible in a high-temperature oven, and those with lower Li_2O content in a corundum crucible in a kryptol oven. The completely clear and homogeneous melts obtained were quickly cooled in metal forms (100 x 7 x 7 mm). After a heat treatment of 10 minutes* and temperature change

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* One in such a way of limited heat treatment to avoid the appearance of a crystallization process in the higher temperature range.

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in 10° steps there followed the electron-microscopic investigation of the test pieces in order to establish the course of the curve of the mutual solubilities of both coexistent phases. Also investigated were freshly crushed flakes, previously treated with 2% hydrofluoric acid, which afterward were rinsed in doubly distilled water, carefully dried and coated with carbon and platinum by simultaneous evaporation; the coated pieces obtained are easily separated by treatment with 10% hydrofluoric acid.

Table

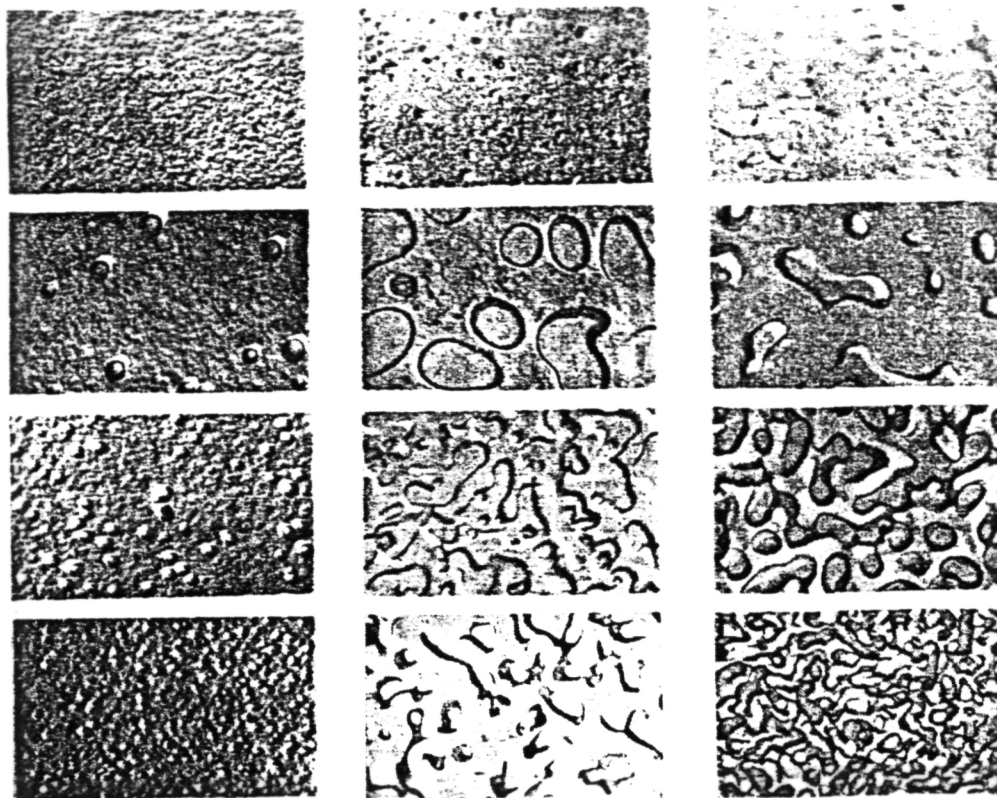| Glass No.	Oxide Content Li_2O	In Mole % SiO_2	Visual Characteristic	t^o of mutual solubility, both dissociation phases
1	29.53	70.47	transparent glass	720
2	28.46	71.54	"	740
3	25.97	74.03	"	820
4	23.37	76.63	Slight opalescence	870
5	18.10	81.90	"	920
6	12.45	87.55	"	950
7	9.57	90.43	"	930

Fig. 2

Fig. 2 shows the electron-microscopic photographs in 20,000 times magnification which correspond to the composition of a Li_2O content of 29.53, 18.10 and 12.45 mole percent (Electron Microscope EIMI D-2, K. Z. Jena). The metastable dissociation region is shown in Fig. 3.

The illustration obtained in this manner shows with satisfactory accuracy the temperature at which, at the corresponding composition, the transition of micro-heterogeneous mixing to the condition of mutual solubility occurs on heating.

The metastable dissociation in the simple glasses can be described as an ordinary phase transition. The speed of the new phase nucleation would be given by the usual formula for phase transitions.[5] The lowest point of the stable dissociation nucleation, that is the critical radius for the solution of the so-called "dissociation drops" at a particular temperature, is
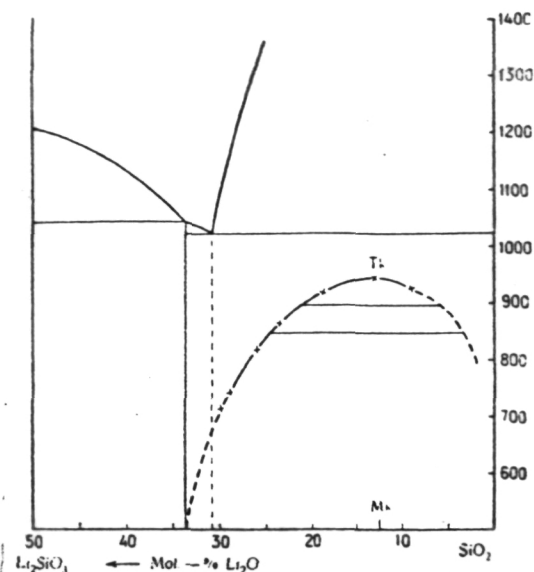
Fig. 3

$$r_k = \frac{3\sigma_{1.2}}{\Delta\varphi},$$

where

r_k = critical radius for the dissolution of the so-called "dissociation drops"

σ = limiting surface tension between the dissociation phases

$\Delta\varphi$ = thermodynamic potential difference of both phases.

With temperature increase, which was considered by us, in order to determine the metastable dissociation region it was shown that the smaller dissociation region with a radius $r < r_k$ is dissolved, if it cannot be induced to increase to critical radius during the temperature increase. Thereby the supercritical range of the so-called "dissociation drops" is increased as a temperature function with simultaneous change in the composition of the conjugated-coexisting liquid phase, and new nuclei are formed in a new composition. Moreover, the dissociation phase decreases with the approach of the temperature of mutual solubility, and with the progression of the isoconcentration points laying quantitatively to the right or left of the critical temperature T_k, and to be sure in favor of the matrix which contains them. In practice, in this temperature range a numerical decrease of the dissociation region expressed as unit of surface, and an increase of its extent is established; that is, the process, which applies at the lower temperature values, in order to reach completion by attainment of the corresponding temperature

/920

of mutual solubility of the co-existent phases, must reveal a curve maximum. This complicated kinetic formation mechanism of glass structure is very clearly observed in Fig. 2.

In contrast to some investigators,[6] we found the dissociation range not to be of universal validity, although definitely in the form of distinct aggregations. Thereby it is clear from the above presentation that in the dissociation region the altered constituent composition also has as a result an alteration in the percentage amount of the coexisting phases; that is, the change of the matrix arises through a dissociation phase and reverses (see Fig. 2).

It should therefore be logically accepted that the altered composition of the curves of the glass properties through a curve maximum or a turning point is denoted in the M_k-region. The work presented , however, did not select the experimental treatment of this question as an object of investigation, and therefore cannot be discussed thoroughly here.

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