

Původní práce

PHASE RELATIONS IN THE SILICA RICH AREA
OF THE SYSTEM $\text{Li}_2\text{O—SnO}_2\text{—SiO}_2$

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The glasses of the composition $\text{Li}_2\text{O} \cdot n \text{SiO}_2$ (where $n = 2, 3, 4, 5$ and 6) with the additions of the amount of SnO_2 up to 30 % were melted in air at 1500—1600 °C. Their crystallization was studied by the gradient method in ceramic boats and by the quenching method. The liquidus surface of the portion of the diagram $\text{Li}_2\text{O—SnO}_2\text{—SiO}_2$ tested is characterized by the fields of primary crystallization of cassiterite, tridymite, lithium metasilicate and lithium disilicate. A ternary eutectic point was found at the temperature 965 °C. Glasses exhibit metastable liquid immiscibility which decreases with the raising amount of SnO_2 . Our results and the comparison with the system $\text{Na}_2\text{O—SiO}_2\text{—SnO}_2$ suggests that SnO_2 belongs to network formers and it is copolymerized with silica tetrahedra in the silicate network. The subsolidus part of the system showed at 880 °C the phase of brennockite $\text{Li}_4\text{Sn}_2\text{Si}_{12}\text{O}_{30}$ which is formed in high silica runs extremely slowly.

INTRODUCTION AND EARLIER STUDIES

The high silica portion of the system $\text{Li}_2\text{O—SnO}_2\text{—SiO}_2$ was studied to follow the behaviour of tetravalent tin in a simple alkali silicate system. The smaller ionic size of lithium ($r = 0,06 \text{ nm}$) compared to Na (0,095 nm) and K (0,133 nm) decreases the volume of alkali ions in the structure of a silicate melt and makes it possible to follow more distinctly the bonding of tin with silicon.

The system $\text{Li}_2\text{O—SiO}_2$ was studied in the thirties by Kracek [1] who found two binary compounds, Li_2SiO_3 with the melting point at 1201 °C and the lithium disilicate $\text{Li}_2\text{Si}_2\text{O}_5$ with the melting point at 1033 °C. A binary eutectic exists between SiO_2 and $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2$ at 1028 °C. A part of the ternary system $\text{Li}_2\text{O—Al}_2\text{O}_3\text{—SiO}_2$ was studied by Krishna and Hummel [2]. No comprehensive survey of the phase relations is recorded in the system $\text{SiO}_2\text{—SnO}_2$ in the literature [3] and the system $\text{Li}_2\text{O—SnO}_2$ does not have binary compounds reported. There is a single ternary phase in the system with K corresponding to the mineral brennockite $\text{Li}_3\text{KSn}_2\text{Si}_{12}\text{O}_{30}$ described from lithium-bearing pegmatites [4] and among the products of experiments, in hydrothermal environment as the phase $\text{Li}_4\text{Sn}_2\text{Si}_{12}\text{O}_{30}$ (5). The properties of glasses in the system $\text{Li}_2\text{O—SiO}_2\text{—SnO}_2$ were tested by Vakhrameev and Evstrop'ev [6]. The role of tin dioxide as nucleation agent in lithium disilicate glasses was studied by Thakur and Thiagarajan [7] and Thakur [8]. The influence of a small addition of Sn on the crystallization of glasses in the system $\text{Li}_2\text{O—Al}_2\text{O}_3\text{—SiO}_2\text{—TiO}_2$ was followed by Khodakovskaya et al. [9].

Table I
The composition of melts in the high silica portion of the system $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$

Classification	Composition (mass . %)			Composition (mol . %)			Colour of glass
	SiO_2	Li_2O	SnO_2	SiO_2	Li_2O	SnO_2	
$\text{Li}_2\text{O} \cdot 1.5 \text{SiO}_2 + x \text{SnO}_2$							
L — S	66.78	33.22	—	50.00	50.00	—	fully crystallized, cracks glass in a thin layer, strongly crystallized grey-brown fully crystallized in total mass grey-brown fully crystallized in total mass
L — 1.5 S	75.09	24.91	—	60.00	40.00	—	
L — 1.5 S — 5	71.52	23.72	4.76	59.06	39.37	1.57	
L — 1.5 S — 10	68.26	22.65	9.09	58.14	38.78	3.08	
$\text{Li}_2\text{O} \cdot 2 \text{SiO}_2 + x \text{SnO}_2$							
L — 2 S — 0	80.08	19.92	—	66.67	33.33	—	greenish, occasionally crystalline spherulites in view through smoky brown, at bottom slightly clouded in view through smoky brown, in thicker layer clouded, crystalline margins dark brown, semitransparent light brown, sings of clouding dark brown, non transparent light brown, transparent dark brown, semitransparent blackbrown, non transparent
L — 2 S — 5	76.27	18.97	4.76	65.58	32.79	1.63	
L — 2 S — 7.5	74.49	18.53	6.98	65.17	32.59	2.44	
L — 2 S — 10	72.80	18.11	9.09	64.53	32.26	3.21	
L — 2 S — 15	69.63	17.32	13.05	63.51	31.75	4.74	
L — 2 S — 20	66.73	16.60	16.67	62.52	31.26	6.22	
L — 2 S — 25	64.06	15.94	20.00	61.56	30.78	7.66	
L — 2 S — 27.5	62.81	15.62	21.57	61.20	30.41	8.39	
L — 2 S — 30	61.60	15.32	23.08	60.64	30.31	9.05	

continued Table I

Classification	Composition (mass. %)			Composition (mol. %)			Colour of glass
	SiO_2	Li_2O	SnO_2	SiO_2	Li_2O	SnO_2	
$\text{Li}_2\text{O} \cdot 3 \text{SiO}_2 + x \text{SnO}_2$							
L—3	85.78	14.22	—	75.00	25.00	—	milk white clouding, in thinner layers translucent in view through light brown (bluish opalescence) light brown (bluish opalescence) light brown, very weak opalescence light brown, very weak opalescence light brown, without opalescence light brown, clouded, transparent dark brown, transparent non transparent, light grey brown with rosa tinge
L—3	81.69	13.55	4.76	73.72	24.57	1.71	
L—3	79.79	13.23	6.98	73.19	24.25	2.56	
L—3	77.98	12.93	9.09	72.48	24.15	3.37	
L—3	74.59	12.37	13.04	71.28	23.76	4.96	
L—3	71.48	11.85	16.67	70.12	23.36	6.52	
L—3	68.62	11.38	20.00	68.99	23.00	8.01	
L—3	65.98	10.94	23.08	67.91	22.63	9.46	
L—3	63.54	10.53	25.93	66.93	22.16	10.91	
$\text{Li}_2\text{O} \cdot 4 \text{SiO}_2 + x \text{SnO}_2$							
L—4	88.94	11.06	—	80.00	20.00	—	opaline, translucent very strong opalescence (bluish), non transparent in view through light brown, distinctly opalescent in view through light brown, weaker opalescence in view through light brown, very weak opalescence in view through light brown, milky streaks dark brown, non transparent
L—4	84.70	10.53	4.77	78.60	19.64	1.76	
L—4	80.86	10.05	9.09	77.24	19.30	3.46	
L—4	77.34	9.62	13.04	75.92	18.98	5.10	
L—4	74.12	9.22	16.66	74.66	18.66	6.68	
L—4	71.16	8.84	20.00	73.43	18.34	8.23	
L—4	68.42	8.51	23.07	72.24	18.06	9.70	

continued Table I

Classification	Composition (mass . %)				Composition (mol . %)				Colour of glass
	SiO ₂	Li ₂ O	SnO ₂		SiO ₂	Li ₂ O	SnO ₂		
Li₂O . 5 SiO₂ + SnO₂									
L — 5 S — 0	90.95	9.05	—		83.33	16.67	—		opaline, only in thinner layers transparent
L — 5 S — 5	86.62	8.62	4.76		81.84	16.37	1.79		in view through light brown, strong bluish opalescence
L — 5 S — 10	82.69	8.22	9.09		80.41	16.07	3.52		in view through, light brown, strong bluish opalescence
L — 5 S — 15	79.09	7.87	13.04		79.01	15.80	5.19		light brown, very weak opalescence
L — 5 S — 20	75.79	7.54	16.67		77.66	15.53	6.81		light brown, weak opalescence
L — 5 S — 25	72.76	7.24	20.00		76.36	15.27	8.37		light brown, in total mass non transparent
L — 5 S — 30	69.96	6.96	23.08						
Li₂O . 6 SiO₂ + SnO₂									
L — 6 S — 0	92.34	7.66	—		85.71	14.29	—		opaline, in total mass non transparent, cracks
L — 6 S — 5	87.94	7.30	4.76		84.21	13.97	1.82		opaline, in total mass non transparent
L — 6 S — 10	83.95	6.96	9.09		82.72	13.70	3.58		in view through light brown, blue opalescence
L — 6 S — 15	80.30	6.66	13.04		81.26	13.47	5.27		light brown, strong bluish opalescence
L — 6 S — 20	76.95	6.38	16.67		79.86	13.23	6.31		light brown, very weak blue opalescence light
L — 6 S — 25	73.87	6.13	20.00		78.49	13.01	8.49		brown, in total mass non transparent
L — 6 S — 30	71.03	5.89	23.08						

METHODS OF INVESTIGATION

Glass preparation and methods of study

The mixture of the starting materials were prepared in the compositional sections $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2$, $\text{Li}_2\text{O} \cdot 3 \text{SiO}_2$, $\text{Li}_2\text{O} \cdot 4 \text{SiO}_2$, $\text{Li}_2\text{O} \cdot 5 \text{SiO}_2$ and $\text{Li}_2\text{O} \cdot 6 \text{SiO}_2$ with added SnO_2 from the following starting materials: SiO_2 — ground sand Dörentrupp 99.83 mass. % SiO_2 , Li_2O added in the form of lithium carbonate (technical purity supplied by firma Kaznějov) and SnO_2 (chemically pure from Lachema in Brno) (Table I). The mixtures of the starting materials were sintered at the temperature 800–900 °C and then melted in the Pt-Rh crucibles in the total amount of about 0.5 kg at the temperatures between 1500–1600 °C in the Kanthal-Super furnaces. The melts were stirred during melting by a Pt-Rh propeller. Various amount of SiO_2 changed considerably the viscosity of the melts and hence the time of melting was changed respectively. The melts of the composition $\text{Li}_2\text{O} \cdot 1.5 \text{SiO}_2$ had a very low viscosity on melting and could have been easily casted. However, they easily crystallized on cooling and could not have been quenched to glass. The mixtures of the composition $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2$ to $\text{Li}_2\text{O} \cdot 4 \text{SiO}_2$ were quenchable without crystallization, however the glasses after cooling showed various degree of unmixing. The mixtures with the composition $\text{Li}_2\text{O} \cdot 5 \text{SiO}_2$ and $\text{Li}_2\text{O} \cdot 6 \text{SiO}_2$ were highly viscous and hence the time of melting was extended from 5 to 10 hours and the time of stirring was prolonged as well. The position of ternary invariant points was followed by 2 experiments with 81 mass. % SiO_2 and 5 mass. % SnO_2 and with 75 mass. % SiO_2 and 5 mass. % SnO_2 . The survey of the melting conditions is given in Table I. The resulting glasses were either completely recrystallized glasses, or transparent glasses with a different degree of unmixing or white glasses in which the starting material was not dissolved in the melt even in extended time (cassiterite).

The areas occupied by individual glasses of this kind are given in the Fig. 1 where the thick line represents the SnO_2 solvus in the melts at the temperatures between 1500–1600 °C.

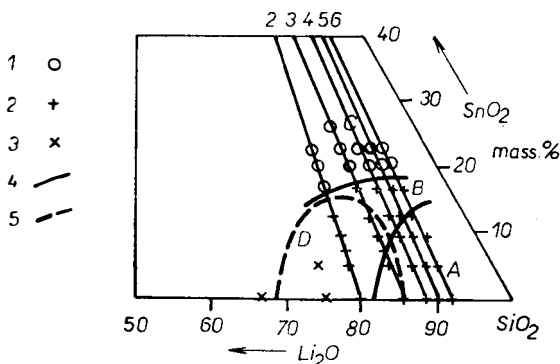


Fig. 1. The area of transparent glasses in the high silica portion of the system $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ showing strong (A) and weak (B) metastable liquid immiscibility. It is separated from clouded glasses with undissolved SnO_2 at 1600 °C which represents the tin dioxide solvus. The area of clear glasses according to Vakhrameev and Evstrop'ev (6) is marked by the field D. 1 — glasses with admixture of SnO_2 , 2 — clear or opalescent glasses, 3 — unquenched glasses, 4 — field boundaries, 5 — boundary of the field D.

The samples of the glasses were tested by the gradient methods in ceramic boats in the temperature interval 700—1300 °C. The details of the methods are described in Kopecký and Voldán [10]. The accuracy for the determination of the temperatures of crystallization is believed to be ± 5 °C which includes the inaccuracies for the control of the temperature in runs and the accuracy of reading of the beginning of crystallization. The time of the runs was 3 hours. Several selected samples were tested by the quenching method using suspended platinum envelopes with quenching on a metallic plate. The temperature of these runs was measured by PtRh thermocouples calibrated against the melting points of gold and sodium chloride, respectively.

The products of runs were studied by optical and X-ray studies. The optical observations included the tests of phase transitions in ceramic boats which were easily detected as the beginning of clouding in glass rods induced by melting or by relatively sharp boundaries of crystallization at univariant or invariant equilibria.

The optical identification was done on a petrographic microscope or by X-ray diffraction studies. These X-ray studies were done in the laboratory of the Geological Survey and in the laboratory of the State Glass Research Institute in Hradec Králové. The data obtained were compared with the data from ASTM tables. Some selected samples were studied under the electron microscope. The etching of fragment faces was done by 2 mass. % HF or 5 mass. % HNO₃ during 1 s and after rinsing by distilled water. One step positive prints were made by a contemporaneous evaporation of carbon and platinum under the angle 25°. The photographs were taken on electron microscope Tesla BS 242 E on a photographic plate ORWO DU 25. The glasses prepared were also tested by the DTA method on the apparatus Derivatograph type OD 102 (by MOM Budapest). The runs were carried out at 6 °C/min., grain size of the sample was 0.1—0.063 mm, the sensitivity 1 : 10, as standard heated Al₂O₃ served.

RESULTS AND DISCUSSION

The phases identified in the studies

The solid phases which were identified during the phase equilibria studies include cristobalite, tridymite, lithium disilicate, lithium metasilicate, cassiterite and brennockite.

Lithium metasilicate Li₂SiO₃

White dense aggregates of prismatic crystals negatively elongated, with parallel extinction; $N_p = 1589$ and $N_g = 1600$.

Lithium disilicate Li₂Si₂O₅

Dense, white-grey aggregates, under the microscope in the form of fibrous crystals. It was identified by X-ray method (according to the ASTM table 17—447).

Tridymite SiO₂

Megascopically greyish clouding in the glasses. Optically, it forms low birefringence basal plates with random orientation in glass.

Cristobalite SiO₂

Disperse grey clouding. Identified by X-ray method as an admixture of some runs with predominance of tridymite at low temperatures.

Cassiterite SnO_2

A rose-white clouding. Under the microscope, short prismatic or acicular, high birefringence crystals occasionally with well developed twinning on {101}.

Brennockite $\text{Li}_4\text{Sn}_2\text{Si}_{12}\text{O}_{30}$ (lithian variety)

Admixture of a high SnO_2 run at 920°C identified by X-ray method according to data by Nekrasov and Dadze (5).

The area of glasses

The melting at $1500-1600^\circ\text{C}$ in the system (see Fig. 1) differentiated the area of translucent glasses showing metastable liquid immiscibility with various degree of opalescence from clouded glasses containing undissolved SnO_2 . The high temperature of experiments did not permit SiO_2 phases (tridymite or cristobalite) to crystallize as a primary phase in the portion tested.

In the area of glasses with metastable liquid immiscibility there can be differed the one showing a strong liquid immiscibility (A) and a weaker liquid immiscibility (B). The weaker liquid immiscibility is in the compositions high in SnO_2 and relatively poorer in SiO_2 as indicated in Fig. 1. Our results are comparable in the silica poorer area with the results of Vakhrameev and Evstrop'ev [6] obtained at lower temperatures ($1300-1400^\circ\text{C}$).

The liquidus surface of the diagram

The phase equilibria on the liquidus surface of the diagram were studied by the tests in ceramic boats. The survey of the important results of runs used in the construction of the diagram is given in Table II.

The portion of the diagram studied is characterized by a steep slope of the liquidus surface of the fields of SiO_2 and SnO_2 primary crystallization of which SiO_2 has the melting points at 1713°C and SnO_2 at 2300°C [3]. These fields of primary crystallization of tridymite and cassiterite occupy the predominant portion of the diagram tested. The fields of primary crystallization of lithium metasilicate and lithium di silicate are restricted to a very small area near the binary $\text{Li}_2\text{O}-\text{SiO}_2$ join. The liquidus temperatures drop from those along the $\text{Li}_2\text{O}-\text{SiO}_2$ join towards the SnO_2 apex and raise again in the area of about 7 to 10 mass. % SnO_2 . The position of the ternary eutectic in the portion of the diagram (Fig. 2) studied has been extrapolated from the data between the $2\text{SiO}_2 \cdot \text{Li}_2\text{O}$ and $3\text{SiO}_2 \cdot \text{Li}_2\text{O}$ sections of the diagram and an additional run at 81 mass. % SiO_2 and 5 mass. % SnO_2 . Its temperature was determined to be equal to $965^\circ\text{C} \pm 5^\circ\text{C}$ at the composition at 78 mass. % SiO_2 and 6 mass. % SnO_2 (± 1 mass. %) (Table III).

The connection of this eutectic with the binary eutectic along the $\text{Li}_2\text{O}-\text{SiO}_2$ side at 82.2 mass. % SiO_2 gives a cotectic line between tridymite and lithium disilicate fields as it has been indicated by a heavy line in Fig. 2.

The course of the cotectic line between the fields of primary crystallization of tridymite and cassiterite could not have been determined within the interval tested in ceramic boats. Therefore three runs were carried out at 1400°C as given in Table IV. These show that the composition $4\text{SiO}_2 \cdot \text{Li}_2\text{O} \cdot 10\text{SnO}_2$ produced a liquid whereas the composition 5 and 6 $\text{SiO}_2 \cdot \text{Li}_2\text{O}$ gave tridymite with some metastable cristobalite as the primary crystallization phases. Hence the course of the cotectic line is

extrapolated to the $4\text{SiO}_2 \cdot \text{Li}_2\text{O} \cdot 10\text{SnO}_2$ composition. The inferred course of cotectic lines between the field of lithium metasilicate and disilicate is shown by dashed line.

Table II
Runs used for interpretation of the fields of primary crystallization

Mass. %			Beginning of (°C) crystallization	Phase(s)
SiO ₂	Li ₂ O	SnO ₂		
66.73	16.60	16.67	> 1250	cas.
69.63	17.32	13.05	> 1253	cas.
71.48	11.85	16.67	> 1230	cas.
72.80	18.11	9.09	1085	cas.
74.12	9.22	16.66	> 1220	cas.
74.49	18.53	6.98	995	dis.
74.59	12.37	13.04	> 1225	cas.
75.00	20.00	5.00	1057	met.
75.79	7.54	16.67	> 1290	cas.
76.27	18.97	4.76	994	dis.
77.34	9.62	13.04	> 1220	cas.
77.98	12.93	9.09	1180	cas.
79.09	7.87	13.04	> 1290	cas.
79.79	13.23	6.98	1220	trid. + cas.
80.30	6.66	13.04	> 1290	trid. + cas.
80.86	10.05	9.09	> 1220	trid. + cas.
81.00	14.00	5.00	> 1131	trid.
81.69	13.55	4.76	> 1230	trid.
82.69	8.22	9.09	> 1280	trid. + cas.
83.95	6.96	9.09	> 1290	trid.
84.70	10.53	4.77	> 1221	trid.
86.62	8.62	4.76	> 1290	trid.

Abbreviations: trid. = tridymite
cas. = cassiterite
cris. = cristobalite
dis. = lithium disilicate
met. = lithium metasilicate

Table III

Runs used for the determination of the temperature of the eutectic point (E)

Mass. %			Temperature of the boundary (°C)	Phases
SiO ₂	Li ₂ O	SnO ₂		
74.49	18.53	6.98	963	dis. + cas.
76.27	18.97	4.76	961	dis. + cas.
78.13	19.43	2.44	970	dis. + cas.
79.79	13.23	6.98	967	cas. + trid. + cris.
81.00	14.00	5.00	965	trid. + dis. + cas.

Abbreviations: trid. = tridymite
cas. = cassiterite
cris. = cristobalite
dis. = lithium disilicate

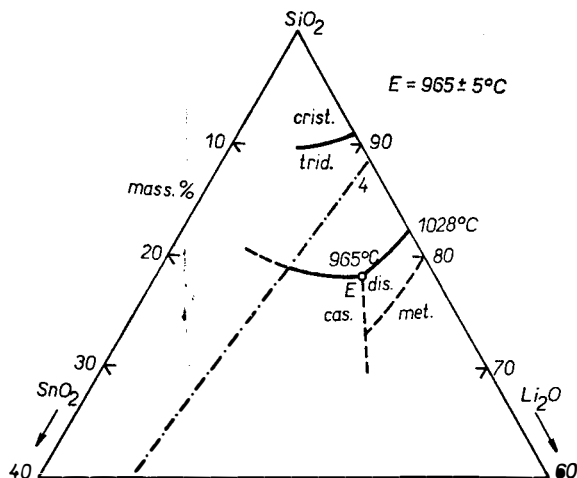


Fig. 2. Liquidus surface of the high silica portion of the system $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ with eutectic point (E) at $965 \pm 5^\circ\text{C}$. Heavy lines indicate field boundaries established by experimental data, the dashed lines are inferred from phase relations. For abbreviations see table 2. The section $\text{Li}_2\text{O} \cdot 4 \text{SiO}_2 + n \text{SnO}_2$ in fig. 4 is marked by 4.

Table IV

Crystallization of glasses at 1400°C

Composition (mass. %)			Products	Notes
SiO_2	Li_2O	SnO_2		
80.86	10.05	9.09	glass	strong opalescence
82.69	8.22	9.09	crist. + trid.	
83.95	6.96	9.09	crist. + trid.	

The subsolidus section of the diagram

The subsolidus diagram was constructed on the basis of data in Table V and shows the relationships of phases below the presence of liquids in the system as given in Fig. 3 in the interval $\sim 800-900^\circ\text{C}$. The diagram in the section $\text{SnO}_2-\text{SiO}_2-\text{Li}_2\text{O}$ has a simple form characterized by four three phase triangles giving the equilibrium of cassiterite-brennockite-tridymite, cassiterite-brennockite-lithium disilicate, tridymite-brennockite-lithium disilicate and cassiterite-lithium metasilicate and lithium disilicate. The appearance of brennockite in the high silica runs has not been recorded and apparently due to sluggish reaction in dry systems in this temperature interval and the equilibrium diagram is constructed from the data in its higher SnO_2 portion.

Brennockite was reported by Nekrasov and Dadze (5) to form in a $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2-\text{H}_2\text{O}$ system at the temperatures 500 and 650°C and the water pressure of $P_{\text{H}_2\text{O}} 10^8 \text{ Pa}$ and it was noted in our experiment to exist below 881°C .

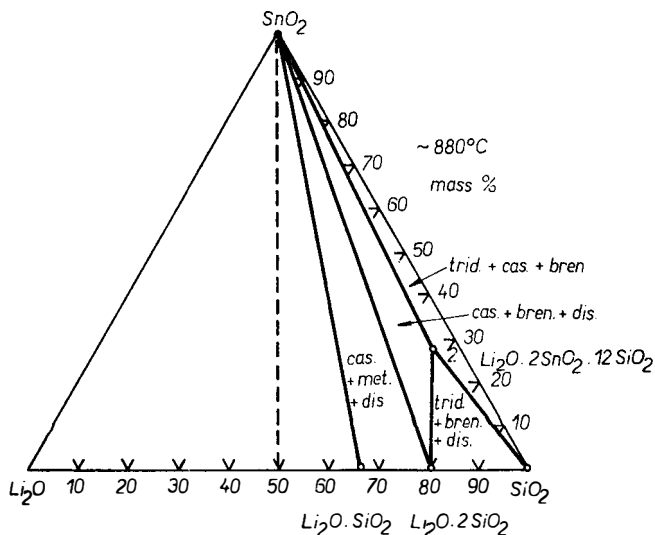


Fig. 4. Schematic cross section through the T - x diagram at $4 \text{ SiO}_2 \cdot \text{Li}_2\text{O} + n \text{ SnO}_2$ with two invariant points (α and β). The section explains the coexistence of tridymite and cassiterite in melts as found in a number of phase determinations.

Table V
Runs for the determination of subsolidus phase equilibria
 $1000 > T > 820^\circ\text{C}$

Mass. %			Temperature	Duration	Product	Methods
SiO ₂	Li ₂ O	SnO ₂	(°C)	(hours)		
65.98	10.94	23.08	920	20	cas. + dis. + trid.	E
68.26	22.65	9.09	820	3	met. + cas.	B
68.42	8.51	23.07	850—881	3	cas. + dis. + bren. + crist. + (coesit?)	B
69.63	17.32	13.05	830—880	3	dis. + cas.	B
72.80	18.11	9.09	873—912	3	dis. + cas.	B
74.49	18.53	6.98	935—965	3	dis. + cas.	B
74.59	12.37	13.04	920	20	dis. + cas. + trid.	E
75.00	20.00	5.00	980—990	3	dis. + metas. + cas.	B
76.27	18.97	4.76	924—961	3	dis. + cas.	B
76.27	18.97	4.76	920	20	dis. + cas.	E
77.34	9.62	13.04	900	20	trid. + cas. + dis.	E
77.98	12.93	9.09	920	20	dis. + cas. + trid.	E
78.13	19.43	2.44	940—960	3	dis. + cas.	B
79.79	13.23	6.98	965—970	3	dis. + cas. + crist.	B
81.00	14.00	5.00	930—940	3	dis. + cas. + trid.	B
81.69	13.55	4.76	920	20	dis. + cas. + trid.	E

Abbreviations: dis. = lithium disilicate
cas. = cassiterite
crist. = cristobalite
trid. = tridymite
met. = lithium metasilicate
bren. = brennockite
E = platinum envelope
B = ceramic boat (gradient crystallization)

Sections through the portion of the system investigated

The sections of the diagram along the $3 \text{ SiO}_2 \cdot \text{Li}_2\text{O}$, $4 \text{ SiO}_2 \cdot \text{Li}_2\text{O}$, $5 \text{ SiO}_2 \cdot \text{Li}_2\text{O}$ and $6 \text{ SiO}_2 \cdot \text{Li}_2\text{O} + n \cdot \text{SnO}_2$ compositions are characterized by two large fields of primary tridymite (cristobalite) and cassiterite crystallization which are contacted at an invariant point β with the field of cassiterite + tridymite + liquid whose existence has been confirmed by a number of phase determinations. The exact position of this point was not determined from the runs but in the $4 \text{ SiO}_2 \cdot \text{Li}_2\text{O} + n \cdot \text{SnO}_2$ join it is close to 1400°C at about 9% SnO_2 (Fig. 4).

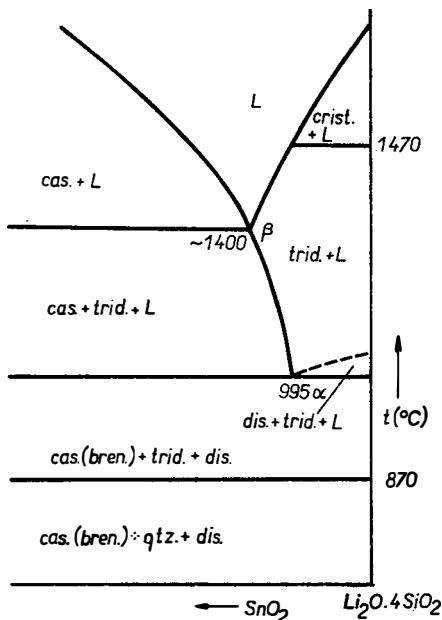


Fig. 3. Subsolidus phase relations of the system $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ at 880°C showing three phase triangles with the equilibria of cassiterite, tridymite, lithium disilicate and brennockite. For abbreviations see table 5.

The position of the second invariant point α with the equilibrium of lithium disilicate, tridymite, cassiterite and liquid was deduced from the literature data and supported by some results of our runs.

Metastable liquid immiscibility

In the samples prepared from the starting materials the metastable liquid immiscibility was observed. The immiscibility appears as a bluish-white cloudint of various intensity. There is a marked decrease in the intensity of clouding with raising amount of SnO_2 . The decrease of metastable liquid immiscibility was well observed on the microphotographs taken under the electron microscope where the

pictures of glasses containing 16.67 mass. % SnO_2 in the section with $\text{Li}_2\text{O} \cdot 5 \text{SiO}_2$ showed abundant oval admixtures (fig. 5) within the matrix whereas the glass with 1.57 mass. % SnO_2 in the section with $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2$ was devoid of them (Fig. 6).

Our data confirm that metastable liquid immiscibility known from the data by Marinov and Radenkova-Yaneva (11) exists also into the ternary system $\text{LiO}_2\text{—SiO}_2\text{—SnO}_2$ in which the presence of SnO_2 tends to decrease the intensity of immiscibility but it does not eliminate it completely.

DTA measurements

The DTA measurements determined the nucleation in the glasses of the sections studied (12, 13). The end members of the sections ($\text{Li}_2\text{O} \cdot 2 \text{SiO}_2$, $\text{Li}_2\text{O} \cdot 3 \text{SiO}_2$, $\text{Li}_2\text{O} \cdot 4 \text{SiO}_2$, $\text{Li}_2\text{O} \cdot 5 \text{SiO}_2$, $\text{Li}_2\text{O} \cdot 6 \text{SiO}_2$) in the system $\text{Li}_2\text{O—SiO}_2$ (without SnO_2) gave exothermic peaks at the temperatures from 600 to 610 °C in the sections studied. The addition of 5 mass. % of SnO_2 gave exothermic peaks at the temperatures 610, 640, 670, 700 and 750 °C respectively which indicates a general temperature increase for the beginning of crystallization as compared with pure systems. The addition of 10 mass. % SnO_2 caused the appearance of exothermic peaks of the crystallization at 690 °C in all series of glasses tested.

The influence of raising amount of SnO_2 on the DTA curves of the glasses in the series $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2 + n \text{SnO}_2$ is shown in Fig. 7.

The curve of the sample without SnO_2 shows one sharp peak at 600 °C indicating the crystallization of $\text{Li}_2\text{Si}_2\text{O}_5$. By the addition of 5 mass. % SnO_2 and more to the glass of this composition, the start of the crystallization of $\text{Li}_2\text{Si}_2\text{O}_5$ is gradually shifted towards higher temperatures. This is related to the raised viscosity caused by the addition of tin dioxide.

At the same time another peak at about 900 °C appears which corresponds to the crystallization of SnO_2 . This peak gradually grows with the raising amount of SnO_2 .

At about 20 mass. % of SnO_2 added to the glass this peak exceeds that of the lithium disilicate and is becoming sharper. This testifies to a more rapid crystallization of SnO_2 compared to that of $\text{Li}_2\text{Si}_2\text{O}_5$. The runs in the section $\text{Li}_2\text{O} \cdot 3 \text{SiO}_2 + n \text{SnO}_2$ are analogous except that with the raising amount of SnO_2 the peaks of SnO_2 and $\text{Li}_2\text{Si}_2\text{O}_5$ crystallization start to coincide and at 25 mass. % SnO_2 there exists a single peak (Fig. 8).

In most of the runs there is an endothermic reaction apparently corresponding to the temperature of melting of lithium disilicate which melts at 1033 °C according to Kracek [1].

Thakur and Thiagarajan [7] studied the nucleation behaviour of glasses of the composition $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2$ with the admixture of SnO_2 by DTA and found that SnO_2 in the amount of about 18 mass. % does not produce heterogenous nucleation and it makes the glasses more stable. The addition of about 24 % SnO_2 by mass gave opaque glasses already on casting at 1440 °C caused by the crystallization of SnO_2 during melting. Our data confirm the increases stability of glasses with the raising amount of SnO_2 as compared with pure systems (without SnO_2) in all the sections studied.

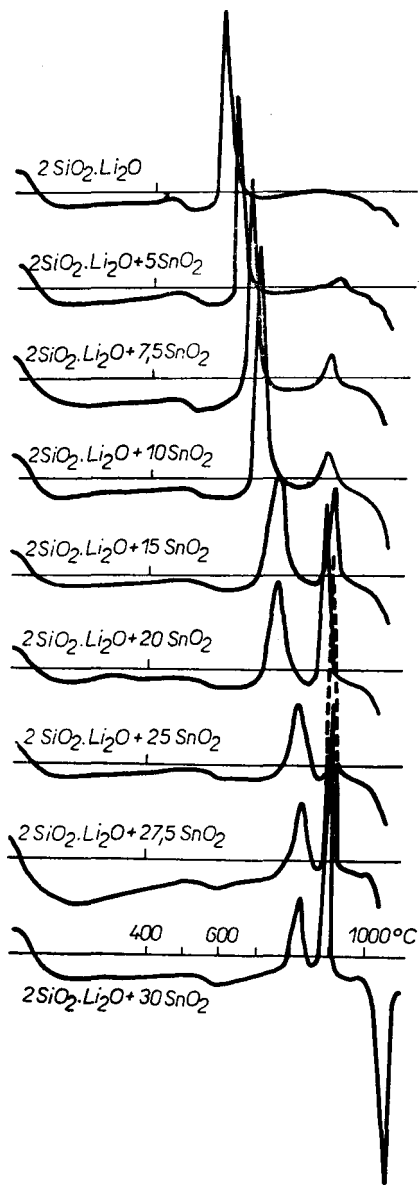


Fig. 7. DTA curves of the samples in the section $\text{Li}_2\text{O} \cdot 2\text{SiO}_2 + n\text{SnO}_2$.

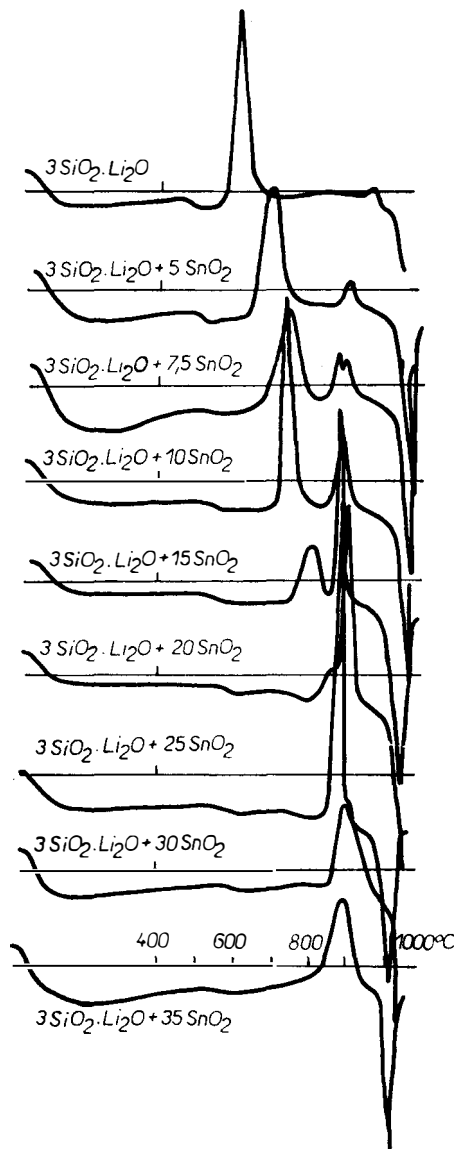


Fig. 8. DTA curves of the samples in the section $\text{Li}_2\text{O} \cdot 3\text{SiO}_2 + n\text{SnO}_2$.

Structural position of SnO_2

The equilibria studies have shown that cassiterite SnO_2 is the typical liquidus phase crystallizing from $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ system over about 7.5 mass. % SnO_2 in melts having approximately lithium disilicate composition. Tetravalent tin with 4 d¹⁰

configuration is more stable than divalent tin in glasses and thus it is present in glasses in high proportion [14]. Tin dioxide belongs to the networkforming oxides and similarly as it was shown in the sodium-silicate system [15] it can be accommodated into the silica network in a limited amount. Its amount dissolved in sodium silicate liquid ranges from 18 to 20 mass. % by mass at 1500–1600 °C and it is very similar to that observed in the $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ system tested in the present study.

Approximately a very similar solubility limit of SnO_2 in the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ (15) compared to that of $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ suggests that the solubility of tin dioxide in the melts is not dependent on the nature of alkali oxide but it is primarily determined by the competence of tin to be copolymerized with silica tetrahedra.

Tin (Sn^{4+}) can be coordinated also with silica and lithium oxide to form a ternary compound (brennockite) at lower temperatures but this reaction is very sluggish in dry system and in most runs in high SiO_2 portion of the diagram SnO_2 appears as a metastable phase. The formation of brennockite is accelerated by the presence of water as shown by Nekrasov and Dadze [5]. The coordination of tetravalent tin in silicate glasses differs from that of divalent tin. SnO can be dissolved in SiO_2 glasses in the amount up to 75.9 mass. % [16].

CONCLUSIONS

The solubility of SnO_2 in high silica lithium silicate glasses at 1600 °C is up to about 18 mass. %. The glasses of such compositions show a metastable liquid immiscibility which is decreased with the raising amount of SnO_2 . The portion of the system studied is occupied by the fields of primary crystallization of cassiterite, lithium disilicate, lithium metasilicate, and of tridymite. The cotectic lines of these fields form a ternary eutectic point at 965 °C.

Our data show the ranges of SnO_2 solubility are similar to the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ which suggest that its extent is not dependent on the nature of the alkali ion. Hence, tin (Sn^{4+}) is probably copolymerized with silicon tetrahedra in alkali glasses and it belongs in silicate melts to network forming oxides.

Acknowledgement

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FÁZOVÉ VZTAHY V ČÁSTI SOUSTAVY $\text{Li}_2\text{O}-\text{SnO}_2-\text{SiO}_2$ BOHATÉ SiO_2

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Byla utavena skla o složení $\text{Li}_2\text{O} \cdot n \text{SiO}_2$ (kde $n = 2, 3, 4, 5$ a 6) s přidavkem SnO_2 až do množství 30 % (hmot.) při teplotě 1500—1600 °C. Byla určena oblast existence skel obsahujících rozpuštěný SnO_2 , která jsou charakterizována metastabilní likvací, jejíž podíl se zmenšuje s přidáním SnO_2 . Krystalizace takto připravených skel byla sledována gradientovou metodou a v zavěšených platinových obálkách. Byla určena pole primární krystalizace kasiteritu, tridymitu, lithného disilikátu, která vytvářejí eutektický bod s teplotou 965 °C. V oblasti subsolidu byla potvrzena existence fáze $\text{Li}_4\text{Sn}_2\text{Si}_{12}\text{O}_{30}$, která odpovídá lithné varietě minerálu brennockitu. Tato fáze vzniká při experimentech jenom velmi pomalu a většina pokusů v části bohaté SiO_2 poskytuje nerovnovážný SnO_2 . Naše výsledky a srovnání s dříve studovanou soustavou $\text{Na}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ ukazují na to, že kyslíčnick ciničitý v jednoduchých alkalických silikátových sklech patří síťotvořičům a je vázán pravděpodobně na tetraedry SiO_4 .

Obr. 1. Oblast průhledných skel v části soustavy $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ bohaté oxidem křemíku se silnou (A) a slabou (B) metastabilní likvací. Oblast je oddělena hranicí od zakalených skel s SnO_2 nerozpuštěným při 1600 °C, která představuje solvus oxidu cínu. Oblast čirých skel podle Vachramejeva a Jevstropěva (6) je označena písmenem D. 1 — skla s příměsí SnO_2 , 2 — čirá nebo opalizující skla, 3 — nezchladitelná skla, 4 — hranice polí, 5 — hranice pole D.

Obr. 2. Poloha likvidu části soustavy $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ bohaté SiO_2 s eutektickým bodem (E) při teplotě 965 °C \pm 5 °C. Silné čáry označují hranice polí určených podle experimentů, čárkované jsou odvozeny z fázových vztahů. Zkratky jsou v tab. II. Řez $\text{Li}_2\text{O} \cdot 4 \text{SiO}_2 + n \text{SnO}_2$ je v obr. 4 označen číslicí 4.

Obr. 3. Fázové vztahy v oblasti subsolidu soustavy $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ při teplotě 880 °C ukazující třífázové trojúhelníky s rovnovahami kasiteritu, tridymitu, lithného disilikátu a brennockitu. Zkratky v tab. V.

Obr. 4. Schematický řez diagramem T-x o složení $4 \text{SiO}_2 \cdot \text{Li}_2\text{O} + n \text{SnO}_2$ se dvěma invariantními body (α a β). Řez vysvětluje koexistenci tridymitu a kasiteritu v taveninách, jak bylo zjištěno v řadě fázových stanovení.

Obr. 5. Obráz z elektronového mikroskopu skla o složení 75,79 % hmot. SiO_2 a 16,67 % hmot. SnO_2 ukazující hojné projevy metastabilní likvace.

Obr. 6. Obráz z elektronového mikroskopu skla o složení 62,81 % hmot. SiO_2 a 21,57 % hmot. SnO_2 bez projevů likvace.

Obr. 7. Křivky DTA vzorků v řezu $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2 + n \text{SnO}_2$.

Obr. 8. Křivky DTA vzorků v řezu $\text{Li}_2\text{O} \cdot 3 \text{SiO}_2 + n \text{SnO}_2$.

ФАЗОВЫЕ РАВНОВЕСИЯ В ЧАСТИ СИСТЕМЫ
 $\text{Li}_2\text{O}-\text{SnO}_2-\text{SiO}_2$, БОГАТОЙ SiO_2

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Была приготовлена стекла составом $\text{Li}_2\text{O} \cdot n \text{SiO}_2$ (где $n = 2, 3, 4, 5$ и 6) с добавкой SnO_2 до количества 30 % по весу при температуре 1600—1500 °С. Была установлена область существования стекол, содержащих растворенный SnO_2 , характеризующая метастабильной ликвицей, доля которой уменьшается с нарастающей добавкой SnO_2 . Кристаллизация полученных таким образом стекол исследовалась с помощью градиентного метода и метода охлаждения. Установлены поля первичной кристаллизации каситерита, тридимита, литиевого дисиликата, образующих эвтектическую точку с температурой 965 °С. В области субсолидуса было доказано существование фазы $\text{Li}_4\text{Sn}_2\text{Si}_{12}\text{O}_{30}$, отвечающей литиевой разновидности минерала бреннокита. Рассматриваемая фаза образуется при экспериментах весьма медленно и в большинстве экспериментов в части, богатой SiO_2 получается неравновесный SnO_2 . Наши результаты в сопоставлении с до сих пор исследованной системой $\text{Na}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ показывают, что окись олова (IV) в простых щелочных силикатных стеклах относится к решеткообразователям и вероятно связывается с тетрадрами SiO_4 .

- Рис. 1. Область прозрачных стекол в части системы $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$, богатой окисью кремния со сильной (А) и слабой (Б) метастабильной ликвицей. Область разделена пределом от глухеных стекол с SnO_2 нерастворенным при 1600 °С представляющий собой сольвус окиси олова. Область прозрачных стекол по Вахрамееву и Естропьеву (6) обозначена D: 1 — стекла с примесью SnO_2 , 2 — прозрачные или опализирующие стекла, 3 — неохлаждаемые стекла, 4 — границы полей, 5 — граница поля D.
- Рис. 2. Поверхность ликвидуса части системы $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$, богатой SiO_2 с эвтектической точкой (E) при температуре 965 ± 5 °С. Толстые линии обозначают пределы полей, установленных на основе экспериментов, штриховые линии из фазовых равновесий. Сокращения см. табл. 2. Сечение $\text{Li}_2\text{O} \cdot 4 \text{SiO}_2 + n \text{SnO}_2$ находится на рис. 4 и обозначено через 4.
- Рис. 3. Фазовые равновесия в области субсолидуса системы $\text{Li}_2\text{O}-\text{SiO}_2-\text{SnO}_2$ при температуре 880 °С, показывающие трехфазные треугольники с равновесием каситерита, тридимита, дисиликата лития и бреннокита. Сокращения см. табл. 5.
- Рис. 4. Схематическое сечение диаграммой T-x составом $4 \text{SiO}_2 \cdot \text{Li}_2\text{O} + n \text{SnO}_2$ с двумя инвариантными точками (α и β). Сечение объясняет сосуществование тридимита и каситерита в расплавах, как это было установлено на основе экспериментов.
- Рис. 5. Электронмикроскопические снимки стекла составом 75,79 % SiO_2 , и 16,67 % SnO_2 (по весу) показывающие метастабильную ликвицию.
- Рис. 6. Электронмикроскопические снимки стекла составом 62,81 % SiO_2 , и 21,57 % SnO_2 (по весу) без явной ликвиции.
- Рис. 7. Кривые ДТА образцов в сечении $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2 + n \text{SnO}_2$.
- Рис. 8. Кривые ДТА образцов в сечении $\text{Li}_2\text{O} \cdot 3 \text{SiO}_2 + n \text{SnO}_2$.

NOVÝ SPŮSOB ZÍSKAVANIA VZÁCNÝCH MINERÁLNYCH LÁTOK Z MORSKEJ VODY navrhli sovietski výskumníci. Metóda využíva obrovské siete filtračných zariadení so špeciálnymi sorbentami ponorené v miestach silných morských prúdov, ktoré zabezpečujú samoočisne dynamické aspekty filtrácie. Výpočty ukázali, že ekonomika tohoto postupu (napr. pri získavaní uránu) je zrovnateľná s ekonomikou banskej ťažby (Sputnik 12, 1985, 107).

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