[CONTRIBUTION FROM SCHOOL OF MINERAL INDUSTRIES, THE PENNSYLVANIA STATE COLLEGE]

The System Lithium Metasilicate–Spodumene–Silica[1]

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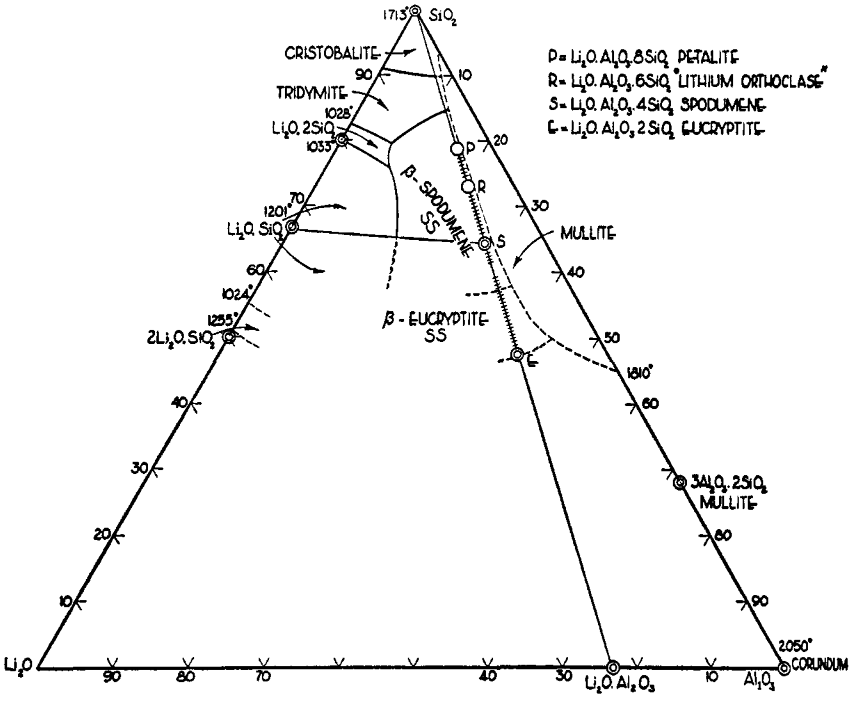
Introduction

The ternary system Li_2O–Al_2O_3–SiO_2 is noteworthy for the many interesting, but still unsolved, compositional and structural problems which it contains. The three minerals petalite, spodumene and eucryptite appear in the system. Of these petalite has not been synthesized, and its chemical formula is in doubt. Spodumene, likewise, has not been synthesized but a high temperature polymorphic form can be crystallized from a glass of the spodumene composition. The same form also appears on heating spodumene above about 700°. The transformation, however, is monotropic, and spodumene cannot be obtained from the high temperature form. Crystals of eucryptite composition have been made, but these are apparently a high temperature form structurally different from the mineral. Glass of the eucryptite composition has a density and refractive index greater than that of the corresponding crystals—an interesting phenomenon still not satisfactorily explained.



Weight per cent.

Fig. 1.—The system Li_2O–Al_2O_3–SiO_2, after Kracek,[4] Hatch,[5] Bowen and Greig[6] and Roy and Osborn.

Related to compositions in the system Li_2O–Al_2O_3–SiO_2 are the lithia micas of the lepidolite series. During recent attempts to synthesize members of this series,[3] the desirability of having phase equilibrium data on systems containing Li_2O, Al_2O_3, and SiO_2 became evident. Besides contributing toward a solution of the problems mentioned above, therefore, data for the system Li_2O–Al_2O_3–SiO_2 can serve as a basis for understanding the more complex mixed alkali–alumina–silica systems.

In the present work, phase equilibrium data were obtained for the ternary system, lithium metasilicate – spodumene – silica. The location of this system within the system Li_2O–Al_2O_3–SiO_2 is shown in Fig. 1. The data of Kracek,[4] of Hatch,[5] and of Bowen and Greig,[6] have established the relations as shown along the joins Li_2O–SiO_2, $Li_2O \cdot Al_2O_3$–SiO_2, and Al_2O_3–SiO_2, respectively.

Inasmuch as lithium is a monovalent cation as are sodium and potassium, but has an ionic radius similar to that of magnesium, it might be expected that the system lithia–alumina–silica would bear a family resemblance both to the alkali–alumina silica systems[7] and to the magnesia–alumina–silica system.[8] Such is the case. The series of compounds $LiAlSiO_4$, $LiAlSi_2O_6$ and $LiAlSi_3O_8$,[9] have analogs in both the soda and potash systems. In all of the alkali systems, the field of mullite approaches closely but does not cross the join on which the ternary compounds appear. The β-spodumene solid solution series does not have a counterpart in the other alkali systems but resem-

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[1] Abstracted from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The Pennsylvania State College.

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[3] Rustum Roy, "Decomposition and Re-synthesis of the Micas," paper presented before the 50th Annual Meeting of the Am. Ceram. Soc., Chicago, Ill., April, 1948.

[4] (a) F. C. Kracek, *J. Phys. Chem.*, **34**, Pt. II, 2645 (1930); (b) F. C. Kracek, THIS JOURNAL, **61**, 2870 (1939).

[5] R. A. Hatch, *Am. Min.*, **28**, 471 (1943).

[6] N. L. Bowen and J. W. Greig, [4] **7**, 242 (1924).

[7] J. F. Schairer and N. L. Bowen, *Am. J. Sci.*, **245**, 196 (1947).

[8] G. A. Rankin and H. E. Merwin, *Am. J. Sci.*, [4] **45**, 322 (1918).

[9] $LiAlSi_3O_8$ is a suggested formula for petalite.

bles the cordierite solid solution series in the system $MgO–Al_2O_3–SiO_2$. It is of interest in this connection that one of our colleagues has found that extensive solid solution exists between β-spodumene and cordierite.[10] The wide application of mixtures in the $MgO–Al_2O_3–SiO_2$ system in the ceramic industry would lead one to expect an increasing use of mixtures in the $Li_2O–Al_2O_3–SiO_2$ system, probably in the same fields.

Method of Investigation

The raw materials used in the preparation of the mixtures were lithium carbonate, alumina and silicic acid.

The lithium carbonate was obtained from a freshly opened bottle of J. T. Baker Analyzed Chemicals with the only significant impurities being 0.200% SO_4 and 1.200% other alkalies. It was dried at 300° in a platinum beaker, and stored in a desiccator.

The alumina used was anhydrous aluminum hydroxide, C. P. (J. T. Baker) with an analysis indicating the presence of 0.28% heavy metals as the only significant impurity. The material was boiled in ammonium chloride, washed thoroughly on a Buchner funnel, and dried. It was then ignited in platinum at 1000° for twenty hours, and 1400° for another fifteen hours. Below 200° it was cooled in a desiccator.

Silica was prepared from anhydrous silicic acid C. P., an Eimer and Amend purity reagent, with the only significant impurity being 0.055% Cl. The ignition loss was tested against the theoretical formula loss and agreed within 0.025%. Water was driven off at 1000° for twenty hours and 1250° for twelve hours.

The mixtures were made by weighing the silica directly into the crucible, and adding weighed amounts of lithium carbonate and alumina. Mixtures were thoroughly stirred with a platinum rod, and melted in an electric "Globar" furnace. After crushing the quenched glass in a steel mortar, the iron was removed with a magnet and the glass remelted. The entire procedure was repeated three or four times, the glasses being checked for homogeneity under the microscope. Part of each glass was crystallized for 24–36 hours at temperatures between 600–800°. Hatch[5] used similar techniques and analyses made indicated that the melted glasses were within 0.2% of the batch composition. The refractive indices of the glasses were measured in Na light (D line). The regular change of the indices (and also of the liquidus temperatures) indicated an accuracy of the melted compositions within the desired limits.

The well-known quenching technique, developed at the Geophysical Laboratory of the Carnegie Institution of Washington and frequently described[11] was used throughout. The platinum–platinum 90%, rhodium 10% thermocouples were calibrated regularly at the gold (1062.6°) and diopside (1391.5°) points. For a more frequent check on the accuracy of the thermocouples, a calibrated standard thermocouple was used. In the long runs (longer than two hours) temperatures were automatically controlled. In general the limit of accuracy was approximately ±2.5°, over extended periods. For short periods of time up to an hour, a large heat capacity furnace was used which could be controlled manually to within ±1°. Unless otherwise stated, the limit of error in runs less than two hours is approximately ±2° and for longer runs ±3°. Various samples were tested to find whether equilibrium had been attained in a certain length of time. Equilibrium was attained rapidly, usually in fifteen minutes. All runs were thirty minutes or longer.

Identification of the phases was performed with the petrographic microscope and from X-ray diffraction patterns. The latter method was used extensively and almost all samples with crystals were examined with X-ray techniques. A General Electric XRD unit with a photographic recording camera of diameter 143.2 mm. and Fe Kα(λ = 1.936) radiation, and a Norelco Geiger counter type X-ray spectrometer with CuKα (λ = 1.53736) radiation were used, the latter much more than the former.

Properties of the Crystalline Phases and Corresponding Glasses

Lithium Metasilicate.—Lithium metasilicate ($Li_2O·SiO_2$) appears in this system as well-formed, uniaxial positive, negatively elongated, prismatic crystals with parallel extinction. Indices measured were: $\epsilon_{Na} = 1.590$, $\omega_{Na} = 1.610$.

Lithium Disilicate.—Crystals of lithium disilicate ($Li_2O·2SiO_2$) usually form in the mixtures studied as subrounded, subequant prisms. A distinct micaceous cleavage is noticeable especially in large crystals. Elongation is negative and the extinction parallel. Indices of refraction were determined as $N_g = 1.558$ and $N_p = 1.546$. The crystals are biaxial positive, probably orthorhombic.

TABLE I

X-RAY DATA

Values given by Austin for $Li_2O·2SiO_2$		Values obtained in this study $Li_2O·2SiO_2$		β-spodumene	
'd' Values	Rel. int.	'd' Values	Rel. int.	'd' Values	Rel int.
7.32	0.06	7.35	0.04	4.61	0.10
4.70	0.11[a]	5.39	.12	3.97	0.40
4.08	0.04	4.10	.04	3.48	1.0
3.75	0.33	3.73	.80	3.173	0.12
3.67	1.00	3.64	.65	2.33	.04
3.34	0.03[a]	3.58	1.00	2.26	.01
2.72	.11[a]	2.93	0.10	2.13	.015
2.40	.03	2.385	.3	1.943	.04
2.37	.04	2.36	.1	1.89	.10
2.31	.02	2.30	.05	1.653	.06
1.975	.24	2.06	.07	1.542	.01
1.84	.02	2.00	.05	1.458	.005
1.57	.04[a]	1.96	.15	1.434	.02
1.50	.04	1.84	.04	1.411	.007
1.47	.18	1.81	.06 (?)	1.385	.005
1.41	.03	1.528	.06 (2)	1.2415	.02
1.30	.03	1.47	.04		
1.255	.06	1.46	.04		
		1.44	.04		
		1.425	.04		
		1.37	.03		
		1.25	.03		
		1.22	.02		

[a] These values correspond with those of the strongest $Li_2O·SiO_2$ lines.

No changes in refractive index indicative of solid solution were noticed, although irregular shifts in the X-ray diffraction patterns were found. In this connection it was found that the X-ray diffraction data were not the same as those recently published by Austin.[12] It appears that the data given by Austin contain the spacings for lithium metasilicate as well as those for the disilicate (see Table I). This might be expected inas-

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[10] F. A. Hummel, personal communication.

[11] E. S. Shepherd, G. A. Rankin and F. E. Wright, *Am. J. Sci.*, **28**, 293 (1909).

[12] A. E. Austin, *J. Am. Ceram. Soc.*, **30**, 218 (1947).

TABLE II

MOLAR REFRACTION DATA

Substance	Av. index	Density	Molar vol.	Total refracn., R	$R_{Al_2O_3}$	$R_{O^{2-}}$	Reference
Eucryptite							
Natural (low)	1.545	2.667	94.5	29.74	10.26	3.62	Dana, "System of Mineralogy"
Synthetic (high)	1.5225	2.352	107.1	32.71	12.71	3.996	Winkler[18]
Glass	1.541	2.429	103.8	32.61	12.61	3.984	Hatch,[5] Gmelin's H. buch d. anorg. Chem., 8th ed.
Spodumene							
Natural (low)	1.67	3.16	120.5	43.7	9.84	3.56	Dana, "System of Mineralogy"
Synthetic (high)	1.5205	2.406	155.0	47.15	12.25	3.85	Hatch,[5] Roy and Osborn
Glass	1.518	2.37	156.0	47.27	12.37	3.88	Roy and Osborn
Petalite (1:1:8)							
Mineral	1.510	2.4	255.0	76.1	11.4	3.75	Dana, "System of Mineralogy"
Glass	1.495	2.358	259.3	75.6	10.9	3.73	Hatch,[5] Roy and Osborn
Petalite (1:1:6)							
Mineral	1.510	2.4	205.0	61.3	11.5	3.76	Dana, "System of Mineralogy"
Glass	1.495	2.36	208.5	60.8	11.0	3.73	Hatch,[5] Extrapolated

[a] The value used for Li_2O is 5.1, an average obtained from the total refractions of Li_2O, $Li_2O{\cdot}Al_2O_3$, $Li_2O{\cdot}SiO_2$, $Li_2O{\cdot}2SiO_2$ and $2Li_2O{\cdot}SiO_2$. [b] For the method of calculation see Safford and Silverman[16]: 7.19 the value for quartz was used in the "low" forms, and 7.45 the value for silica glass was used in the high and vitreous forms, as the subtraction for the refraction contribution of silica. [c] $R_0{}^{2-}$ values were calculated according to the method of Fajans and Kreidl,[17] although a major change in $R_0{}^{2-}$ in the arrangement of one molecule of Al_2O_3 is progressively diluted as one proceeds to higher molecular weights. [d] It should be noted that refractive indices and densities especially, differ widely as given in the literature, often by as much as 5%.

much as Austin used a commercial source of silica, and furthermore he obtained the compound "merely by allowing the crucible to cool from 1200°."[13] An inspection of the equilibrium diagram for the system Li_2O–SiO_2 (Kracek[4a]) will suggest that such a procedure might give a mixture of metasilicate and disilicate.

Spodumene, β-Spodumene and Eucryptite.—In most cases β-spodumene ($Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$) appears as small anhedral grains. Rarely well-developed, tetragonal dipyramids form. The indices for β-spodumene were found to be $\epsilon_{Na} = 1.522$, and $\omega_{Na} = 1.516$ (± 0.002) which are essentially the same as those given by Hatch.[5] The birefringence of the solid solutions, however, did not seem to decrease with increasing silica content to the same extent as shown by Hatch, for even in the highest silica member it appeared to be considerably greater than 0.001.

Spodumene, the natural, low temperature form of $Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ did not appear in this study, nor has its synthesis ever been confirmed. Spodumene inverts to the high temperature polymorph rapidly above 900°, but the change may be brought about at 700°[14] by extremely fine grinding followed by heating for periods of time of the order of two hundred hours. Some attempts were made to synthesize the mineral form. From analogy with the use of calcium vanadate as a "flux" in the synthesis of wollastonite, lithium vanadate and tungstate were used as fluxes. Additions of 5, 10 and 15% of flux were made to β-spodumene and the mixtures heated to 500, 550 and 600° for lengths of time varying between twenty-four and two hundred hours. In no case was spodumene obtained. The synthesis and inversion were attempted by hydrothermal methods. Pressure vessels of the type used by Ingerson and Morey[15] were used at temperatures between 400 and 700°, the pressure being varied between 500 and 12,000 p.s.i. Both β-spodumene and glass of the spodumene composition were used, and additions of 5% of KF, or of acid or alkali were tried. In none of the experiments did spodumene form.

Data were obtained concerning the probable structures of the high and low temperature forms of both spodumene and eucryptite. The use of molecular refraction values as an index to structure in silicates is illustrated in two recent papers by Safford and Silverman,[16] and by Fajans and Kreidl.[17] With the use of the Lorenz–Lorentz equation

$$R = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{\mathrm{d}}$$

and the best available values for the density and refractive indices of the polymorphs and of the glass of each composition, values of the total molar refraction, R, the refraction contribution of alumina, $R_{Al_2O_3}$, and of each oxygen ion $R_{O^{2-}}$ were calculated and are shown in Table II. The calculations of Safford and Silverman give an average value of $R_{Al_2O_3}$ of 12.31 for the four network structure type minerals, albite, nephelite, carnegieite and anorthite. For corundum and kyanite where the Al^{3+} is in sixfold coördination, the alumina refraction contribution was found by these writers to be approximately 10.5. These data coupled with those in Table II suggest the follow-

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(13) Austin, *op. cit.*, p. 219.

(14) First shown by Meissner, *Z. anorg. Chem.*, **110**, 187 (1920).

(15) E. Ingerson and J. Morey, *Am. Mineral.*, **22**, 1121 (1937).

(16) H. Safford and A. Silverman, *J. Am. Ceram. Soc.*, **30**, 203 (1947).

(17) K. Fajans and N. J. Kreidl, *ibid.*, **31**, 105 (1948).

ing: (1) that both natural eucryptite and spodumene have different crystal forms from the synthetic crystals; (2) that on analogy with spodumene, synthetic eucryptite is a high temperature polymorph of the mineral; (3) that the coördination number of Al^{3+} in the low temperature forms of both spodumene and eucryptite is 6, whereas the high temperature forms possess a network of AlO_4 and SiO_4 tetrahedra; and (4) that the structure of the high temperature form in each case is closely similar to that of its glass. The evidence of Winkler[18] on the structure of synthetic eucryptite, and the accepted structure of spodumene are in accordance with these deductions.

Petalite.—Hatch[5] found that petalite has no existence above the solidus in the binary system β-spodumene–silica. It was not encountered in the present study. The chemical formula for petalite, usually written as $Li_2O{\cdot}Al_2O_3{\cdot}8SiO_2$, has often been questioned. The most recent analysis of the problem by Mikkola and Wiik[19] suggests the composition $4Li_2O{\cdot}5Al_2O_3{\cdot}40SiO_2$. Ballo and Dittler[20] suggested the formula $Li_2O{\cdot}Al_2O_3{\cdot}6SiO_2$, and this composition is shown in Fig. 1 as "lithium orthoclase." The evidence from molar refraction data (Table II) indicates that neither the 1:1:8 nor the 1:1:6 formula gives very satisfactory correspondence in the $R_{Al_2O_3}$ values.

Silica.—Silica appeared in all three polymorphic forms, quartz, tridymite and cristobalite. Quartz appeared as a metastable phase above 867°[21] in practically every case where silica was a phase, if the starting material was all crystalline and the duration of the run was less than twenty-four hours at a temperature below 1100°. It persisted for shorter periods of times in runs at temperatures up to 1200°. In no case was quartz found in any mixture which had been heated above 1200°. The explanation of the existence of quartz above 867° is found in the fact that quartz formed during the crystallization of the glass at 600–800° and as has often been reported[22] failed to invert. It was also found that many mixtures especially those in the vicinity of the 980° invariant point (Fig. 6) when introduced as a glass into a furnace at about 1000°, and held at this temperature for times ranging from fifteen minutes to twenty-four hours, usually contained quartz as the silica phase. It appeared therefore that quartz was crystallizing out of a melt in the stability range of tridymite. Further investigation showed, however, that the quartz crystallized from the glasses during the short time (usually fifteen to twenty seconds) during which the temperature of the sample rose from room temperature to 867°. It was, however, not proven that this quartz does not grow further at temperatures above 867°. The spacings of the lines in the X-ray pattern of the quartz which persisted in these mixtures (patterns made at room temperature) were quite definitely displaced, and corresponded more nearly to those of high quartz than low quartz. The pattern for high quartz used in comparison was obtained with a high-temperature unit[23] for the Geiger counter spectrometer at 600°. The remarkable persistence of quartz above 867° as well as the displaced X-ray patterns suggest that a low quartz solid solution was present or that high quartz is stabilized to room temperature by the presence of the lithium ion. It may be noted that Winkler[18] in a recent analysis of the eucryptite structure has demonstrated that the Li^+ ion is of just the right size to fit into the "holes" in the high quartz structure.

Tridymite was the stable phase in the temperature range in which the work was done, and although it seldom crystallized out first, the other forms of silica tended to invert to tridymite on being held for a sufficiently long time.

Cristobalite usually crystallized out in the silica field. Near the boundary with β-spodumene, and especially near the eutectic it appeared as fine octahedra. The refractive index though not accurately determinable was apparently that of high cristobalite; the X-ray patterns showed the presence of both high and low cristobalite. This is another case of the quenching of high cristobalite to room temperature while imbedded in glass.[24] On crushing very fine, the crystals of high cristobalite inverted to the low form as shown by the X-ray patterns.

Glasses.—The refractive index of the glass of each of the mixtures, quenched usually from about 100–200° above the liquidus, was determined in sodium light (D line). From these data the isofracts in the system lithium metasilicate–β-spodumene–silica were drawn and are shown in Fig. 2. The index of refraction and density of a quenched glass of spodumene composition were found to be, respectively, 1.518 and 2.37 as compared with reported[5] values for β-spodumene of 1.5205 and 2.406. With annealing of the glass, its index and density would increase and approach even more closely to those of β-spodumene. A glass of eucryptite composition has actually a higher index and a greater density than crystals of high eucryptite (Table II).

Binary Systems

Lithium Metasilicate–Silica.—This is part of the system lithia–silica worked out by Kracek[4a]; Fig. 3 presents the latest revision of the system by Kracek.[4b]

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[18] H. G. F. Winkler, *Acta. Cryst.*, **1**, 27 (1948).

[19] T. Mikkola and H. B. Wiik, *Bull. Comm. Geol. Fin.*, **140**, 281 (1947).

[20] R. Ballo and E. Dittler, *Z. anorg. Chem.*, **76**, 39 (1912).

[21] Revised value for the quartz-tridymite inversion given by Kracek, ref. 4b.

[22] F. C. Kracek, N. L. Bowen and G. W. Morey, *J. Phys. Chem.*, **41**, 1188 (1937).

[23] R. Roy, E. T. Middleswarth and F. A. Hummel, *Am. Mineral.*, **30**, 458 (1948).

[24] First reported by J. W. Greig, This Journal, **54**, 2846 (1932). All recorded cases are summarized by A. Grenall, *ibid.*, **70**, 423 (1948).

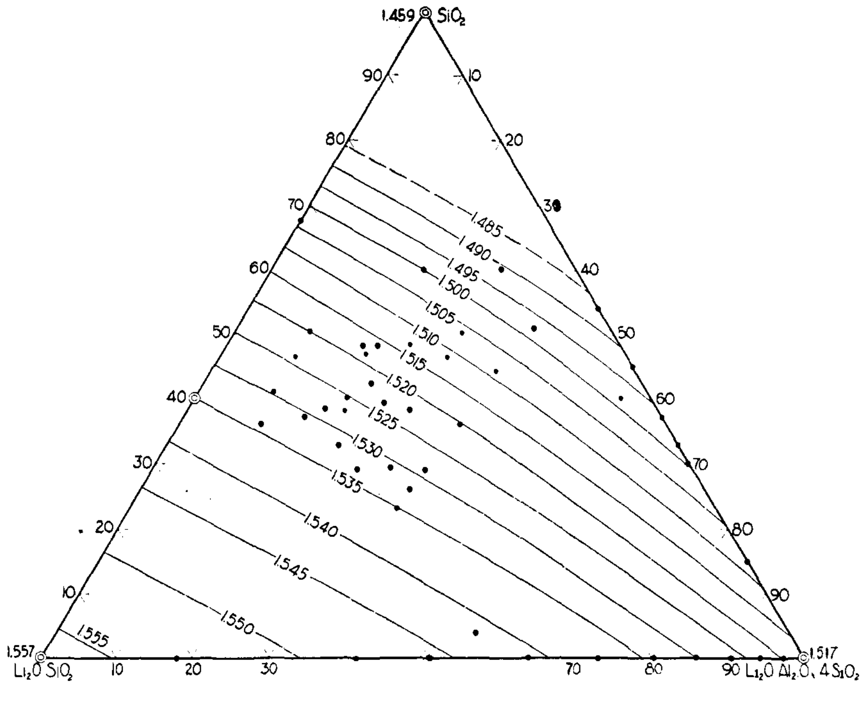

Fig. 2.—Isofracts for the quenched liquids in the system lithium metasilicate–β-spodumene–silica.

β-Spodumene–Silica.—This system is part of the one investigated by Hatch[5] and the relevant portion is presented as Fig. 4. Because of its bearing on phase relations in the ternary system, runs were made to try to establish more closely the limit of the solid solution series extending from β-spodumene toward silica and to find the slope of the line indicating the limit of the solid solution series as the temperature is decreased below 1356°. From the data obtained on two mixtures, 26.54 and 39.27% silica, Hatch[5] estimated the limit of solid solution at 1356° to be about midway between these two points, and he indicated the boundary of the solid solution field below 1356° as a vertical, dashed line.

The data obtained on six mixtures in this study are summarized in Table III. These did not serve to establish the limits of solid solution much more accurately than the data of Hatch because of the inability either to determine the presence of small amounts of a second phase or to determine accurately by optical or X-ray means the composition of a β-spodumene solid solution. On the basis of slight shifts of X-ray pattern lines, five different solid solutions were considered to be present in the mixtures, indicated in Table III as SS (1), SS (2), SS (3), SS (4), and SS (5). The limit of solid solution at 1356° is taken as 34 ± 2% silica, with no change indicated with decreasing temperatures.

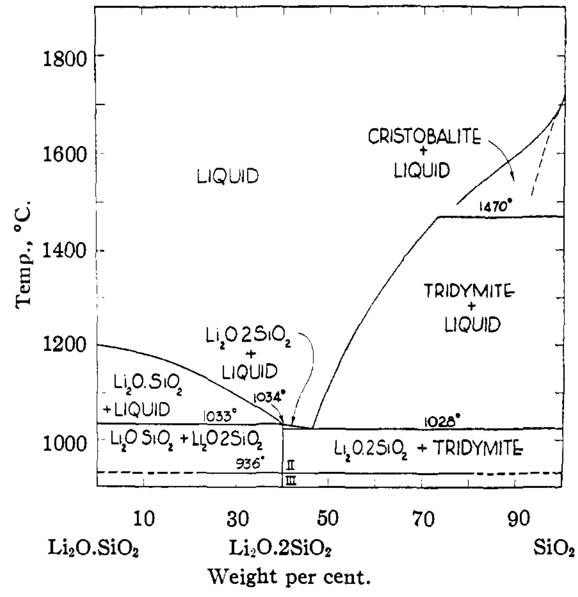

Fig. 3.—Equilibrium diagram of the system lithium metasilicate–silica, after Kracek.[4]

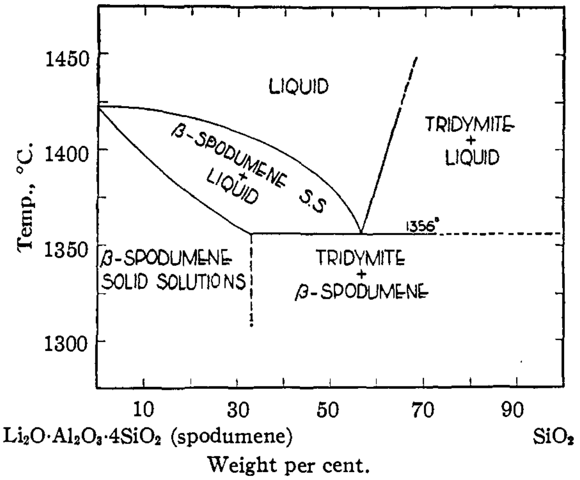

Fig. 4.—Equilibrium diagram of the system spodumene–silica, after Hatch.[5]

Lithium Metasilicate-β-Spodumene.—Thirteen mixtures were prepared and studied in this system. The equilibrium diagram constructed from the data obtained is shown as Fig. 5.

TABLE III

BINARY SYSTEM SPODUMENE–SILICA

Composition in wt. % Spodumene	Silica	Temp., °C.	Time, hours	Phases present
46	54	1360	3	SS (1), glass (?)
46	54	1350	8	SS (1), Tr
46	54	975	100	SS (1), Tr
55	45	1360	3	SS (1), glass
55	45	1350	8	SS (1), Tr
55	45	975	100	SS (1), Tr
63	37	1360	3	SS (1), glass
63	37	1350	8	SS (1)
63	37	975	100	SS (1), Tr (?)
67	33	1360	3	SS (2)
67	33	1350	8	SS (2)
67	33	975	100	SS (2)
70	30	1360	3	SS (3)
70	30	1350	8	SS (3) ?
70	30	975	100	SS (3) ?
65	35	1360	3	SS (4)
65	35	1350	8	SS (4)
65	35	975	100	SS (5) ?

TABLE IV

BINARY SYSTEM LITHIUM METASILICATE–SPODUMENE

In this and succeeding tables the following abbreviations are used: Cr = cristobalite, Tr = tridymite, Qz = quartz, Sp = β-spodumene, DS = lithium disilicate, MS = lithium metasilicate, V = very.

Composition in wt. % Metasilicate	Spodumene	Temp., °C.	Time, minutes	Phases present
100	0	1202	30	All glass
100	0	1200	35	Rare MS, glass
100	0	1199	30	All MS
82	18	1190	30	All glass
82	18	1186	30	Rare MS, glass
82	18	1028	30	MS, glass
82	18	1025	30	MS, Sp
58	42	1116	30	V Rare MS, glass
58	42	1028	30	MS, glass
58	42	1025	30	MS, Sp
49	51	1065	30	All glass
49	51	1060	30	Rare MS, glass
49	51	1030	30	MS, glass
49	51	1025	45	MS, Sp
36	64	1116	30	All glass
36	64	1100	40	Rare Sp, glass
36	64	1030	30	Sp, glass
36	64	1023	30	Sp, MS
27	73	1200	35	V Rare Sp
27	73	1030	30	Sp, glass
27	73	1023	30	Sp, MS
20.5	79.5	1275	30	All glass
20.5	79.5	1265	30	Rare Sp, glass
20.5	79.5	1023	30	Sp, glass
20.5	79.5	1018	60	Sp, MS
14	86	1335	30	All glass
14	86	1325	30	Rare Sp, glass
14	86	1024	40	Sp, glass
14	86	1015	30	Sp, MS
9.5	90.5	1380	30	All glass
9.5	90.5	1372	30	Rare Sp, glass
9.5	90.5	1024	720	Sp, glass
9.5	90.5	1018	60	Sp, MS
5.8	94.2	1408	30	All glass
5.8	94.2	1400	30	Rare Sp, glass
5.8	94.2	1028	30	Sp, glass (?)
5.8	94.2	1013	30	Sp, MS
2.8	97.2	1415	30	All glass
2.8	97.2	1408	30	Rare Sp, glass
2.8	97.2	1024	720	Sp, glass (?)
2.8	97.2	1018	30	Sp, MS (?)
0	100	1425	45	All glass
0	100	1421	40	Sp, little glass
0	100	1415	30	All Sp

A eutectic occurs at 1026° at the composition 54.6% spodumene, 45.4% lithium metasilicate. No appreciable solid solution is present. This is in contrast to the work of Ballo and Dittler[20] who found a series of solid solutions extending from lithium metasilicate to 60% spodumene, and in addition a 1:1 molar compound. The melting point of spodumene was determined as 1423 ± 2°, in agreement with Hatch,[5] in contrast to numerous other workers. A slight anomaly is found at the spodumene end, the temperature of appearance of the second phase being about 5° lower than 1026°. This is not a matter of undercooling, for crystalline material containing both lithium metasilicate and β-spodumene was used as starting material. No explanation was found for this phenomenon. The data from which the diagram was constructed are given in Table IV.

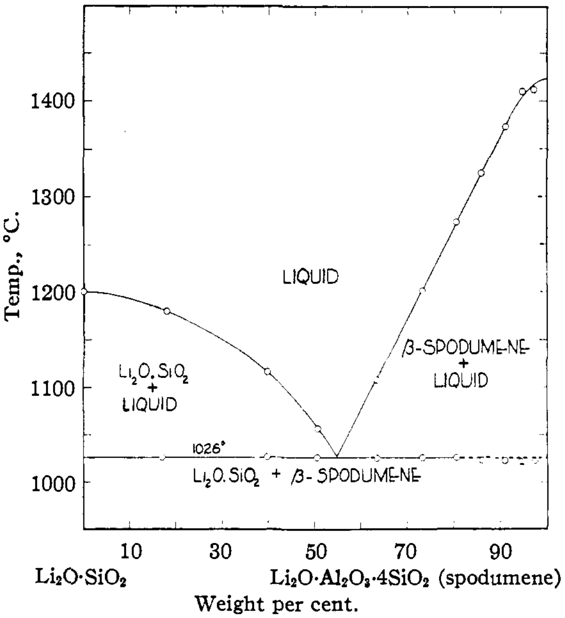

Fig. 5.—Equilibrium diagram of the system lithium metasilicate–β-spodumene.

The Ternary System Lithium Metasilicate–β-Spodumene–Silica

The phase equilibrium diagram for the system lithium metasilicate–β-spodumene–silica is shown

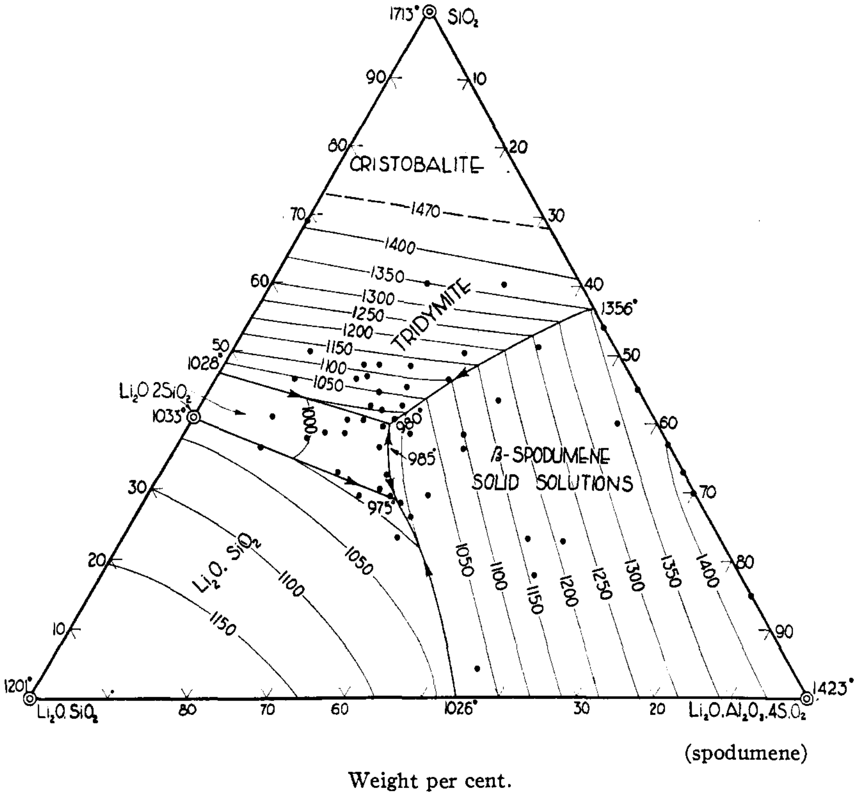

Fig. 6.—Equilibrium diagram of the system lithium metasilicate–β-spodumene–silica. Dots represent compositions of mixtures studied; heavy lines are boundary curves; light lines are isotherms.

in Fig. 6, constructed from data obtained on the forty-seven mixtures whose compositions are indicated by dots, and data from the binary systems. A summary of the essential data obtained for these mixtures is given in Tables V and VI. Heavy lines in Fig. 6 represent boundary curves; arrows shown indicate the direction of falling temperature. Lighter lines are isotherms.

The ternary system contains two invariant points, both eutectics, and a maximum on the boundary curve joining these two points. At one invariant point, lithium disilicate, tridymite and a β-spodumene solid solution (33% SiO_2) are in equilibrium at 980° with a liquid of the composition 39.2% silica, 26% spodumene and 34.8% lithium metasilicate (± 0.25% oxides). At the second invariant point lithium metasilicate, lithium disilicate and a β-spodumene solid solution (24% SiO_2) are in equilibrium with a liquid of the composition 39.2% metasilicate, 28.2% silica and 32.6% spodumene at 975°. At the maximum (point M in Fig. 7), lithium disilicate and a β-spodumene solid solution containing approximately 29.5% silica are in equilibrium with a liquid of approximately the composition, 36% silica, 37% metasilicate and 27% spodumene, at 985°.

Data for establishing the composition and temperature of the two eutectics are included in Table V. The location of the maximum could not be obtained directly from liquidus data, except as a rough approximation because of the very low temperature gradient along the boundary AB (Fig. 7). Two other considerations were used to fix the position of M. First, M must lie within the triangle DRT as all mixtures in this field crystallize only to two phases, lithium disilicate and a β-spodumene solid solution. Secondly, M must lie at the junction of the boundary curve with a three-phase boundary (*vide infra*) which when extended as a straight line passes through D.

To understand relationships in a ternary system of this type with solid solution it is essential that the positions of the three-phase boundaries[25] be known.[26] Accurate determination of most three-phase boundaries in this system is not possible because of the low temperature gradient along the boundary curve AB (Fig. 7), the inability to determine the composition of crystals of β-spodumene by either optical or X-ray methods, and the difficulty of recognizing very small amounts of a third phase especially if it is glass or some form of silica. It was possible, however, to establish with fair accuracy the positions of the two most significant three-phase boundaries, AT and BR. Other three-phase boundaries were drawn in at reasonable locations as shown in Fig. 7. The three-phase boundary AT (Fig. 7) joins liquid A with the β-spodumene solid solution which is in equilibrium with silica at 980° in the binary system β-spodumene–silica. Because the extent of solid solution in this binary system at 980° could not be determined accurately (Table III and Fig. 4), ternary data were necessary to fix the position of T. These data along with those used to establish the position of BR are listed in Table VI. The position of T was found to be 33% silica. This is corroboratory evidence therefore that the dashed line in Fig. 4 delimiting the β-spodumene solid solution field is approximately

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(25) The concept of three-phase boundaries is defined and described by N. L. Bowen, *Am. J. Sci.*, **38**, 222 (1914).

(26) Discussion of methods of determination of three-phase boundaries are given by N. L. Bowen, *ibid.*, **40**, 151 (1915), and (b) E. F. Osborn and J. F. Schairer, *ibid.*, **23**, 726 (1941).

vertical from 1356° to 980°. The silica content of R, which is not determined by binary relations, was found to be approximately 24%.

TABLE V

TERNARY SYSTEM LITHIUM METASILICATE–β-SPODUMENE–SILICA

Composition in wt. %			Temp., °C.	Time, minutes	Phases present
Meta-silicate	Spodumene	Silica			
Silica Field					
20	20	60	1350	120	All glass
20	20	60	1335	120	Rare Cr, glass
20	20	60	1050	30	Cr, glass
20	20	60	1030	30	Cr, Sp, glass
20	20	60	990	30	Cr, Sp, glass
20	20	60	985	45	Cr, Sp, DS
10	30	60	1360	100	Rare silica
10	30	60	1220	90	Cr, Sp, glass
10	30	60	990	30	Cr, Sp, glass (?)
10	30	60	985	30	Cr, Sp, DS (?)
40	10	50	1100	30	Glass, silica
40	10	50	1010	45	Tr, glass
40	10	50	1007	45	Tr, DS, glass
40	10	50	980	60	Tr, DS, Sp (?)
40	10	50	975	600	Tr, DS, Sp
20	30	50	1160	30	Rare silica, glass
20	30	50	1110	40	Qz, glass
20	30	50	1100	45	Qz, Sp, glass
20	30	50	980	30	Sp, Qz, glass (?)
20	30	50	975	30	Sp, Qz, DS
34	18	48	1110	40	All glass
34	18	48	1100	45	Cr, glass
34	18	48	990	40	Cr, glass
34	18	48	985	30	Qz, DS
34	18	48	975	30	Tr (?), Sp, DS
32	20	48	1105	30	Silica, glass
32	20	48	990	30	Tr, Qz, glass
32	20	48	985	60	Tr, DS, Qz
32	20	48	975	30	DS, Sp, Qz
28	24	48	1105	30	Cr, glass
28	24	48	995	40	Cr, Qz, glass
28	24	48	985	30	Qz, Sp
28	24	48	980	30	Qz, Sp, DS
34	19	47	1105	30	All glass
34	19	47	995	30	Cr, glass
34	19	47	985	45	Cr, glass
34	19	47	980	120	DS, Cr, Sp
36	19	45	1075	50	V rare silica, glass
36	19	45	990	50	Tr, glass
36	19	45	985	30	Cr, DS
36	19	45	980	30	Sp, DS, Qz
44	10	46	1050	40	V rare silica, glass
44	10	46	1015	30	Tr, glass
44	10	46	1012	30	Tr, DS, glass
44	10	46	983	30	Tr, DS, Sp (?)
44	10	46	975	40	Tr, DS, Sp
34	22	44	1050	40	Rare Cr, glass
34	22	44	985	30	Cr, glass
34	22	44	980	30	DS, Sp, Qz (?)
30	25	45	1075	50	Cr, glass
30	25	45	985	30	Qz, glass
30	25	45	980	60	Qz, Sp, glass (?)
30	25	45	975	60	Sp, DS, Qz (?)
36	22	42	1015	30	Rare Cr, glass
36	22	42	990	30	Cr, glass
36	22	42	985	30	DS, Qz, glass
36	22	42	980	180	DS, Sp, Qz (?)
35	24	41	1015	30	V rare Cr, glass
35	24	41	985	60	Qz, DS, Sp (?)
35	24	41	980	30	Qz, DS, Sp
24	30	46	1110	40	All glass
24	30	46	1105	30	Rare Cr, glass
24	30	46	1075	50	Cr, Sp, glass
24	30	46	985	30	Qz, Sp, glass (?)
24	30	46	980	30	Qz, Sp, DS
32	26	42	1025	120	Rare Cr, glass
32	26	42	995	40	Qz, Sp (?), glass
32	26	42	985	30	Qz, Sp, glass (?)
32	26	42	980	180	Qz, Sp, DS
34	26	40	990	50	Rare Cr, glass
34	26	40	985	30	Cr, Sp, glass
34	26	40	980	30	Qz, DS, Sp
Spodumene Field					
9.6	39.4	51	1250	60	V rare Sp, glass
9.6	39.4	51	1220	60	Sp, silica, glass
9.6	39.4	51	980	30	Sp, Qz, glass (?)
9.6	39.4	51	975	5000	Sp, Qz, DS (?)
33	29	38	1000	30	Rare Sp. glass
33	29	38	985	30	Sp, glass
33	29	38	980	50	Sp, DS
33	29	38	975	720	Sp, DS, silica (?)
18.5	38.2	43.3	1165	30	V rare Sp, glass
18.5	38.2	43.3	1105	30	Sp, silica (?), glass
18.5	38.2	43.3	980	130	Sp, silica (?), glass
18.5	38.2	43.3	975	720	Sp, DS, silica (?)
5.0	55	40	1360	100	Rare Sp, glass
5.0	55	40	1000	30	Sp, glass
5.0	55	40	980	30	Sp, silica (?), DS (?)
5.0	55	40	975	720	Sp, silica (?), DS (?)
34.8	36.1	29.1	1025	120	Rare Sp, glass
34.8	36.1	29.1	985	30	Sp, glass
34.8	36.1	29.1	980	30	MS, DS, Sp
39	33	28	985	30	Rare Sp, glass
39	33	28	980	30	MS, Sp
39	33	28	975	1000	MS, DS, Sp
38.3	35.7	26	1000	35	V rare Sp, glass
38.3	35.7	26	993	30	Sp, glass
38.3	35.7	26	985	60	MS, Sp, glass
38.3	35.7	26	980	100	MS, Sp, glass (?)
38.3	35.7	26	975	600	MS, DS, Sp
2.7	79	18.3			Only Sp detected below liquidus
41	55	4	1050	120	All glass
41	55	4	1035	30	Sp, glass
41	55	4	975	600	MS, Sp
Disilicate Field					
49	10	41	1020	30	All glass
49	10	41	980	30	DS, glass
49	10	41	975	30, 600	DS, Sp, Silica (?)
40	20	40	987	30	All glass
40	20	40	980	30	DS, glass

TABLE V (*Continued*)

Composition in wt. %			Temp., °C.	Time, minutes	Phases present
Meta-silicate	Spodu-mene	Silica			
40	20	40	975	30, 600	DS, Sp, silica (?)
38	22	40	990	30	All glass
38	22	40	987	30	Rare DS
38	22	40	980	30	Sp, DS, silica (?)
36	25	39	985	30	Rare DS, glass
36	25	39	980	30	Sp, DS, glass (?)
36	25	39	975	600	Sp, DS, silica (?)
47	16	37	1000	30	V rare DS, glass
47	16	37	985	30	DS, glass
47	16	37	980	30	DS, Sp
41.4	20.6	38	987	30	Rare DS, glass
41.4	20.6	38	985	30	DS, glass
41.4	20.6	38	980	70	DS, Sp
41.4	20.6	38	975	600	DS, Sp
44	18	38	1000	30	Rare DS, glass
44	18	38	985	30	DS, glass
44	18	38	980	30	DS, Sp (?)
44	18	38	975	2700	DS, Sp
38	26	36	985	30	DS, little glass
38	26	36	980	30, 600	DS, Sp
44	21	35	990	30	V rare DS, glass
44	21	35	985	35	DS, glass
44	21	35	980	30	NS, DS, Sp
45	22.5	32.5	1000	30	All glass
45	22.5	32.5	980	30	DS, glass
45	22.5	32.5	975	30	DS, MS, glass
39	29	32	990	30	All glass
39	29	32	980	30	DS, Sp, glass
39	29	32	975	30	DS, MS, Sp
41	29	30	990	30	All glass
41	29	30	975	30	SD, glass
41	29	30	970	100	DS, MS, Sp
40	31	29	985	30	All glass
40	31	29	980	30	DS, Sp, glass (?)
40	31	29	975	600	DS, MS, Sp
			Metasilicate Field		
53	11	36	1023	30	All glass
53	11	36	1018	30	Rare MS, glass
53	11	36	1015	40	MS, DS, glass
53	11	36	985	30	MS, DS, glass
53	11	36	980	30	MS, DS, Sp
44	27	29	990	30	Rare MS, glass
44	27	29	985	30	MS, glass
44	27	29	980	45	MS, DS, Sp
42	35	23	1012	30	All glass
42	35	23	1005	35	Rare MS, glass
42	35	23	995	40	MS, Sp, glass
42	35	23	980	30	MS, DS, Sp

TABLE VI

DATA INDICATING POSITIONS OF THREE-PHASE BOUNDARIES

Composition in wt. %			Temp., °C.	Time, minutes	Phases present
Meta-silicate	Spodu-mene	Silica			
20.8	56.7	22.5	1220	60	All glass
20.8	56.7	22.5	1210	30	Rare Sp, glass
20.8	56.7	22.5	990	75	Sp, MS (?), glass
20.8	56.7	22.5	986	60	Sp, MS, glass
20.8	56.7	22.5	975	600	Sp, MS, DS (?)
26.9	55.6	17.6	1160	60	All glass
26.9	55.6	17.6	1150	50	Rare Sp, glass
26.9	55.6	17.6	998	30	Sp, glass
26.9	55.6	17.6	995	30	Sp, MS, glass
25	52	23	1105	50	V rare Sp, glass
25	52	23	990	75	Sp, MS (?), glass
25	52	23	986	60	Sp, MS, glass
25	52	23	975	720	Sp, MS, DS, (?)
26.9	37.1	36	1100	30	V rare Sp
26.9	37.1	36	985	60	Sp, glass
26.9	37.1	36	980	100	Sp, DS
26.9	37.1	36	975	960	Sp, DS
26	36	38	1105	30	All glass
26	36	38	1075	50	Sp, glass
26	36	38	990	60	Sp, silica, glass
26	36	38	985	60	Sp, silica, glass (?)
26	36	38	975	960	Sp, DS, silica

Courses of crystallization and phase relations for other silicate systems of a similar type have been considered by various authors.[25,26,27] Consequently a series of isothermal planes and a detailed analysis of the crystallization and melting phenomena are not given. In Fig. 7, however, an isothermal plane for the temperature 970° is shown. This diagram illustrates the phase relationships existing 5° below the lowest temperature at which liquid can exist under equilibrium conditions. The ternary diagram is divided into four triangular areas by heavy lines. At equilibrium all mixtures within the triangle LKR will consist of lithium metasilicate and a β-spodumene solid solution whose composition will lie between K and R, the exact composition of the final solid solution depending on the original composition of the mixture. All mixtures in the triangle LRD will be composed of the three crystalline phases, lithium metasilicate, lithium disilicate and β-spodumene solid solution R. Within the area RDT, mixtures will have crystallized to only two phases, lithium disilicate and a β-spodumene solid solution of a composition between R and T. Finally mixtures lying within the area DTS contain the three phases, lithium disilicate, β-spodumene solid solution T, and tridymite.

During crystallization if equilibrium were not maintained, silica might appear in other forms, and it has already been mentioned that both quartz and cristobalite were present in the stability range of tridymite, inverting to the stable phase only after a very long time. Furthermore, failure to maintain equilibrium throughout the crystallization process may result in incompleteness of the continuous reaction between β-spodumene solid solutions and liquid. Thus, for example, although under equilibrium conditions mixtures in the area LRK crystallize to only two phases, if equilibrium is not maintained the liquid may not disappear until the eutectic B is reached

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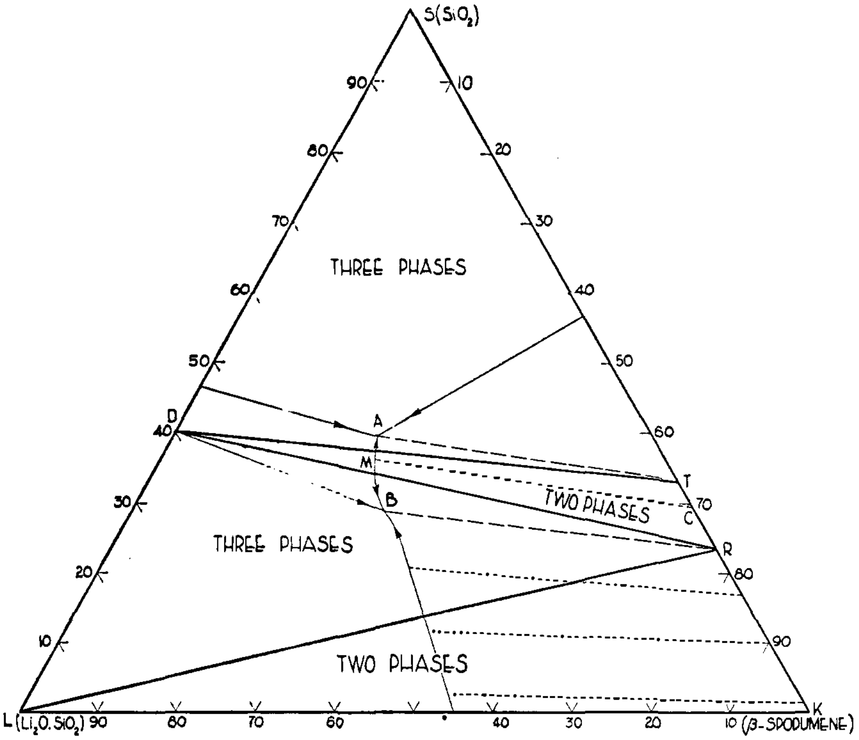
(27) N. L. Bowen, J. E. Schairer and E. Posnjak, *Am. J. Sci.*, **26** (5th series), 193 (1933).

at 975°. Hence some lithium disilicate will be present in the final mixture and furthermore the β-spodumene crystals may appear zoned, the outer zones being higher in silica content. It is possible for certain mixtures in this system to exhibit a reversal of zoning, even though the mixtures are cooled continuously.[27b] This is true for all mixtures in the area BRCM (Fig. 7), M being the position of the maximum on the boundary curve AB, and MC being the three-phase boundary intersecting the boundary curve at M. During the cooling of these mixtures from the liquidus temperature until they meet the boundary curve, the composition of the solid solution in equilibrium with liquid changes toward silica. On further cooling, as the composition of the liquid moves toward the eutectic B along the boundary curve, the composition of the solid solutions in equilibrium with these liquids moves away from silica. If reaction of crystals with liquid is not complete, zoned β-spodumene crystals may appear having an inner and outer zone both poorer in silica than an intermediate zone.



Weight per cent.

Fig. 7.—An isothermal plane indicating phase equilibrium relations at 970°. Heavy solid lines bound four composition triangles within which either two or three phases are present as indicated; light solid lines are boundary curves; light dashed lines are three phase boundaries; A and B are eutectics; M is a maximum on the boundary curve AB.

Summary

Phase equilibrium relations in the binary system lithium metasilicate–β-spodumene and in the ternary system lithium metasilicate–β-spodumene–silica are presented. In the binary system no solid solution or binary compound is present, a eutectic occurring at 1026° and at the composition 45.4% lithium metasilicate. In the ternary system two eutectics and a maximum appear, as shown in Figs. 6 and 7. The positions of three-phase boundaries and the phase relations below the temperature at which liquid is present in the ternary system are shown in Fig. 7.

Evidence is presented for believing that the coördination number of Al^{3+} in the high temperature forms of spodumene and eucryptite is four whereas in the low temperature, natural modifications the coördination number is six. Neither petalite nor the natural form of spodumene was synthesized, and the composition of the former is still in doubt.

Quartz commonly appears in the ternary system at temperatures above its stability range. X-Ray data obtained on this quartz at room temperature suggest that ions other than Si^{4+} and O^{2-} are present in the quartz in sufficient quantities either to shift the X-ray lines of low quartz or to stabilize the high form. High cristobalite appears at room temperature in some mixtures.

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