PHASE EQUILIBRIUM IN THE SYSTEM: $Li_2O \cdot Al_2O_3–SiO_2$*

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CONTENTS

ABSTRACT

Liquidus and solidus temperatures for almost all of the 21 preparations along the line $Li_2O \cdot Al_2O_3–SiO_2$, from 85 to 22 per cent silica, have been determined. Three component compounds in the system are β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, high temperature form, melts congruently at 1423°C.) and β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$, melts with dissociation at 1397°C.). No compounds having the compositions of petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$) or "lithium orthoclase" ($Li_2O \cdot Al_2O_3 \cdot 6SiO_2$) are stable above the solidus. Petalite dissociates at 950°C. or less.

This system includes five or six fields: (1) the silica field, (2) the field of β-spodumene-silica solid solution, (3) the field of β-spodumene solid solution, (4) the field of β-eucryptite solid solution, (5) the γ-alumina field, and (6) the lithium aluminate field (?). Fields (1) and

(2) appear to be binary; fields (3) and (4) are essentially binary at the liquidus but show ternary behavior 10° to 80° below the solidus, small amounts of mullite and/or α-alumina separating from the solid solution series; field (5) is ternary.

Attempts to synthesize α-spodumene (mineral) hydrothermally at pressures below 100 atmospheres and at temperatures of 400° to 550°C. failed. In every case β-spodumene crystallized from the spodumene glass.

INTRODUCTION

The alkali aluminosilicates are among the most important rock-forming minerals in nature. The phase equilibrium relationships in the potassium and sodium aluminosilicate systems have been partly determined. However, little is known about such relationships in the lithium aluminosilicate system.

The ternary system, Li_2O–Al_2O_3–SiO_2, contains three compounds that occur in nature: eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$), spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$), and petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$). Because these three compounds all have a molecular ratio of one to one between lithia and alumina, it seemed desirable to first investigate the composition line extending from silica to $Li_2O \cdot Al_2O_3$.

The lithium aluminosilicate minerals are not abundant in nature but they are important constituents of lithium pegmatites. A possible clue to the physical-chemical conditions under which these minerals are formed in the pegmatites is furnished by this investigation. The existence or absence of other compounds in the system, such as "lithium orthoclase" ($Li_2O \cdot Al_2O_3 \cdot 6SiO_2$) also may be of interest to the geologist and the mineralogist.

Furthermore, because lithia imparts many desirable properties to glasses and glazes, and because spodumene and petalite are sometimes used as a source of lithia, the investigation may be of interest to the ceramic and glass industries.

PREVIOUS INVESTIGATIONS

Investigations of the system $Li_2O \cdot Al_2O_3$–SiO_2 have been confined mainly to the synthesis of eucryptite, spodumene, and petalite, and to the determination of the melting and inversion temperatures of these compounds. Most of the investigations were made before 1914, all of them before 1921. Since then, our knowledge of silicate systems has increased manyfold and the techniques of thermal, microscopic, and x-ray analysis have been perfected and coordinated to an ever-increasing degree. It is to be expected, therefore, that much of the earlier data are inaccurate, especially the temperature determinations.

Possibly the earliest attempt to synthesize lithium aluminosilicates was reported by Hautefeuille[15] in 1880. He prepared compounds of

$LiO \cdot Al_2O_3 \cdot 5SiO_2$ (1:1:5),* (1:1:6), and (3:4:30) by fusion of the ingredients with lithium vanadinate or tungstate as a flux. In 1890, Hautefeuille and Perrey[16] reported the synthesis of the lithium equivalent of nepheline, now known as eucryptite (1:1:2).

Many other attempts to synthesize eucryptite, spodumene, and petalite have been made by Weyberg[31] (1905), Stein[27] (1907), Ginsberg[14] (1912), Endell and Rieke[10] (1912), Ballo and Dittler[2] (1912), and Jaeger and Simek[17] (1914). It was generally recognized by these men that the physical properties of the synthetic compounds differed from those of the mineral of corresponding composition.

Investigations on the inversion of the lithium aluminosilicate minerals were confined almost entirely to spodumene. Brun[6] (1902) and Tammann[28] (1903) noted that the density of spodumene decreased markedly when heated for a short time at a temperature of about 1000°.† By means of specific gravity—temperature and refractive index—temperature curves Endell and Rieke[10] showed that spodumene underwent a change at 950° but thought this to be the melting temperature. Ballo and Dittler,[2] Jaeger and Simek,[17] and Meissner[22] (1920) concluded that the inversion of α-spodumene (mineral) to the high temperature β-form was monotropic. Endell and Rieke also noted that petalite became isotropic-amorphous at 1050°.

Of the several determinations of the melting temperatures of the lithium aluminosilicate minerals (M) and synthetic products (S) (see Table 1), only the method of "quenching" used by Jaeger and Simek gave

TABLE 1. REPORTED MELTING TEMPERATURES OF PETALITE, SPODUMENE, AND EUCRYPTITE

Name	Date	Petalite	Spodumene	Eucryptite	Method
Cusack[8]	1897	—	(M) 1173°	—	Meldometer
Brun[6]	1902	(M) 1270°	—	—	—
Doelter[9]	1907	—	(M) 1080°	—	PtRh thermel, heating curve.
Ginsberg[14]	1912	—	—	(S) 1307°	Cooling curve
Endell,[10] Rieke	1912	(M) 1050° (1340°)	(M) 950° (1380°)	—	PtRh thermel, heating curve.
Ballo,[2] Dittler	1912	(S) 1200°	(S) 1275°	(S) 1330°	PtRh thermel, cooling curve.
Fletcher[12]	1913	—	(M) 1223°	—	Meldometer
Jaeger,[17] Simek	1914	—	(M) 1418–1428° (S) 1401–1420°	(S) 1388°	PtRh thermel, quench method.

* Hautefeuille used the formula LiO for lithium oxide.

† All temperatures in this report are in degrees Centigrade.

good results. The cooling curve method gave low results because of the marked undercooling of lithium aluminosilicate melts. Another source of error in the determination of the melting temperature of spodumene was the failure of several early workers to recognize that the swelling and powdering of spodumene when heated above 900° were inversion phenomena instead of melting.

For a more general review of the literature the reader is referred to Mellor's[23] treatise.

<div align="center">EXPERIMENTAL PROCEDURE</div>

MATERIALS

The silica was obtained from colorless rock crystal quartz that contained only a few small inclusions of gas bubbles and magnetite. The crystals were crushed in a steel mortar, the powder treated with hot hydrochloric acid to remove traces of iron, and then inverted to cristobalite by heating in an electric furnace to a temperature of about 1400° for about twelve hours. The silica was then ground in an agate mortar, the powder treated with hot aqua regia to remove traces of platinum. The purified silica yielded a residue of 0.02 per cent when evaporated with hydrofluoric and sulfuric acids.

The alumina was obtained from the General Chemical Company. A spectrographic analysis of the alumina revealed the presence of sodium as the most abundant impurity. The material was purified by boiling three times in ammonium chloride solution followed by washing with hot water. The alumina was then fired. A quantitative spectrographic analysis of the purified material showed that most of the sodium had been removed and that not more than 0.05 per cent soda remained.

As a source of lithia, Baker's lithium carbonate was used. A quantitative spectrographic analysis indicated that the amount of soda present was not greater than 0.15 per cent ($Li_2O + Na_2O = 100\%$). The material was used without further purification.

THE $Li_2O \cdot Al_2O_3$–SiO_2 PREPARATIONS

The lithium aluminosilicate glasses were prepared by three methods: (1) by adding a constant amount of alumina and a variable amount of silica to previously prepared lithium silicate glass or crystalline material; (2) by mixing two lithium aluminosilicate glasses; and, (3) by adding a variable amount of silica to crystalline $Li_2O \cdot Al_2O_3$.

The advantage of the first method is that no further volatilization of lithia is detected when the alumina and silica are added to the lithium silicate. Also, this method permits the fixation of lithia at a much lower

temperature than is possible in any other way. The second method allows additional intermediate glasses to be prepared quickly and easily. The third method is probably best for mixtures low in silica. Most of the preparations were made by the first two methods.

The lithium aluminosilicate glasses were made in a platinum crucible by melting the ingredients in an electric furnace at about 1500°. To ensure homogeneity of the glasses, the batches were crushed, mixed, and melted five successive times. The products appeared to be homogeneous when examined under a petrographic microscope.

As a check on the accuracy of the synthesis of the glasses, seven of them were analyzed chemically. One-half gram samples were fused with sodium carbonate, dissolved in hydrochloric acid, and dehydrated and filtered twice to separate the silica from the filtrate. Pure silica was determined by evaporating the impure silica with hydrofluoric and sulfuric acids. Alumina was determined by precipitation with 8-hydroxyquinoline.

The results of the chemical analyses (Table 2) show that all of the glasses contain silica and alumina within ± 0.2 per cent of the intended values. The probable limit of error of the analyses for both silica and alumina is ± 0.2 per cent.

TABLE 2. QUANTITATIVE CHEMICAL ANALYSES OF $Li_2O \cdot Al_2O_3$–SiO_2 GLASSES

No. of Prep.	Weight per cent SiO_2		Weight per cent Al_2O_3	
	Calc.	Anal.	Calc.	Anal.
3	78.5	78.4	16.7	16.8
6	64.6	64.6	27.4	27.5
8	56.0	56.0	34.0	34.2
9	53.0	53.0	36.4	n.d.
10	47.7	47.8	40.5	40.4
19	46.0	45.9	41.8	n.d.
20	44.0	44.1	43.3	n.d.

As a further check on the accuracy of the synthesis of the glasses, their refractive indices were determined (Table 3) and plotted as a curve (Fig. 1). The measurements were made on the water-quenched, unannealed glasses, using the oil immersion method and sodium (D) light. The temperature varied from 22° to 28°. After matching the refractive indices of glass and oil, the index of the oil was determined immediately by means of the Abbe refractometer.
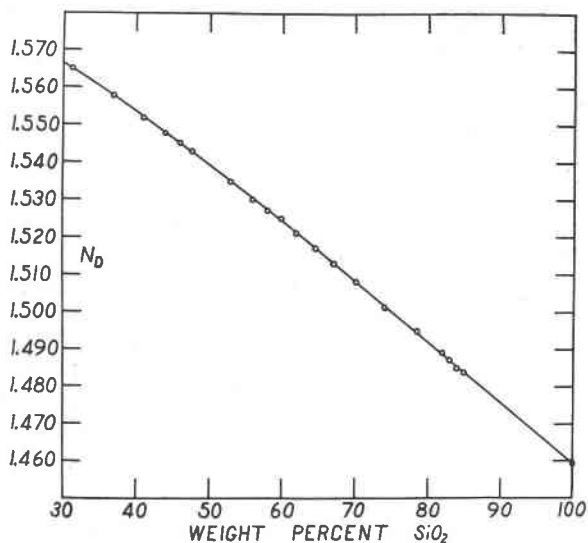
FIG. 1. Refractive index—composition curve of $Li_2O \cdot Al_2O_3$–SiO_2 glasses.

TABLE 3. REFRACTIVE INDICES OF $Li_2O \cdot Al_2O_3$–SiO_2 GLASSES

No. of Prep.	Weight per cent SiO_2	Refr. Index
*	100	1.459
1	85.0	1.484
16	84.0	1.485
15	83.0	1.487
2	82.0	1.489
3	78.5	1.495
4	74.0	1.501
5	70.0	1.508
33	67.0	1.513
6	64.6	1.517
32	62.0	1.521
7	60.0	1.525
24	58.0	1.527
8	56.0	1.530
9	53.0	1.535
10	47.7	1.543
19	46.0	1.545
20	44.0	1.548
21	41.0	1.552
13	37.0	1.558
12	31.3	1.565

* R. B. Sosman, The Properties of Silica, *Monograph Am. Chem. Soc.*, No. **37**, 592–4 (1927).

The limit of error in index is believed to be ± 0.001; all the determined points lie within this range of the curve. From 100 per cent silica to about 55 per cent, the relationship is linear, within the limit of error. Below about 55 per cent the curve departs from the straight line in increasing amount. Because of the high melting point and the great rapidity of crystallization, it is not possible to extend the curve much below 31 per cent silica.

THE PHYSICAL EQUIPMENT AND EXPERIMENTAL CONDITIONS

A detailed description of the furnaces, the thermoregulator, and the thermocouple that were used in the investigation was given by Faust[11] who constructed the physical plant. The only noteworthy change in equipment was the substitution of a Leeds and Northrup type K potentiometer for the Wolff model used by Faust. The potentiometer-thermocouple system was not shielded.

Most of the temperature measurements were in the range from 1340° to 1430°. At these elevated temperatures it was difficult to keep the temperature of the "hot spot" constant. Most serious in its effect on temperature control was the fluctuation in the current output of the motor-generator. Unless compensated for manually, temperature fluctuations of 10° to 15° would occur several times a day. In spite of this difficulty, however, the temperature was kept constant to within five degrees during most runs and to within three degrees on most of the critical runs made to locate melting temperatures more accurately.

It was not possible to make accurate night runs due to the current fluctuations and also to volatilization of the platinum wire with which the furnace was wound. The latter caused a drop in temperature of three to ten degrees overnight.

All temperature measurements were made with a Pt: 90Pt 10Rh thermocouple that was calibrated at the following fixed points:

Gold...1062.6°C.
Diopside ($CaMgSi_2O_6$)...........................1391.5°C.

Because most of the temperatures measured were within $\pm 40°$ of the diopside melting temperature, this calibration point was used almost exclusively to correct the potentiometer readings. A calibration was made after almost every determination of a liquidus or solidus temperature. Electromotive force readings were converted into temperatures by means of standard tables.[1] The diopside was kindly furnished by the Geophysical Laboratory.

TABLE 4. LIQUIDUS AND SOLIDUS TEMPERATURES OF $Li_2O \cdot Al_2O_3$–SiO_2 PREPARATIONS

Prep. No.	Composition, weight per cent			Liquidus temp. °C	Time, hours	Primary phase	Solidus temp. °C	Time, hours	Phases
	Li_2O	Al_2O_3	SiO_2						
1	3.4	11.6	85.0	1382 ± 5	8–12	Tridymite	1356 ± 3	3–5	Tridymite+β-spodumene-silica solid solution
16	3.6	12.4	84.0	1367 ± 3	6–10	β-spodumene-silica s.s.	n.d.		S.S.+tridymite
15	3.9	13.1	83.0	1371 ± 3	3–6	Ditto	n.d.		Ditto
2	4.1	13.9	82.0	1380 ± 3	2–6	Ditto	n.d.		Ditto
3	4.9	16.6	78.5	1397 ± 3	6–10	Ditto	1355 ± 5	10–12	Ditto
4	5.9	20.1	74.0	1413 ± 3	8–12	Ditto	1365 ± 5	10–12	β-spodumene-silica s.s.
5	6.8	23.2	70.0	1420 ± 4	12–15	Ditto	n.d.		Ditto
33	7.5	25.5	67.0	n.d.		Ditto	1404 ± 5	8–11	Ditto
6	8.0	27.4	64.6	1423 ± 3	6–20	β-spodumene	None		β-spodumene s.s.
32	8.6	29.4	62.0	n.d.		β-spodumene s.s.	1407 ± 5	11–12	β-spodumene s.s.+β-eucryptite s.s.
7	9.1	30.9	60.0	1418 ± 4	11–12	Ditto	1408 ± 5	9–13	β-eucryptite s.s.
24	9.5	32.5	58.0	1412 ± 4	6–11	Ditto	1402 ± 4	7–11	Ditto
8	10.0	34.0	56.0	1406 ± 4	7–11	β-eucryptite s.s.	n.d.		Ditto
9	10.6	36.4	53.0	1403 ± 4	10–12	Ditto	1399 ± 4	9–11	Ditto
10	11.8	40.5	47.7	1397 ± 4	9–11	β-eucryptite	None		γ-alumina+β-eucryptite-like s.s. (dissociates)
19	12.2	41.8	46.0	1421 ± 3	3–4	γ-alumina	1390 ± 4	8–12	Ditto
20	12.7	43.3	44.0	1450 ± 5	3–4	Ditto	1387 ± 5	7–13	Ditto
21	13.4	45.6	41.0	1490 ± 5	2–6	Ditto	1376 ± 5	7–13	Ditto
13	14.3	48.7	37.0	n.d.		Ditto	1361 ± 5	7–14	Ditto
12	15.7	53.1	31.3	n.d.		Ditto	1340 ± 5	6–12	γ-alumina+lithium aluminate-like s.s. (?)
22	17.7	60.6	21.7	n.d.		Ditto	1371 ± 5	9–12	Ditto
TERNARY COMPOSITIONS OFF THE LINE									
17	5.9	10.1	84.0	1290 ± 5	4–13	Tridymite	1140 ± 20	12–24	Tridymite+an unidentified phase
18	3.0	13.0	84.0	n.d.		Mullite	n.d.		Mullite
28	6.3	28.9	64.8	1425 ± 5	2–12	β-spodumene-like phase	1385 ± 5	2–15	Mullite+β-spodumene-silica s.s.
29	10.0	24.4	65.6	1415 ± 6	2–12	β-spodumene-like phase	1400 ± 10	6–12	Peculiar dissociation of homogeneous phase, no mullite
31	20.4	39.0	40.6	1343 ± 20	24	γ-alumina	n.d.		

Note: s.s. = solid solution.

The high viscosity of the lithium aluminosilicate melts made it necessary to employ the "quench method" for determining melting temperatures. This method was originally described by Shepherd, Rankin, and Wright[26] in 1909 and has since been mentioned many times in the reports of the members of the Geophysical Laboratory of the Carnegie Institution. As is usually the case in investigations of this kind, these experiments were carried out in an oxidizing atmosphere and under a pressure of one atmosphere.

EXPERIMENTAL RESULTS

The data presented in Table 4 and Fig. 2 represent a summary of the many quenching experiments made during the investigation of this problem. A brief outline of the principal facts follows.

From 100 per cent silica to 64.6 per cent (β-spodumene) the system appears to be binary and is divided into fields of silica and β-spodumene-silica solid solution by a eutectic point at 84.5 per cent and 1356°. The solid solution extends up to about 76 per cent silica beyond which tridymite crystallizes as the secondary phase. Petalite (78.5 per cent) or "lithium orthoclase" (73.2 per cent) are not stable at the liquidus. Only β-spodumene has a clearly defined congruent melting temperature at about 1423°.

From 64.6 to 47.7 per cent silica (β-eucryptite) the system behaves essentially like a binary system above the solidus and is divided into fields of β-spodumene solid solution and β-eucryptite solid solution by a peritectic point at about 57.3 per cent. Above the solidus in both of the fields the solid solutions show an increasing amount of dissociation into an unknown fibrous product as the silica decreases. At temperatures ranging from 10° to 80° below the solidus these fields show ternary behavior with small amounts of mullite forming in the β-spodumene solid solutions and somewhat larger amounts of mullite and/or α-alumina forming in the β-eucryptite solid solution. The compound β-eucryptite is unstable and dissociates into γ-alumina and a β-eucryptite-like substance just below 1397°, the liquidus temperature.

From 47.7 to less than 22 per cent silica the system is ternary and passes through the γ-alumina field. A secondary phase of β-eucryptite-like solid solution (unstable) extends from 47.7 to 31.3 per cent and at a lower silica content than 31.3 per cent the secondary phase is a lithium aluminate (?) solid solution.

With this brief summary of the system to serve as a guide, some of the fields will be described in greater detail.
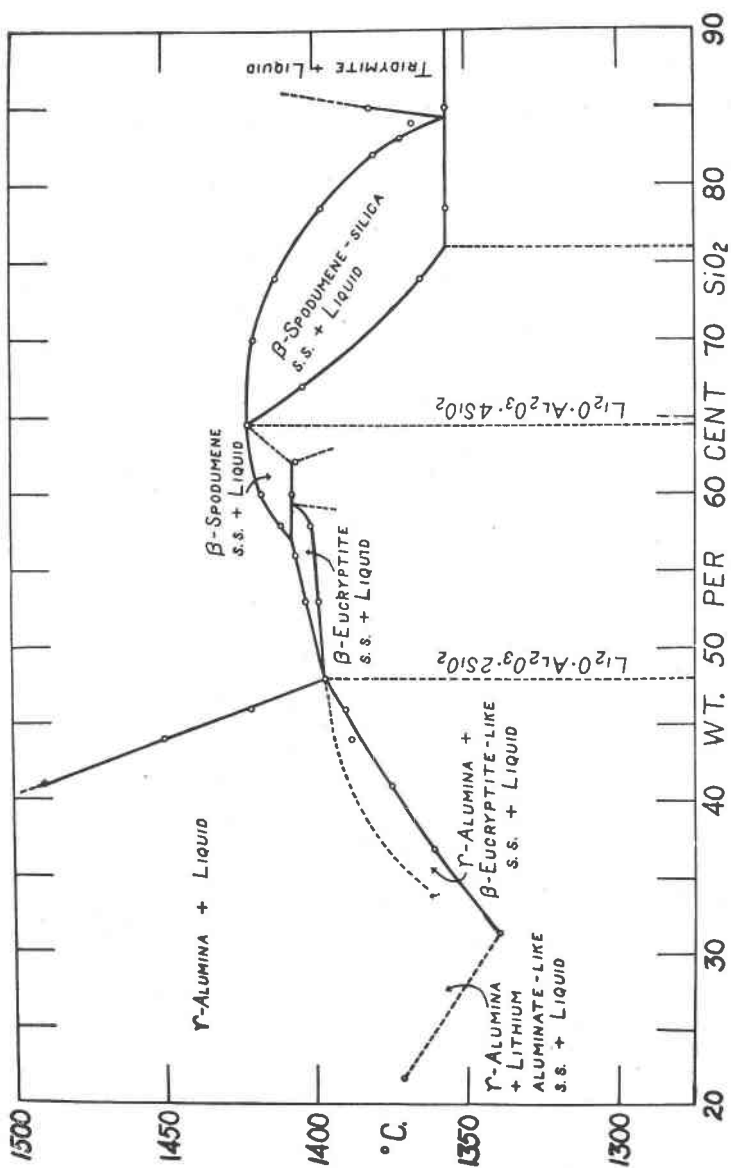
FIG. 2. Liquidus and solidus curves of $Li_2O \cdot Al_2O_3 - SiO_2$ preparations.

THE SILICA FIELD

The liquidus curve was not determined for this field because the high temperature causes rapid burning out of the furnace. An additional difficulty is the very great viscosity of the melts in the silica field. The reluctance of crystalline phases to go into solution makes it difficult to prepare homogeneous glasses.

The liquidus curve may be located approximately by constructing a curve through the points 100 per cent, 1713° and 85 per cent, 1382°. The
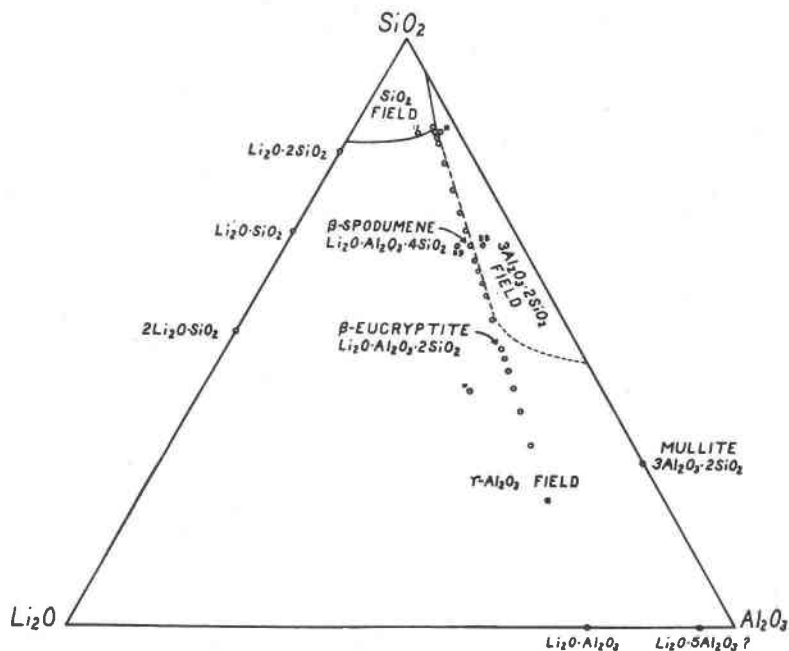
FIG. 3. Fields in the system Li₂O–Al₂O₃–SiO₂.

latter point lies just within the silica field with tridymite the primary phase. The shape of the liquidus is probably similar to that determined by Kracek[20] for the silica field in the system, Li₂O–SiO₂.

The approximate boundary of the silica field in the ternary system Li₂O–Al₂O₃–SiO₂ may now be established from the data of Kracek, Bowen and Greig,[5] and the writer. This and the location of all compositions investigated by the writer are plotted in Fig. 3.

THE FIELD OF β-SPODUMENE-SILICA SOLID SOLUTION

The determination of the liquidus curve for this field presented no great difficulty. Although the viscosity of the melts increases directly

with the silica content, the time necessary to obtain equilibrium decreases markedly. It is doubtful if twelve hours is sufficient time to obtain equilibrium in melts with a silica content less than 70 per cent.

The solidus curve is located only approximately but the general character of the curve is probably correct. The existence of solid solution was established by optical and x-ray powder examination of the crystalline products. A fairly regular variation in the spacing of the lines on the x-ray photographs and a small but regular variation of the refractive indices constitute the evidence for solid solution.

No compound or solid solution with the composition of petalite exists at temperatures above about 950°. Synthetic material of the composition of petalite was held at temperatures ranging from 1356° down to about 1140°, and all contained 10 to 15 per cent of an interstitial glass-like phase which probably is silica in some form.

Samples of the mineral petalite when heated at temperatures of about 950° and 1050° for 12 and 7 hours, respectively, dissociated to a crystalline product having the same optical properties as the synthetic material of the same composition and contained 10 to 15 per cent of the same interstitial glassy phase. X-ray powder photographs of both of these products were quite similar. The liquidus temperature of an unaltered, pure-looking petalite from Greenwood, Maine (U.M. no. 4170), was determined to be 1399°. This value compares favorably with the 1397° obtained for the artificial product.

The Solid Solution Fields of β-Spodumene–β-Eucryptite

General considerations: The determinations of liquidus and solidus temperatures in these fields were especially difficult because all compositions tend to superheat and the refractive indices of the glasses are very close to those of the crystalline products. According to Morey,[24] "overheating is a common occurrence," especially in complex silicate melts. That superheating takes place in this system is not surprising because this phenomenon has long been recognized in the corresponding potassium and sodium aluminosilicate systems.

In order to approach equilibrium conditions the samples must be held for long periods of time at a constant temperature. For reasons mentioned previously, it was not possible to make constant temperature runs of much longer duration than about twelve hours. Runs of one hour duration gave liquidus temperatures about five degrees higher than the values indicated in the phase diagram. It does not appear likely that periods of heating for longer than twelve hours would lower the liquidus temperatures appreciably.

The crystalline products have a marked tendency to recrystallize and to become coarse-grained when held near their melting temperatures, both above and below. When the grains begin to melt, the product is a granular aggregate of crystalline material with discrete grains of glass and not the normal interstitial arrangement of glass. Measurements of the refractive indices of the glasses indicate that the crystal aggregates melt to liquids having compositions within one per cent silica of the composition of the sample, the compositions usually lying on the high silica side of the point rather than on the low silica side as expected. All this is indicative of superheating.

Glasses in the β-spodumene–β-eucryptite fields devitrify readily when heated between 1000° and 1100° for fifteen minutes. X-ray powder photographs of the devitrified materials reveal a fairly regular shift of the lines of high-angle reflection indicating complete solid solution between the two end components. Beta-eucryptite solid solutions when heated near the solidus temperature give x-ray patterns which are closely similar, if not entirely identical, with those obtained from the devitrified glasses, but preparations in the β-spodumene field when subjected to the same treatment show patterns similar to the devitrified glasses but contain more lines of high-angle reflection. This probably indicates minor structural changes in the β-spodumene solid solution, possibly due to the exsolution of a second crystalline phase.

In addition to the thermal evidence for a peritectic point at 57.3 per cent silica and 1408°, there is ample optical evidence of such a reaction. The β-spodumene-like material is uniaxial positive while the β-eucryptite solid solution is uniaxial negative; also, there is a small but easily determined difference in their refractive indices. An examination of samples of preparation no. 24 reveals all stages in the transition of the crystalline product from the β-spodumene phase to the β-eucryptite phase, with decrease in temperature. Attention is called to the material no. 24-I (Table 5) which originally formed β-eucryptite solid solution when heated at about 1355° but inverted back to a β-spodumene-like phase when heated between 1400° and 1405°. This indicates that the inversion temperature may be somewhat lower than the 1408° indicated in the phase diagram.

The field of β-spodumene solid solution: As a check on the melting temperature of artificial β-spodumene, that of kunzite from Pala, California, was determined to be 1423° while that of spodumene from the Black Hills, South Dakota, was 1419°. The artificial material fuses at 1423°. These values fall within the 1418° to 1428° range given by Jaeger and Simek[17] for natural spodumenes.

The evidence for at least a limited solid solution in the β-spodumene field is revealed by: (1) a slight increase in the refractive indices of the crystalline products from 64.6 to 60 per cent silica; (2) x-ray powder photographs which show a small but fairly regular shift in the lines of high-angle reflection; (3) a solidus temperature for preparation no. 32 which is the same, or slightly less, than is shown by preparation no. 7; and, (4) the presence of a β-eucryptite-like phase as rims around the β-spodumene in preparation no. 7, when it is heated below the solidus for several hours. The writer tentatively interprets the β-spodumene field as consisting of a limited solid solution, extending between 64.6 and 62 per cent silica.

When preparations in this field are heated for about three to twelve hours or more, varying amounts of a fine-grained fibrous product exsolves from the solid solution. The resulting intergrowth may be likened to a film and fine string perthite, commonly observed in potash feldspar. The dissociation takes place above the solidus as well as below it; both substances, however, appear to melt at the same time, probably due to the superheating effect. The amount of this material and the rate at which it exsolves increase with decreasing silica, beginning with a trace in β-spodumene and increasing to a maximum at about 57 per cent silica. It develops first as short fibers perpendicular to the grain borders and spreads inward. The marked ability of the β-spodumene solid solution to recrystallize appears to cause expulsion of a part of this material from the grains and the development of interstitial stringers around the grains. Because of the very fine-grained nature of this exsolution product and the resulting interference of the host material, its optical properties are extremely difficult to determine. The coarser stringers are weakly birefringent and probably have positive elongation. The refractive index is noticeably greater than that of the host. Nothing is known about the composition of the exsolution product and therefore the direction of change in composition of the β-spodumene solid solution can not be predicted. Investigations off the $Li_2O \cdot Al_2O_3 - SiO_2$ line may reveal the true nature of this dissociation.

Before leaving this subject several points concerning the peritectic reaction between β-spodumene and β-eucryptite solid solutions may be worth recording. The β-spodumene solid solution of preparation no. 24 dissociates rather rapidly above the inversion temperature and eventually completely, producing the typical intergrowth with the exsolution product. Below the inversion temperature the two phases react slowly to give a β-eucryptite solid solution which contains only a trace of the exsolution product.

In preparation no. 7 the phase that develops with long heating below

the solidus as wide rims around the β-spodumene solid solution is optically positive, like β-spodumene, but it has refractive indices which are close to those for β-eucryptite. This material contains much of the exsolution product, probably giving aggregate indices, while the β-spodumene cores are comparatively free of the exsolution product. The supposition is that the material composing the rims will invert to β-eucryptite solid solution if given sufficient time.

The field of β-eucryptite solid solution: The case for solid solution in the β-eucryptite field is amply supported by optical and x-ray evidence. The refractive indices of the solid solution increase slightly with decreasing silica and the x-ray photographs show a regular shift in the lines of high-angle reflection.

This field consists essentially of one phase although a fine-grained fibrous material tends to exsolve with long heating, beginning along the borders of the grains and working inward. In appearance and behavior this exsolution product seems to be identical with the fibrous material described in the β-spodumene field.

Beta-eucryptite itself is a very unstable compound which dissociates with short periods of heating just below the melting temperature to a β-eucryptite-like phase that contains γ-alumina plus the above-mentioned fibrous material. The β-eucryptite-like substance has lower refractive indices than the true β-eucryptite compound, $\omega = 1.528$, $\epsilon = 1.521$, as compared to $\omega = 1.531$, $\epsilon = 1.523$.

It was not feasible to determine the melting temperature of natural eucryptite because it seems to occur always as a very fine-grained intergrowth with albite. The material that Jaeger and Simek[17] used was undoubtedly such a mixture. Dr. Foshag of the U. S. National Museum kindly furnished the writer with a sample of the eucryptite-albite material from Branchville, Connecticut (U.S.N.M., no. 81106), that was described by Brush and Dana.[7] The material melted to a glass having a refractive index of 1.506, the same value obtained by Jaeger and Simek. Artificial eucryptite glass has a refractive index of 1.543. According to Penfield's chemical analysis the intergrowth is composed of eucryptite and albite in a molecular ratio of one to one. If this ratio is changed into weight per cent; if 1.543 and 1.489 are used as the refractive indices of eucryptite and albite glasses, respectively; and, if perfect additivity is assumed; the refractive index of the glass obtained from such a mixture should be 1.506.

Ternary behavior of the β-spodumene–β-eucryptite fields: Several weeks before the experimental work was discontinued it was discovered that preparation no. 24 develops a small amount of a mullite-like phase when held at a temperature of 1355° for 28 hours. In the remaining time the

writer attempted to discover how many other preparations exhibit a similar type of dissociation. The results of the few runs made are given in Table 5.

TABLE 5. EXPERIMENTS ON THE DISSOCIATION OF β-SPODUMENE–β-EUCRYPTITE SOLID SOLUTIONS

Prep. no.	Temp. °C.	Time, hours	Results
3-P	1337–1350	37	No mullite.
5-C	1337–1350	37	1–2% mullite needles in β-spodumene-like phase.
33-C	1376–1392	70	Homogeneous solid solution.
6-C	1400–1405	9	Used 6-B. Mullite needles redissolved completely to form homogeneous β-spodumene.
6-A	1376–1392	70	Trace of mullite needles in β-spodumene.
6-B	1326–1340	30	1–3% mullite needles and wormy interstitial material in β-spodumene.
7-F	1376–1392	70	Typical exsolution product in β-eucryptite-like rims around the β-spodumene.
7-G	1326–1340	30	3–5% mullite needles in β-spodumene-like phase.
24-I	1400–1405	9	Used 24-G. Mullite needles redissolved completely leaving β-spodumene solid solution plus the fibrous exsolution product.
24-H	1384–1392	13	β-eucryptite solid solution, very little exsolution product. No mullite.
24-G	1348–1362	28	5–8% mullite needles, trace of α-alumina, in β-eucryptite-like phase.
8-A	1326–1340	30	3–5% mullite needles plus α-alumina in β-eucryptite-like phase.
9-C	1376–1392	70	5–10% α-alumina, trace of γ-alumina, no mullite, in β-eucryptite-like phase. Small amount of fibrous exsolution product.
9-D	1326–1340	30	3–5% α-alumina, trace of γ-alumina, no mullite, no fibrous exsolution product.
10-A	1376–1392	70	3–5% γ-alumina, trace of α-alumina, in β-eucryptite-like phase.
10-B	1337–1350	37	10–15% γ-alumina, trace of α-alumina, in β-eucryptite-like phase.

Several conclusions may reasonably be drawn from these experiments.
1. The region of dissociation to mullite extends from 70 per cent or greater to 56 per cent or less silica.
2. The β-eucryptite solid solutions dissociate to form an increasing amount of α-alumina and a decreasing amount of mullite as the β-eucryptite compound is approached.

3. The β-eucryptite compound dissociates mostly to γ-alumina with only a trace of α-alumina and no mullite.

4. Within certain limits, the amount of mullite or alumina increases with decreasing silica content, with decreasing temperature, and with increasing time.

5. The temperature of dissociation appears to be progressively higher with decreasing silica.

6. Very little or no fibrous exsolution product such as that which forms near the melting temperature is found associated with the mullite. Small amounts of it occur in some of the β-eucryptite samples that contain α-alumina and it seems to be more abundant in samples of 10 which contain γ-alumina.

7. The facts that good crystals of mullite in preparations nos. 6-C and 24-I completely redissolve when heated between 1400° and 1405° and that the fibrous exsolution product is present, lead one to doubt that the fibrous exsolution product is mullite in the incipient stage of formation. However, final judgment on this matter should await further experimental work in the ternary system.

The optical properties of the crystals thought to be mullite and α-alumina so far as they can be determined agree with the usual values for these substances. These data are presented in the section on Optical Data.

Conclusions: In the foregoing description of the β-spodumene–β-eucryptite fields of solid solution, the writer has attempted to show that the behavior of this part of the system above the solidus is essentially that characteristic of a binary system. The exsolution of a fine-grained fibrous product with long periods of heating, above as well as below the solidus temperatures, is strongly indicative of the metastability of the solid solutions. The development of small amounts of mullite or α-alumina at temperatures ranging from 10° to 80° below the solidus apparently indicates ternary behavior of the system at these temperatures.

Complete understanding of the unusual behavior of this part of the system must await further investigations in the ternary system. However, a clue was obtained from preparation no. 28 which is located on the alumina side of the line near the spodumene composition. This preparation lies in the mullite field and has liquidus and solidus temperatures of 1425° and 1385°. Mullite crystallizes out to the extent of 10 or 15 per cent before a lithium aluminosilicate, which probably has a composition close to 70 per cent silica, begins to crystallize at a temperature of about 1390°. This one observation suggests that the mullite field lies close to the $Li_2O·Al_2O_3–SiO_2$ line, probably on the alumina side of the line but possibly extending slightly over the line to the lithia side (see Fig. 3).

This interpretation is supported by the marked similarity of the systems $MgO-Al_2O_3-SiO_2$[25] and $Li_2O-Al_2O_3-SiO_2$, due probably in part to the close similarity in the atomic radii of magnesium and lithium.

THE γ-ALUMINA FIELD

In the fields of β-spodumene and β-eucryptite solid solutions the tendency for a part of the alumina to break away from the lithium aluminosilicate solid solution is clearly recognizable below the solidus and is probably due to a gradual weakening of the chemical bonds that hold alumina in the structure. At a silica content of about 47.7 per cent the break is complete and γ-alumina becomes the primary phase in a field of ternary behavior. The γ-alumina field extends at least as far as 22 per cent. The writer has not investigated preparations of lower silica content because of the high melting temperatures. The liquidus and solidus curve do not reveal the changes in phase composition that take place in this field because the compositions of the phases lie off the $Li_2O \cdot Al_2O_3-SiO_2$ line.

In 1932 during an investigation of the $Li_2O-Al_2O_3-SiO_2$ system, Barlett[3] described what she thought to be a new cubic modification of alumina, called zeta-alumina. Subsequently, other investigators, such as Beljankin,[4] Verwey,[30] and Kordes,[19] expressed the opinion based on a comparison of refractive index, density, and x-ray measurements that zeta-alumina and γ-alumina are identical. The writer is not aware that any opinions to the contrary have been published. As the term γ-alumina was apparently first used by Ulrich[29] in 1925 for the cubic modification of alumina, it clearly has priority over the term "zeta-alumina."

The identification of γ-alumina was made more difficult when Kordes in 1935 claimed that he had synthesized a compound with a formula of $LiAl_5O_8$ which has physical properties that are nearly identical with those of γ-alumina. Both compounds have the spinel type of structure and give almost identical x-ray powder photographs.

In order to check on the identity of the γ-alumina produced in the study of this system, the writer had a quantitative spectrographic analysis made of the material. To separate the tiny crystals from the lithium aluminosilicate matrix, the material was decomposed with hydrofluoric acid and the lithium and aluminum salts dissolved in hydrochloric acid. After repeating this treatment, the γ-alumina crystals were separated from the acid solution by repeated decantations. The crystals appeared to be free from contamination when viewed under the microscope. The spectrographic analysis gave values of 2.2, 2.4, and 2.8 per cent lithia, which is about one-half of the 5.5 per cent contained in the lithium spinel.

The lithia content may have been due to (1) occluded lithium salt, (2) a mixture of lithium spinel and γ-alumina, or (3) solid solution between the two compounds. In view of the structural similarity of the two compounds, it is reasonable to expect partial if not complete solid solution between them. However, until the existence of the lithium spinel is verified, it is probably best to assume that this system contains only γ-alumina.

Barlett[3] noted that "crystals of the material (γ-alumina) remain unaltered when subjected to a temperature of 1600° for several hours. Fusing it, however, results in an inversion, apparently over a considerable period, to the alpha form. The presence of silica accelerates this change and causes it to occur at lower temperatures." The writer also observed a few small crystals of α-alumina associated with the γ-alumina in some of the samples that were heated at about 1400° for the longer periods of time. Many writers have indicated temperatures ranging from about 900° to 1200° for the γ- to α-alumina inversion. In most cases these results were obtained on γ-alumina prepared by dehydrating various hydrates of alumina. Both Verwey[30] and Kordes[19] state that the presence of a small amount of lithia stabilizes the lattice of γ-alumina. It appears likely that the γ-alumina in this system is metastable at temperatures above the solidus although the matter is not yet proved.

The marked similarity between this part of the system and the corresponding part of the MgO–Al₂O₃–SiO₂ system is worth noting. A large field of the structurally similar MgO·Al₂O₃ spinel occurs in the latter.

It is readily seen in Fig. 2 that the temperature range through which γ-alumina crystallizes as the sole phase, increases rapidly between 47.7 and 31.3 per cent. The approximate boundary curve between γ-alumina and the secondary phase is shown in part by dashes. The secondary phase, from 47.7 through 37 per cent, shows a type of metastability similar to that observed in the β-eucryptite field. Under certain time-temperature conditions one homogeneous phase resu'ts; under different conditions there is extensive dissociation of this homogeneous phase into two phases. Lower temperature and longer periods of heating seem to be the conditions that favor the dissociation.

X-ray study of preparations nos. 19, 20, 21, and 13 reveals close similarity in structure between the homogeneous secondary phase and β-eucryptite; in fact there must be a β-eucryptite-like solid solution although neither x-ray nor refractive index measurements show unmistakable evidence of it. The uncertainty in estimating the amount of γ-alumina in the samples is too great to venture more than a guess on the compositions of the secondary solid solution phases. It appears likely, however, that they vary between β-eucryptite and some such possible

compounds as $3:1:3$ or $2:1:2$. The dissociation of the secondary phase may take place into the end members of the solid solution series.

X-ray photographs of preparations nos. 12, 22, and $Li_2O \cdot Al_2O_3$ all show similar patterns with a progressive shift in some of the lines of high-angle reflection. The refractive indices of the three materials rise progressively and uniformly toward lithium aluminate and the birefringence is nearly identical in all. This is suggestive of a lithium aluminate-lithium aluminosilicate solid solution.

Inversion Temperatures

The lowest temperatures of α- to β-inversion on record are summarized as follows:

eucryptite,	never observed.
spodumene,	720° Meissner[22]
petalite,	950° (dissociates), this report.

Although the principal workers [2,10,17,22] concluded that the inversions of α- to β-spodumene and α- to β-eucryptite are monotropic, their experimental data are insufficient to prove it. However, all attempts to synthesize the natural compounds have failed even though the materials were mixed with tungstate and vanadinate fluxes and were fused at temperatures as low as about 600°. The marked decrease in density of spodumene when it inverts, from about 3.2 to 2.4, would seem to favor the monotropic inversion hypothesis for that mineral.

It is interesting to note that one method for the beneficiation of spodumene makes use of the α- to β-inversion.[13] In this process the spodumene-bearing rock is heated at 1050° to 1080° for about one hour to bring about the inversion. The β-spodumene powder is then easily separated from the quartz and feldspar gangue by a selective grinding process followed by a particle-size separation.

A similar treatment of petalite does not cause the mineral to powder because the change of volume which accompanies the dissociation is very small.

Hydrothermal Experiments

The hydrothermal synthesis of spodumene and petalite has never been attempted so far as the writer knows. The probable hydrothermal origin of these minerals made it highly desirable to attempt hydrothermal syntheses under different temperature and pressure conditions.

It may be stated at the outset that the results of these experiments thus far have been negative. No products resembling the natural minerals were formed. The data relating to the experiments are given in Table 6.

Exp. No.	1.	2.	3.
Temperature °C.	390°–430° aver. = 410°	ca. 550° (?)	410°–470° aver. = 440°
Pressure, (calc.)	11–15 atmos. aver. = 13 atmos.	ca. 20 atmos. (?)	60–90 atmos.
Time	14 days	ca. 5 hours, glass softened, bomb exploded	7 days or more, bomb exploded sometime during 14 day run.
Results	*Spodumene glass*, about ½ crystallized to fine-grained aggregate of β-spodumene. *Petalite glass*, no change.	*Spodumene glass*, entirely crystallized to β-spodumene. *α-spodumene*, no change. *Petalite glass*, no change. *α-petalite*, no change.	*Spodumene glass*, entirely crystallized to β-spodumene. *α-spodumene*, no change. *Petalite glass*, mostly glass, contains unidentified crystallites. *α-petalite*, no change.

The materials were wrapped in individual platinum foil envelopes and placed in the bombs with a known amount of distilled water. From the effective volume of the bomb (actual volume minus volume of samples) and the weight of water added, the reciprocal vapor density was calculated. With this figure and the temperature of the furnace during the run, the pressure was obtained from the steam tables of Keenan and Keyes.[18]

The bombs were heated to the desired temperature by placing them in an electric furnace, the "crystallizing furnace" described by Faust.[11] The temperature was measured before or after a run by means of a mercury in glass thermometer. The temperature range shown in Table 6 was caused by fluctuations in the voltage of the direct current source.

Pyrex glass tubing was used for the bombs but was serviceable only for relatively short runs at low pressures. The water vapor caused the crystallization of a thin layer of the glass on the inside of the tubes. Transverse and longitudinal cracks also formed on the inside and in time the weakened tube would explode.

Although the results of these experiments are negative, they indicate that spodumene and petalite probably do not form under low pressure

hydrothermal conditions. It is always possible, however, that the time factor is of prime importance. If we recall the difference in density of α- and β-spodumene, it seems reasonable to expect that high pressure (500 to 1000 atmospheres) is a necessary condition for the formation of natural spodumene. The same can not be said for petalite because its density is about 2.5, not much greater than that of the high temperature dissociation product.

OPTICAL DATA

Tridymite: Crystals of tridymite are very small and not well developed. The refractive index is slightly less than 1.480, birefringence very weak.

β-spodumene-silica solid solution: Crystals of this solid solution series take the form of tetragonal bipyramids, well developed when formed in sufficient liquid, but becoming more granular as the amount of liquid
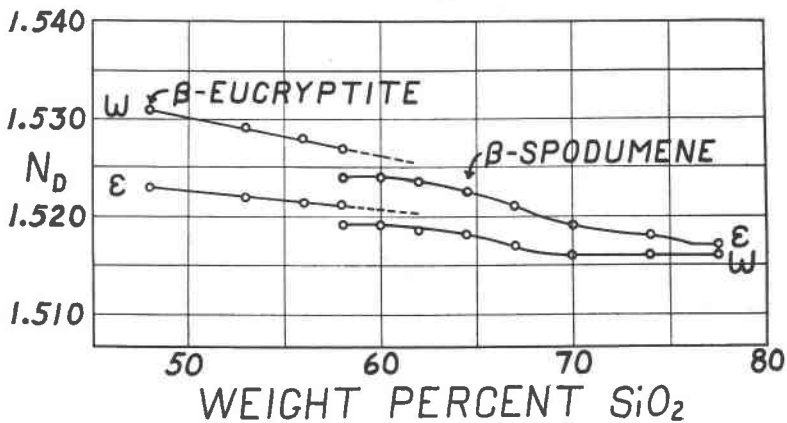
FIG. 4. Refractive index—composition curves of β-spodumene—β-eucryptite solid solutions.

decreases. The grain size ranges from a very fine-grained eutectic inter-growth of solid solution and tridymite, or siliceous glass, to grain diameters of 0.1 to 0.2 millimeter for β-spodumene. The solid solution material is uniaxial positive, $\omega = 1.516$ to 1.518, $\epsilon = 1.517$ to 1.523. The birefringence increases regularly from about 0.001 for the end member at 76 per cent silica up to about 0.005 for β-spodumene (see Fig. 4).

β-spodumene solid solution: Crystalline material in this field forms irregular grains; no tetragonal crystals were ever seen. The material is uniaxial positive, probably tetragonal because of the close similarity in x-ray patterns of this material and that of the high silica solid solution

field, $\omega = 1.518$ to 1.519, $\epsilon = 1.523$ to 1.524. The refractive indices increase very slightly with decreasing silica content. Jaeger and Simek[17] reported β-spodumene to be biaxial with a small 2V. However, such figures are obtained only on grains that show wavy extinction, as many of them do, which in some cases at least is due to overlapping crystals with different optical orientations.

β-eucryptite solid solution: This material takes the form of granular aggregates much like the β-spodumene. The material is uniaxial negative, probably tetragonal, $\omega = 1.527$ to 1.531, $\epsilon = 1.521$ to 1.523. The refractive indices increase slightly with decreasing silica content. A comparison of Figs. 1 and 4 reveals the interesting fact that the refractive indices of the glasses become greater than the mean index of the crystalline material for silica compositions below about 58 per cent. This indicates that the density of such glasses must be greater than that of the corresponding crystalline phases. Jaeger and Simek noted a three per cent increase in volume when eucryptite glass was devitrified. It is of interest to note that cordierite, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ is quite similar optically to β-spodumene and β-eucryptite and also melts to a glass which has a refractive index greater than that of the crystalline material.

β-eucryptite-like solid solution: This material includes the homogeneous secondary phase in preparations nos. 19, 20, 21, and 13. All tend to crystallize as coarse-grained aggregates. The different materials seem to have identical optical properties. They are uniaxial negative, $\omega = 1.528$, $\epsilon = 1.521$.

Lithium aluminate-like solid solution (?): This material includes the secondary phase in preparations nos. 12 and 22 as well as lithium aluminate. All are uniaxial negative. The refractive indices are:

	12.	22.	Li$_2$O · Al$_2$O$_3$
$\omega =$	1.586	1.605	1.624
$\epsilon =$	1.570	1.589	1.606

A small amount of a third phase appears in preparation no. 22. It has refractive indices of about $\alpha = 1.576$, $\gamma = 1.583$, uniaxial negative (?).

γ-alumina: Crystals of γ-alumina are usually less than 0.01 millimeter in diameter. They are isotropic with octahedral habit, granular when poorly developed, refractive index of 1.733.

α-alumina: Crystals of α-alumina are usually about the same size as those of γ-alumina but can be readily distinguished from the latter by their hexagonal habit, forming thin hexagonal plates. These crystals are uniaxial negative and have a refractive index greater than 1.74. The relief and birefringence appear to be identical with known α-alumina placed in the same liquid.

Mullite: Crystals of mullite are developed the best in preparation no. 28 which lies in the mullite field. They occur as rectangular, needle-shaped crystals and have lengths up to about 0.05 millimeter. They have weak birefringence, parallel extinction, positive elongation, and a refractive index close to 1.65. The crystals which form in the β-spodumene–β-eucryptite fields are usually smaller but otherwise they have optical properties that agree with those above. The small size of the needles prevents satisfactory refractive index measurements. However, the needles in all stages of development and size appear like the mullite needles of corresponding development and size in preparation no. 28.

Conclusions

The system, $Li_2O \cdot Al_2O_3$–SiO_2, as far as it has been investigated, may be divided into five fields: (1) the silica field, (2) the field of β-spodumene-silica solid solution, (3) the field of β-spodumene solid solution, (4) the field of β-eucryptite solid solution, and (5) the γ-alumina field.

The compounds that exist in this system are silica (SiO_2, M.T. 1713°), β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, M.T. 1423°), β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$, M.T. 1397°), and lithium aluminate ($Li_2O \cdot Al_2O_3$, M.T. above 1600°). No compounds having the composition of petalite (1:1:8) or "lithium orthoclase" (1:1:6) are stable above the solidus. Petalite dissociates at 950° or less.

From 100 per cent silica to 64.6 per cent (β-spodumene) the system behaves like a binary system. A eutectic point exists between the fields of silica and β-spodumene-silica solid solution at 84.5 per cent and a temperature of 1356°.

The solid solution fields of β-spodumene and β-eucryptite extend from 64.6 to 47.7 per cent (β-eucryptite) and are separated by a peritectic point at 57.3 per cent and a temperature of 1408°, or slightly less. The relations in these two fields are essentially binary near the melting temperatures although a small amount of a very fine-grained fibrous material exsolves both above and below the solidus. At temperatures varying from 10° to 80° below the solidus, this portion of the system exhibits ternary behavior with the solid solutions partly dissociating to form small amounts of mullite or α-alumina. It is suggested that the unusual behavior of this part of the system may be due to the mullite field closely approaching or possibly crossing the $Li_2O \cdot Al_2O_3$–SiO_2 line as it does in the remarkably similar MgO–Al_2O_3–SiO_2 system.

With less than 47.7 per cent silica the system is ternary with γ-alumina the primary phase. The liquidus curve rises steeply to well over 1500° with a ten per cent decrease in silica. The γ-alumina appears to invert

slowly with long heating near 1400° to α-alumina, thereby suggesting the metastability of the γ-form.

The attempts to synthesize α-spodumene hydrothermally at pressures below 100 atmospheres and at temperature of 400° to 550° all failed. In every case the high temperature β-form crystallized from the spodumene glass. Either higher pressures or longer time seem to be needed to form the mineral.

Although it is evident that this investigation is far from completion, the war makes it necessary to cease work on this problem. Most of the essential features of the system have been determined and it therefore seems advisable to publish the data as they now stand. The writer hopes that this work will provide a basis for further investigations in the ternary system $Li_2O–Al_2O_3–SiO_2$.

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