STABILITY RELATIONS OF LiAlSi$_2$O$_6$ AT HIGH PRESSURES

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ABSTRACT

The pyroxene end member spodumene (α-LiAlSi$_2$O$_6$) crystallizes in three stable polymorphic forms. Only one of these, a $C2$ pyroxene structure, is found in nature. One of the remaining two polymorphs (β-spodumene) is tetragonal, is isomorphous with keatite, and is the high-temperature form at pressures between 1 atm and about 9 kbar. The other polymorph (β-quartz$_{ss}$) is hexagonal, isostructural with β-quartz, and is the high-temperature polymorph in the pressure range 10–26.5 kbar. At pressures above 26.5 kbar the pyroxene form is stable at all subsolidus temperatures.

β-Spodumene melts congruently at 1429°C at 1 atm and persists as the liquidus phase with increasing pressure up to 8.5 kbar, 1455°C. At higher pressures spodumene melts incongruently, forming β-quartz$_{ss}$ + liquid, and the slope of the liquidus increases markedly. In the subsolidus β-spodumene is unstable at all pressures above 10 kbar.

The inversion between spodumene and β-quartz$_{ss}$ was determined reversibly; the curve has an average slope of 40°/kbar and terminates at the high-pressure end in a singular point, spodumene + β-quartz$_{ss}$ + liquid, at 26.5 kbar, 1510°C. By extrapolation to low pressures the spodumene $\rightleftarrows$ β-spodumene inversion must lie below 520°C at 1-atm pressure and may be found as low as 400°C.

Above 10 kbar a complete series of β-quartz solid solutions are stable along the join SiO$_2$-LiAlSi$_2$O$_6$; thus, pressure greatly increases the solid solution of Li and Al ions in the β-quartz structure. In the range 10–25 kbar a simple eutectoid relation probably exists in the subsolidus between the phases α-quartz, β-quartz$_{ss}$, and spodumene.

INTRODUCTION

Spodumene is a bonafide pyroxene. It has received less attention than the more common pyroxenes because of its somewhat unusual chemistry and its restricted natural occurrences. Nonetheless, as one of the primary sources of lithium, spodumene is of considerable economic importance. Moreover, spodumene plays an important role in the crystallization processes of lithium-bearing granitic pegmatites and as such is part of the intriguing petrologic problem bearing on the origin of these rocks. Finally, spodumene as a pyroxene is interesting from a crystal-chemical viewpoint, its chemistry and phase relations being markedly different from those of other pyroxenes.

The ideal (end-member) composition for spodumene is LiAlSi$_2$O$_6$. Most natural spodumenes approach this composition closely; the common contaminants are Na$_2$O and Fe$_2$O$_3$. On the basis of the analyses in Deer *et al.* (1963, p. 93) these components account for a theoretical maximum of 10 mole percent jadeite (NaAlSi$_2$O$_6$) + acmite (NaFeSi$_2$O$_6$), although 5 percent of these "excess components" is a more typical value. Thus, extensive solid solution of other pyroxene components with spodumene does not occur in nature. Inasmuch as most common natural pyroxenes show extensive solid solutions, spodumene is in this sense unique.

Polymorphism and its significance undoubtedly constitute one of the prime problems in pyroxene mineralogy. In this respect, spodumene is a simplified member of the group—only one natural polymorph is known. Three polymorphs of LiAlSi$_2$O$_6$ are reported from synthetic studies, however, and it is largely the relationships between these three structures which complicate the synthetic phase studies of spodumene and spodumene-bearing assemblages.

The stability of LiAlSi$_2$O$_6$ composition in the P-T plane is investigated in this report, which is the first study of equilbrium phase relations in the system Li$_2$O-Al$_2$O$_3$-SiO$_2$

with the use of solid-media pressure apparatus. All details regarding experimental techniques and procedures, synthesis and identification of phases, and the results of critical experiments are given in the appendix.

CRYSTAL DATA FOR THREE SPODUMENE POLYMORPHS

The three polymorphs of LiAlSi$_2$O$_6$ can be distinguished as follows:

1. Spodumene: monoclinic, $C2$ (α-LiAlSi$_2$O$_6$). This is the only natural polymorph. The crystal structure of spodumene has been shown by Appleman and Stewart (1968) to be very similar to that of jadeite (Prewitt and Burnham, 1966) except that the space group symmetry is lowered from $C2/c$ to $C2$. In this paper the term spodumene is used only for that polymorph of LiAlSi$_2$O$_6$ having the monoclinic (pyroxene) crystal structure.

2. β-Spodumene: tetragonal, $P4_32_12$. The crystal structure of this polymorph is based on a three-dimensional aluminosilicate framework. It is isostructural with keatite, a tetragonal silica polymorph, with Li ions stuffed in interstitial positions (Skinner and Evans, 1960). In this paper the term β-spodumene refers only to the tetragonal polymorph having the specific composition LiAlSi$_2$O$_6$; the term β-spodumene$_{ss}$ refers to all solid solutions on the join SiO$_2$-Li$_2$O·Al$_2$O$_3$ that have the keatite structure.

3. β-Quartz$_{ss}$: hexagonal, $P6_222$ (?). This polymorph is assumed to be isostructural with β-quartz. To emphasize the special (but not unique) composition of LiAlSi$_2$O$_6$, parentheses enclosing that composition are used, *e.g.* β-quartz$_{ss}$ (LiAlSi$_2$O$_6$). In the absence of parentheses, the term β-quartz$_{ss}$ refers to a range of solid solutions along the join SiO$_2$-Li$_2$O·Al$_2$O$_3$ having the specified structure. The X-ray powder pattern of β-quartz$_{ss}$ (LiAlSi$_2$O$_6$) is essentially identical with the powder pattern for β-eucryptite$_{ss}$, a hexagonal polymorph that has been shown to be metastable on LiAlSi$_2$O$_6$ composition at 1 atm. (Skinner and Evans, 1960).

TABLE 1. CELL DIMENSIONS AND CALCULATED DENSITIES OF LiAlSi₂O₆ POLYMORPHS

	a, Å	b, Å	c, Å	β	D_{calc}
1. Natural spodumene	9.449(3)	8.386(1)	5.215(2)	110°6.0'	3.201
2. Synthetic spodumene	9.461(3)	8.388(3)	5.215(2)	110°6.4'	3.196
3. β-Spodumene	7.538(1)		9.151(1)		2.377
4. β-Quartz$_{ss}$ (LiAlSi₂O₆)	5.204(2)		5.462(4)		2.412

1. Appleman and Stewart (1968).
2. Synthesized from β-quartz$_{ss}$ (LiAlSi₂O₆) at 40 kb, 1600°C.
3. Synthesized from glass at 1 atmosphere, 1350°C.
4. Synthesized from β-spodumene at 15 kb, 1350°C.
2, 3, and 4 were determined by X-ray powder diffractometer using Cu Kα₁ radiation. Internal standards used were: 2, 4, CaF₂; 3, NaF.

This similarity arises because β-eucryptite (LiAlSiO₄) has a structure analogous to that of β-quartz, except that in β-eucryptite the c axis is doubled when referred to the β-quartz cell (Winkler, 1948). Nonetheless, the c axis of the phase synthesized in this study, subsequently shown to be stable on LiAlSi₂O₆ composition at high pressures, was measured by precession photographs and was found to have a 5.5 Å β-quartz c axis, not the doubled (11 Å) β-eucryptite c axis.

Cell dimensions of all three synthetic polymorphs are presented in Table 1, along with their conditions of synthesis. It is interesting to note the calculated densities of these phases (3.20 for spodumene, 2.38 for β-spodumene, 2.41 for β-quartz$_{ss}$). Spodumene is the only pyroxene that can crystallize in polymorphic forms having densities considerably lower than those of the normal pyroxene range.

PREVIOUS INVESTIGATIONS

All attempts to synthesize spodumene at 1-atm pressure have been unsuccessful. Synthesis of spodumene under hydrothermal conditions at low pressure, however, has been previously reported (*e.g.* Roy *et al.*, 1950; Barrer and White, 1951; Šćavničar and Sabatier, 1957), but in all cases the phase synthesized was apparently contaminated by iron. Substitution of small amounts of ferric iron for aluminum dramatically enlarges the stability field of spodumene (Appleman and Stewart, 1968). Attempts at hydrothermal syntheses of spodumene from pure components at pressures up to 4 kbar routinely result in mixtures of α-eucryptite (LiAlSiO₄) + petalite (LiAlSi₄O₁₀) at lower temperatures and β-spodumene at higher temperatures (Isaacs and Roy, 1958). Isaacs and Roy (1958) suggested that the failure to synthesize spodumene in the pure system could be due to the lack of some minor impurity that might be necessary to stabilize its structure and promote its growth. This is not the case though, inasmuch as spodumene can be readily crystallized from pure components, and in the absence of a fluid phase, at pressures above 10 kbar. Previous difficulties encountered in growing spodumene can thus be attributed to the extremely sluggish nucleation of this phase at low temperatures and pressures.

It has long been known from 1-atm studies that spodumene inverts to β-spodumene at temperatures above about 700°C. The reverse reaction has not yet been reported in the literature, and most workers (*e.g.* Deer *et al.*, 1963, p. 94) consider the inversion to be monotropic. Above the inversion temperature β-spodumene is the stable phase up to the solidus. At about 1430°C β-spodumene melts congruently.

Complications in the 1-atm studies are known, but they invariably relate to phase equilibria extended to the join SiO₂-Li₂O·Al₂O₃. For example, crystallization of LiAlSi₂O₆ glass at 1350°C for a few minutes sometimes produces a polymorph having the structure of β-eucryptite, although with longer crystallization times this phase inverts to the stable polymorph, β-spodumene (Skinner and Evans, 1960). β-Eucryptite solid solutions are apparently stable over a wide range on the join SiO₂-Li₂O·Al₂O₃, although at 1350°C this field is terminated on the silica-rich end by the two-phase assemblage β-eucryptite$_{ss}$ + β-spodumene$_{ss}$ (Skinner and Evans, 1960; Fig. 1).

Under hydrothermal conditions, and at moderately low pressures, phase relations on the join SiO₂-Li₂O·Al₂O₃ are modified by the appearance of petalite, LiAlSi₄O₁₀, and by the existence of a fairly wide field of β-quartz solid solutions at the silica-rich end of the join. The stability relations of petalite have been determined (Stewart, 1964); it does not exist as a stable phase above about 5 kbar. Recently Edgar (1968) determined the α-spodumene → β-

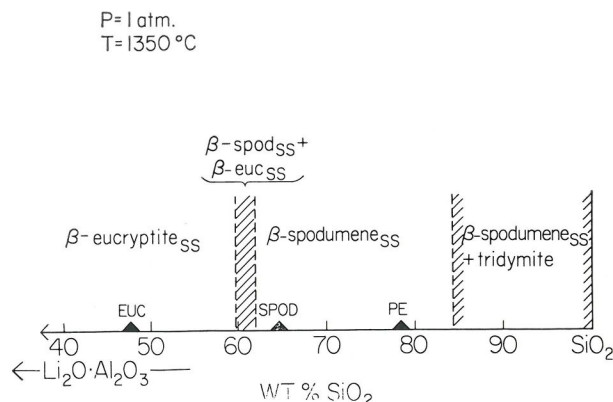FIG. 1. Phase boundaries on the join SiO₂-Li₂O·Al₂O₃ at 1350°C, 1 atm. Adapted from Skinner and Evans (1960).

spodumene inversion temperature in the presence of water at pressures up to 3 kbar. Using three natural spodumenes, he reported the inversion in the range 555° to 630°C, although these values do not represent reversed equilibrium. He also found that the presence of an aqueous gas phase caused leaching of small amounts of lithia from spodumene, with the excess silica being taken up by β-spodumene$_{ss}$.

EXPERIMENTAL RESULTS

Stability of LiAlSi₂O₆ composition in the P-T plane. The following assemblages may be stable for LiAlSi₂O₆ composition in the P-T regions studied: (1) spodumene, (2) β-spodumene, (3) β-quartz$_{ss}$ (LiAlSi₂O₆), (4) β-spodumene$_{ss}$ + β-quartz$_{ss}$, (5) β-quartz$_{ss}$ + liquid, (6) liquid. The geometric relationship of these fields is shown in the P-T diagram (Fig. 2), and the critical experiments are listed in the appendix (Table 4).

β-Spodumene melts at 1429° ± 1°C at 1 atm (J. F. Schairer, personal communication). Congruent melting persists to 8.5 kbar, 1460°C, at which point incongruent melting to β-quartz$_{ss}$ + liquid is observed, with a marked increase in the slope of the liquids curve. The solidus curve β-quartz$_{ss}$ ⇌ β-quartz$_{ss}$ + liquid is interrupted by a singular point (spodumene + β-quartz$_{ss}$ + liquid) at 26.5 kbar, 1510°C; at higher temperatures spodumene melts incongruently to β-quartz$_{ss}$ + liquid. If spodumene ultimately melts congruently, it will have to be well above 40 kbar.

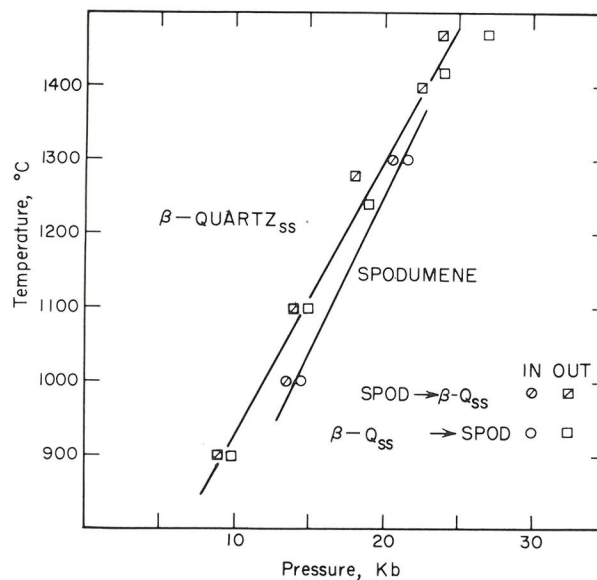In the subsolidus the β-spodumene field is restricted to the high-temperature, low-pressure ($<$ 9 kbar) region of the

FIG. 3. *P-T* projection for the inversion curve spodumene ⇌ β-quartz$_{ss}$ (LiAlSi₂O₆) showing results of both piston-out and piston-in runs.

diagram. With increasing pressure, a cigar-shaped two-phase field which terminates at the solidus separates the field of β-spodumene from the field of β-quartz$_{ss}$.

One problem in determining the maximum stability limit of β-spodumene stems from the rapid rate of inversion of β-spodumene at pressures above 10 kb. For example, at 15 kbar β-spodumene inverts entirely to β-quartz$_{ss}$ (LiAlSi₂O₆) in the length of time required to increase the temperature from 20° to 1200°C (about 1 min.). Thus, all runs in which the appearance or disappearance of β-spodumene is critical must be made with care in order to avoid momentary excursions into the β-quartz$_{ss}$ field. This was done by overpumping the furnace cell at room temperature, bleeding to the desired pressure, and slowly bringing up the temperature while constantly bleeding the ram to maintain the run pressure.

The boundaries of the two-phase field (β-spodumene$_{ss}$ + β-quartz$_{ss}$) were determined by performing two experiments for each P-T region within that field. When both β-spodumene and β-quartz$_{ss}$ (LiAlSi₂O₆) starting materials, run under the same conditions, yielded the two-phase assemblage, it was assumed that the conditions were within the two-phase region.

The upper stability of spodumene defines the only geologically interesting phase boundary in the diagram. This boundary was measured by both piston-out and piston-in methods (see appendix). The two curves thus obtained (Fig. 3) represent the maximum errors due to friction effects in the apparatus; the friction-free curve lies somewhere between them. At about 1300°C the difference between the two curves is only about 1 kbar, but this different increases at lower temperatures. The projection of both curves back to 1 at-

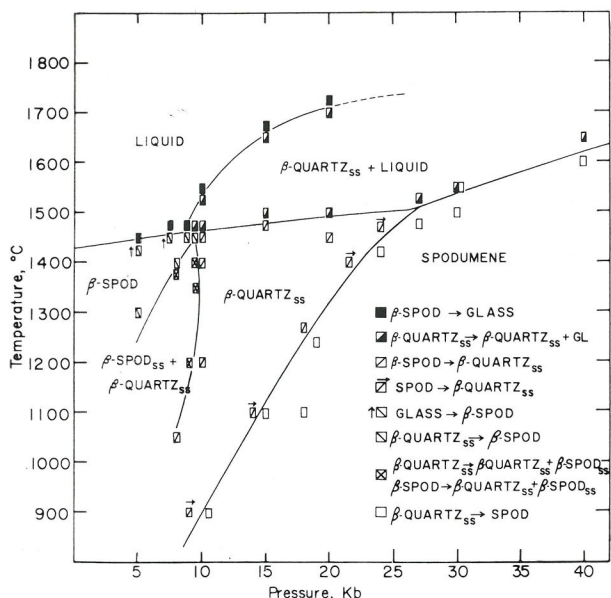

FIG. 2. Stability relations for the bulk composition LiAlSi₂O₆ plotted in *P-T* projection. All runs shown on this diagram are "piston-out" type (see appendix). Reversals, where achieved, are indicated by the appropriate symbol.

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mosphere gives the following (metastable) values for the maximum stability of spodumene at 1 atm: piston-out curve, 520°C; piston-in curve, 395°C. The equilibrium temperature of the metastable inversion spodumene $\rightleftarrows$ β-quartz$_{ss}$ (LiAlSi$_2$O$_6$) lies between these two extremes; the *stable* equilibrium (spodumene $\rightleftarrows$ β-spodumene$_{ss}$) must, of course, be found at a *lower* temperature than the metastable equilibrium. Of particular interest is the large positive slope for both experimentally determined curves (average: 40°C/kbar). Because the density of β-spodumene is very close to that of β-quartz$_{ss}$ (LiAlSi$_2$O$_6$) (Table 1), a similar large positive slope doubtless exists for the spodumene $\rightleftarrows$ β-spodumene inversion. This implies that it will not be possible to apply temperature limits to pegmatite zones, based solely on the presence of spodumene in the zones, without taking pressure into account.

Extrapolation of experimental data to the join SiO$_2$-LiAlSiO$_4$. The detailed study of LiAlSi$_2$O$_6$ composition has not yielded enough information to unravel unambiguously the effect of pressure on phase equilibria on the join SiO$_2$-LiAlSiO$_4$. Nonetheless, two obvious questions arise: (1) Does the absence of β-spodumene above 10 kbar represent a phase disappearance or merely the shift of the β-spodumene solid solution field to a different position on the join?; (2) At high pressure, do β-quartz solid solutions extend in an unbroken series from SiO$_2$ to LiAlSi$_2$O$_6$? A number of additional experiments were performed in an attempt to answer both questions.

Regarding the possibile stability of β-spodumene, mixtures of β-spodumene + quartz in different proportions were held at 10 kbar and reacted at 1350°C for various times. In every case the β-spodumene inverted to β-quartz$_{ss}$ within 1 hour, and the two β-quartz phases present (the second phase resulting from the inversion of α-quartz) progressively homogenized into a single β-quartz phase. As might be expected, this homogenization was very sluggish; however, it could be followed at each stage in a multicycle run by observing the convergence of analogous reflections on the X-ray diffractogram. Inasmuch as the *rate* of homogenization of two β-quartz solid solutions is many times less than the rate of the conversion of β-quartz$_{ss}$ (LiAlSi$_2$O$_6$) to β-spodumene, it seems likely that β-spodumene *solid solutions* are not stable above 10 kb.

Crystallization of glasses on the join SiO$_2$-LiAlSi$_2$O$_6$ at 10, 15, or 20 kbar invariably yields a single phase β-quartz solid solution. Cell dimensions of the phases were determined on quenched materials and are given in Table 2. These synthesis experiments in themselves yield no reliable information regarding stability relations. However, when they are considered in combination with the observed progressive homogenization of two β-quartz solid solutions described above, it is very tempting to conclude that a continuous series of stable solid solutions extends between SiO$_2$ and LiAlSi$_2$O$_6$ at pressures above 10 kbar. If this is true, then the subsolidus phase relations along that join in

TABLE 2. CELL DIMENSIONS OF β-QUARTZ SOLID SOLUTIONS SYNTHESIZED ON THE JOIN SiO$_2$-LiAlSi$_2$O$_6$ AT 15 KBAR, 1350°C[a]

Composition (mole %)	a, Å	c, Å
Sp$_{100}$	5.204 (2)	5.462 (4)
Sp$_{89.7}$Q$_{10.3}$	5.190 (2)	5.459 (4)
Sp$_{79.5}$Q$_{20.5}$	5.172 (1)	5.457 (2)
Sp$_{69.3}$Q$_{30.7}$	5.155 (1)	5.461 (2)
Sp$_{60.2}$Q$_{39.8}$	5.133 (1)	5.455 (2)
Sp$_{49.2}$Q$_{50.8}$	5.105 (5)	5.441 (7)
Sp$_{39.3}$Q$_{60.7}$	5.065 (2)	5.436 (4)
Sp$_{29.3}$Q$_{70.7}$	5.011 (1)	5.429 (1)
Sp$_{19.5}$Q$_{80.5}$	4.936 (1)	5.411 (2)
Sp$_{9.7}$Q$_{90.3}$	4.920 (1)	5.405 (1)

[a] Cell dimensions were determined by computer, using least-squares analysis of indexed powder data (Burnham, 1962). CaF$_2$ was used as an internal standard.

the pressure range 10–25 kbar would appear rather straightforward—in fact, in *T-X* section it suggests the existence of a simple eutectoid involving the phases α-quartz + spodumene + β-quartz$_{ss}$. The temperature of the eutectoid must, of course, be lower than the temperature of the α-quartz $\rightleftarrows$ β-quartz inversion at a given pressure, for instance less than 920°C at 15 kbar (Cohen and Klement, 1967). In view of the difficulties encountered with reaction kinetics along this join at 1350°C, it appears that the determination of the equilibrium composition and temperature of the eutectoid would be impossible in the absence of some suitable flux.

In summary, the phase relations on the join SiO$_2$-LiAlSiO$_4$ become simplified with increasing pressure. What remains enigmatic, however, is the relationship between the β-quartz solid solutions synthesized in this study and the β-eucryptite solid solutions found at lower pressures. Specifically, does β-eucryptite (LiAlSiO$_4$) synthesized at high pressure still retain a doubled c axis when compared to β-quartz, and if so, what is the nature of the transition between these two phases when present as solid solutions? Attempts to synthesize crystals of β-eucryptite (LiAlSiO$_4$) at 20 kbar suitable for single crystal analysis were unsuccessful. Because of this, and in recognition of possible inversions which could occur during quenching, the solution of this important problem apparently requires X-ray photographs of β-quartz$_{ss}$ and β-eucryptite$_{ss}$ taken within their respective stability fields—that is, at both high temperatures and high pressures.

CONCLUSIONS

1. β-Spodumene is a stable polymorph of LiAlSi$_2$O$_6$ only at pressures below 10 kbar; above 10 kbar the stable polymorphs are spodumene and a β-quartz solid solution.

2. The temperature of the spodumene $\rightleftarrows$ β-spodumene inversion at 1 atm must lie below 520°C. The inversion is strongly pressure-sensitive, and probably has a *P-T* slope

of the order of 40°/kbar. This places important limitations on the use of spodumene as a geothermometer in pegmatite zones.

3. The solubility of Li + Al in β-quartz solid solution greatly increases with increasing pressure—above 10 kbar a complete series of solid solutions are stable along the join SiO_2-$LiAlSi_2O_6$ and may extend all the way to $LiAlSiO_4$.

4. β-Quartz solid solutions containing considerable Li and Al have not yet been reported in nature. This is not surprising, inasmuch as lithium-bearing pegmatites probably crystallize at low pressures near the earth's surface, whereas present data indicate that extensive solid solution in β-quartz would be expected only at pressures above 10 kbar, corresponding to a depth of burial greater than 33 km.

APPENDIX

SYNTHESIS OF PHASES

Starting materials were initially crystallized from a glass of $LiAlSi_2O_6$ composition prepared under the direction of J. F. Schairer. The method is analogous to the one described for the preparation of glasses in the K_2O-Al_2O_3-SiO_2 system (Schairer and Bowen, 1955, p. 682), except that Li_2CO_3 was substituted for $KHCO_3$. Glasses used to determine cell dimensions on the join $LiAlSi_2O_6$-SiO_2 were supplied by David B. Stewart and were prepared by a similar technique.

Dry synthesis of the three polymorphs of $LiAlSi_2O_6$ in bulk amounts was most satisfactorily accomplished under the following conditions: β-spodumene, crystallized from glass at 1 atm, 1350°C, overnight; β-quartz ($LiAlSi_2O_6$), synthesized from β-spodumene at 15 kb, 1200°C, 2 hours, synthesized from β-spodumene at 30 kbar, 1250°C, 2 hours. Under these conditions 100 percent yields of all three polymorphs were obtained from single experiments.

IDENTIFICATION OF PHASES

Distinction between the three polymorphs was most easily accomplished by X-ray powder diffraction. The overall diffractometer patterns of β-spodumene and β-quartz$_{ss}$ ($LiAlSi_2O_6$) are remarkably similar, and many of their strongest reflections mutually interfere. Nonetheless, it is fairly easy to tell them apart on the basis of differences in the 19–30° 2Θ region for Cu Kα radiation (Table 3). Spodumene itself is characterized by a distinctive X-ray trace and pyroxene-like optical properties.

EXPERIMENTAL PROCEDURES

All experiments at pressures above 1 atm were performed in the single-stage piston-cylinder apparatus, described originally

TABLE 3. INDEXED *d* VALUES[a] USED TO DISTINGUISH
β-SPODUMENE FROM β-QUARTZ$_{ss}$ ($LiAlSi_2O_6$)

β-Spodumene		β-Quartz$_{ss}$ ($LiAlSi_2O_6$)	
(111)	4.606	(100)	4.507
(102)	3.911	—	
(201)	3.485	(101)	3.476
(211)	3.164	—	

[a] The *d* were calculated from unit-cell dimensions for the respective phases (see Table 2).

by Boyd and England (1960, 1963). The most recent description of this apparatus (Richardson *et al.*, 1968) corresponds exactly to the design of the furnace-cell assembly used in this study. Uncertainties in the magnitude of the true pressure experienced by the sample in the piston-cylinder apparatus are due partly to frictional effects in the apparatus and partly to the presence in the furnace cell of materials having different strengths. One approach to the first problem is to maximize the frictional uncertainties by maintaining as a constant the direction of piston travel. This is accomplished by two different methods—the "piston-out" technique, in which the nominal pressure is always less than the true pressure, and the "piston-in" technique, in which the nominal pressure is always greater than the true pressure. Richardson *et al.* (1968) describe these techniques in detail and give a comprehensive discussion of the entire problem. In this study the piston-out technique was used for most experiments, although a few experiments were performed using the piston-in method in order to obtain an idea of the magnitude of frictional effects present. The pressures reported in this paper are nominal, that is no corrections have been applied. Pt-Pt$_{90}$Rh$_{10}$ thermocouples were used to record temperature; no correction was made for the effect of pressure on thermocouple emf.

Inasmuch as minute amounts of water drastically affect the stability relations of LiAl silicates, it was essential that both the charge and furnace assembly be carefully dried prior to each experiment. Samples containing either spodumene or the β-quartz polymorph could be dried at 800°C for several hours with no discernible inversion to β-spodumene. Sample containing β-spodumene, or samples which were to be used for determination of liquid-crystal equilibria, were dried with their furnace parts in a stream of nitrogen at about 1150°C for 30 minutes; the furnace and charge were then assembled and the experiment was begun immediately, while the assembly was still hot.

DETECTION OF REACTION

Above the solidus, melting was detected by the presence of copious glass in runs of 5 minutes' duration. Below the solidus, conversion of one polymorph to another was commonly total or almost complete; thus there was seldom a problem in determining direction of reaction. In some cases it was convenient to use mixtures of two polymorphs as a starting material once the reaction itself had been defined by reconnaissance experiments. When both polymorphs were present in the reaction product the result was dicarded unless it was obvious from both X-ray and optical studies that a very major change in proportions had occurred; no quantitative X-ray determinative method was found necessary.

The main experimental problem encountered was maintaining the bulk composition of the charge at $LiAlSi_2O_6$ composition This stems both from the volatility of lithia at high temperatures and from the apparent solubility of lithia in water-rich fluids at high pressures (Edgar, 1968).

The first aspect of the problem was recognized by the results

of runs in the β-quartz$_{ss}$ field at temperature above 1200°C for periods in excess of 2 hours. In some cases, the rather large (30 μm) crystals of β-quartz$_{ss}$ contained tiny bluish inclusions of high refractive index, which appeared to be corundum. These inclusions were always less than 1 percent of the total charge, and thus their presence was never detected by X-rays. Inasmuch as the amount of these inclusions tended to increase with both temperature and run time, it is believed that they represent crystallization of corundum due to escape of lithia from the charge, the excess silica being taken up in β-quartz$_{ss}$.

A different and more serious effect was observed in low-temperatures runs to which traces of moisture had been added in hopes of fluxing the reaction. In these cases, at temperatures in the range 900°–1000°C, and pressures around 10 kbar, copious sheaves of needles were found, forming up to 30 percent of the total charge, in addition to large mats of a brown isotropic phase which appeared to be quenched vapor. The needles gave an X-ray pattern similar to mullite. Commonly, very little recognizable lithium silicate was present.

Both problems were either solved or minimized by using extremely dry charges and runs as short as possible at higher temperatures. The wet results suggest that some serious problems may develop in the hydrothermal studies of lithium-bearing systems below 10 kbar if the composition of the gas phase is not known.

Diagnostic runs on LiAlSi$_2$O$_6$ composition are given in Table 4.

TABLE 4. DIAGNOSTIC RUNS ON LiAlSi$_2$O$_6$ COMPOSITION

P, kb[a]	T, °C (± 10)	Run time (hr)	Run time (min)	Starting material[b]	Products[b]
5	1450	0	45	bs	gl
5	1425	0	30	bs	bs+very rare gl fragments
5	1300	0	50	bq	bs
7.5	1475	0	21	bs	gl
7.5	1450	0	20	bs	bs+tr. gl
8	1400	1	50	bq	bs
8	1375	1	50	bq	bq+bs
8	1050	5	7	bs	bq
8	1050	6	45	bq	n.r.
8	900	23	0	bq	n.r.
8.8	1475	0	20	bs	gl
8.8	1450	0	40	bq	bs
8.8	1450	0	30	bs	n.r.
9	1350	2	0	bq	bs+bq
9	1200	9	0	bs	bs+bq
9	900	19	25	sp+bq	bq
9.4	1475	0	20	bs	gl+bq
9.4	1450	1	3	bs	n.r.

TABLE 4—(Continued)

P, kb[a]	T, °C (± 10)	Run time (hr)	Run time (min)	Starting material[b]	Products
9.4	1400	2	10	bs	bs+bq
9.4	1400	0	55	bq	bs+bq
9.5	1350	1	40	bq	n.r.
10	1550	0	10	bs	gl
10	1475	0	40	gl	gl+large bq
10	1450	0	50	gl	bq
10	1450	0	57	bs	bq
10	1400	2	0	bs	bq
10.5	900	6	30	bq (undried)	sp+bq
12*	1000	6	15	sp+bq	bq
13.8*	1000	7	0	sp+bq	n.r.
14	1100	5	20	sp+bq	bq>>sp
14*	1000	5	15	sp+bq	bq
14.5*	1000	7	35	sp+bq	sp>>bq
15	1675	0	10	bs	gl
15	1650	0	10	bs	gl+bq
15	1500	0	5	bs	gl+very rare bq
15	1475	0	10	bq	n.r.
15*	1000	5	20	sp+bq	bq
15	1100	6	25	sp+bq	sp
15.5*	1000	7	0	sp+bq	sp>>bq
15.5*	1000	4	25	bq	n.r.
18	1100	2	50	sp+bq	sp
20	1725	0	5	bs	gl
20	1700	0	5	bs	gl+bq
20	1500	0	20	gl	bq
20	1450	0	50	gl	bq
20*	1300	1	30	sp+bq	bq
20.8*	1300	1	45	sp+bq	bq>>sp
21.5	1400	0	55	sp+bq	bq
21.5*	1300	2	0	sp+bq	sp
23*	1300	1	15	sp+bq	sp
24	1420	0	55	sp+bq	sp>>bq
24	1470	0	30	sp+bq	bq
27	1525	0	30	bq	bq+rare gl
27	1475	0	55	bq	sp+rare bq
30	1550	0	10	bs	sp+bq
30	1550	0	20	bq	bq+rare gl
30	1500	0	20	bq	sp
40	1650	0	10	bq	gl+bq
40	1600	0	15	bq	sp

[a] An asterisk following a nominal pressure designates a piston-in run procedure; pressures quoted without asterisks represent piston-out run procedures.

[b] Abbreviations: bs, β-spodumene; bq, β-quartz$_{ss}$; sp, spodumene; gl, glass; n.r., no reaction detected; tr., trace.

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