Hydrothermal Synthesis of Various Spodumenes

D. J. Drysdale

Division of Mineralogy, CSIRO, W.A. Laboratories, Wembley, Western Australia

Abstract

Spodumenes having the same crystallographic structure as natural α-spodumene but with iron, chromium, vanadium, indium, and scandium substituting for aluminium have been synthesized under water pressures and other conditions in which the synthesis of α-spodumene has failed. It is suggested that the difficulty of producing α-spodumene and the ease of producing these substituted analogs stems from the differing tendency of the corresponding metals to take up octahedral coordination in densest hexagonal as opposed to defective cubic close packed oxygen networks. Cell dimensions of the synthetic materials are given.

Introduction

The manner of occurrence of α-spodumene has led most geologists to conclude that it characteristically crystallizes at temperatures of the order of 400° to 600°C in pegmatite systems rich in volatiles and under pressures of substantially less than 10 kbar \(P_{total}\). These findings are supported by experiments on spodumene stability using the natural mineral (e.g., Edgar, 1968; Munoz, 1971).

However, no hydrothermal synthesis of spodumene has been achieved under these conditions, the nearest approach being that of Kuznetsov, Shternberg, and Ivanova (1970) using aqueous LiCl solution + Al\(_2\)O\(_3\) at pressures of about 6000 atm. All attempts at synthesis at lower pressures, e.g., Roy, Roy, and Osborn (1950), Barrer and White (1951), Isaacs and Roy (1958) have failed, although other compounds with the α-spodumene structure have been synthesized at the lower pressures. In these, aluminum has been replaced by iron, chromium, vanadium, and scandium (e.g., Brown, 1971), and these substitutions, together with gallium and manganese, have been observed in natural spodumenes. However, because natural spodumenes can occur without appreciable substituting elements (Deer, Howie, and Zussman, 1963), it cannot be said that these substitutions have aided spodumene crystallization in nature. Nor, therefore, should the presence of these elements be necessary for its formation in the laboratory.

The α-LiAlSi\(_2\)O\(_6\) structure is very dense (sp gr ≈ 3.2) with Al in 6-fold coordination. Synthesis under geologically realistic conditions requires nucleation and growth of this dense phase at low temperatures where these processes are slow, and there are a number of lower density phases (sp gr ≈ 2.4), e.g., β-spodumene, petalite, α- and β-eucryptite, each with Al in 4-fold coordination, which are more easily nucleated metastably. Fyfe (1960) and Coombs et al (1959) stressed that the use of highly reactive gels to achieve reasonable reaction rates at temperatures below 500°C increases the chance of formation of metastable phases. Furthermore, Carr and Fyfe (1960) and Shorygin (1962) showed that reaction products varied with different starting materials, thus indicating that the state of the Al in solution influences the solid phases produced.

The hydrothermal syntheses of spodumenes described here were conducted to look for possible influence of gel composition. It is assumed that α-LiAlSi\(_2\)O\(_6\) is the stable phase at 2 kbar, 500°C and that β-spodumene was formed metastably.

Experimental Work

All runs were made with the components (noted below) plus water in sealed gold capsules contained in cold seal, externally heated, test tube bombs of Stellite or stainless steel. Temperatures were measured at thermocouple wells in the bomb walls beside the charges and are accurate to ±10°C; pressures were measured by Bourdon gauges rated accurate to ±50 bars. All runs were carried out at 2,000 bars pressure. The bomb was first brought
up to pressure, and then to temperature in about 20 minutes, and at the termination of the run was quenched by air blast, reaching less than 100°C in under one minute.

Phase identification was by X-ray diffraction, and the cell parameters were determined using a Hägg Guinier camera. Gels containing Al, Fe, Cr, V, Sc, In, and Ga were prepared by a method previously used in studies of the Li$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O system (Drysdale, 1971). For Sc, In, and Ga, the starting solution was the chloride.

Results

(a) Synthetic Products

(i) Aluminum spodumene. Gels of LiAlSi$_2$O$_6$ composition yielded β-spodumene at higher temperatures and zeolites at temperatures below 350°C. These crystalline products were the first evidence of structure to appear. (These results are reported in part in Drysdale, 1971). Gels with excess silica produced petalite+quartz and not the spodumene+quartz assemblage seen in nature. It was established that the amorphous Al(OH)$_3$ precipitate prepared from Al(NO$_3$)$_3$·9H$_2$O + LiOH + NH$_4$OH (simulating an intermediate stage in the synthesis) crystallized to boehmite and not diaspore at 440°C.

(ii) Iron spodumene. α-iron-spodumene readily formed, and iron spodumene + quartz assemblages similar in bulk composition to spodumene + quartz pegmatitic cores can be produced from compositions with excess silica. Iron petalite was not formed, nor was β-iron-spodumene.

Amorphous Fe(OH)$_3$, prepared by addition of LiOH + NH$_4$OH to Fe(NO$_3$)$_3$·9H$_2$O solution, dried at room temperature to form FeOOH, goethite (analogous to diaspore) but crystallized hydrothermally at 440°C to hematite (corundum structure).

(iii) Chrome spodumene. A Cr spodumene, α-LiCrSi$_2$O$_6$, forms from gels of ideal composition.

A hydrated Cr oxide, Cr(OH)$_3$·nH$_2$O, was formed from Cr(NO$_3$)$_3$·9H$_2$O + LiOH + NH$_4$OH and at 440°C hydrothermally crystallized to CrO(OH). At 500°C under $P_{N_2O} = 2,000$ bars this forms Cr$_2$O$_3$, eskolaite, with corundum structure.

(iv) Vanadium spodumene. Gels of Li$_2$O·V$_2$O$_5$·4SiO$_2$ composition were prepared using vanadyl sulfate, but these failed to crystallize to an α-spodumene structure. It was found, however, that if vanadium were maintained in the trivalent state, by precipitating the gel in the presence of hydrazine, drying in an inert atmosphere, and then recrystallizing at 600°C also with hydrazine present (or in an inert atmosphere, nitrogen-filled capsule), vanadium α-spodumene could be formed. Preparation of α-V(OH)$_3$, VO(OH)$_2$, and V$_2$O$_5$ was not attempted.

(v) Indium, scandium and gallium. Indium and scandium formed spodumenes as outlined in Table 1, but the gallium analog did not form under these conditions. No attempt was made to determine the intermediate oxides, but it is of interest that InOOH has a particularly dense structure. This is believed to be the first synthesis of indium spodumene.

(b) Results of X-ray Examinations

The parameters for the monoclinic unit cells of the various spodumenes are shown in Table 2, together with the effective ionic radii for the metal atom in the spodumene as calculated by Shannon and Prewitt (1969) on the basis of an oxygen radius of 1.40 Å. These values were refined by least squares methods from measurements made with a Hägg-Guinier powder X-ray camera using ThO$_2$ as standard ($a_0 = 5.5969 ± 0.0005$ Å).

The unit cells show a negligible variation in monoclinic angle and the c dimension. This confirms the expectation of Papke et al (1973). The synthetic spodumenes all have longer $a$ and $b$ dimensions than the natural α-aluminum-spodumene.

<table>
<thead>
<tr>
<th>Table 1. Hydrothermal Experiments</th>
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<tbody>
<tr>
<td><strong>Bulk Composition</strong></td>
</tr>
<tr>
<td>Li$_2$O Al$_2$O$_3$ 4SiO$_2$</td>
</tr>
<tr>
<td></td>
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<td></td>
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<tr>
<td>Al(OH)$_3$</td>
</tr>
<tr>
<td>Li$_2$O Fe$_2$O$_3$ 4SiO$_2$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
</tr>
<tr>
<td>Li$_2$O V$_2$O$_5$ 4SiO$_2$</td>
</tr>
<tr>
<td>Li$_2$O Sc$_2$O$_3$ 4SiO$_2$</td>
</tr>
<tr>
<td>Li$_2$O In$_2$O$_3$ 4SiO$_2$</td>
</tr>
<tr>
<td>Li$_2$O Ga$_2$O$_3$ 4SiO$_2$</td>
</tr>
</tbody>
</table>

* Excess Li$_2$O does not affect the product.
** Synthesized in 4% hydrazine solution.
HYDROTHERMAL SYNTHESIS OF SPODUMENES

Table 2. Cell Sizes of Synthesized α-Spodumene

<table>
<thead>
<tr>
<th>Compound</th>
<th>a Å ±</th>
<th>b Å ±</th>
<th>c Å ±</th>
<th>β° ±</th>
<th>Volume Å³</th>
<th>Ionic* Radius Metal ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium spodumene (natural)</td>
<td>9.48 ± 0.01</td>
<td>8.38 ± 0.01</td>
<td>5.24 ± 0.01</td>
<td>109.5 ± 0.2</td>
<td>392.5</td>
<td>.54</td>
</tr>
<tr>
<td>Chromium spodumene</td>
<td>9.60 ± 0.01</td>
<td>8.63 ± 0.01</td>
<td>5.23 ± 0.01</td>
<td>110.2 ± 0.2</td>
<td>406.8</td>
<td>.615</td>
</tr>
<tr>
<td>Iron spodumene</td>
<td>9.81 ± 0.01</td>
<td>8.64 ± 0.01</td>
<td>5.27 ± 0.01</td>
<td>110.3 ± 0.1</td>
<td>419.0</td>
<td>.64</td>
</tr>
<tr>
<td>Vanadium spodumene</td>
<td>9.78 ± 0.02</td>
<td>8.65 ± 0.03</td>
<td>5.29 ± 0.01</td>
<td>110.0 ± 0.2</td>
<td>420.5</td>
<td>.64</td>
</tr>
<tr>
<td>Scandium spodumene</td>
<td>9.78 ± 0.01</td>
<td>8.91 ± 0.01</td>
<td>5.27 ± 0.01</td>
<td>109.9 ± 0.1</td>
<td>431.8</td>
<td>.75</td>
</tr>
<tr>
<td>Indium spodumene</td>
<td>9.70 ± 0.03</td>
<td>8.95 ± 0.02</td>
<td>5.24 ± 0.01</td>
<td>109.1 ± 0.4</td>
<td>420.9</td>
<td>.80</td>
</tr>
</tbody>
</table>

* Metal in 3+ state and with six coordination based on r(VI O²⁻) = 1.40Å (Shannon and Prewitt (1969)). Bracketed data for cell sizes are from Appleman and Stewart (1968).

and consequently a significantly larger unit cell volume.

**Discussion**

The syntheses reported show that the α-spodumene structure readily nucleates and grows if Al³⁺ is excluded and its place taken by Fe³⁺, Cr³⁺, and V³⁺. Synthesis of α-LiAlSi₂O₆ has only been accomplished at much higher pressures where the dense α-spodumene is favored over the less dense phases which are likely to nucleate (e.g., Blinov and Roy, 1963, 1969; Neuhaus and Meyer, 1965).

It is suggested that this difference in behavior of Al³⁺ stems from the formation of hydroxides, oxyhydroxides, and oxides with Al³⁺ 6-coordinated in relatively open, less dense structures with defective cubic close packing, whereas Fe³⁺, Cr³⁺, and V³⁺ tend to form hydroxides, oxyhydroxides, and oxides with Fe³⁺, Cr³⁺, and V³⁺ 6-coordinated in more dense structures with hexagonal close packing.

Thus Al³⁺ forms γ series compounds gibbsite, boehmite, and γ-Al₂O₃ rather than bayerite, diaspor, and corundum, while Fe³⁺, Cr³⁺ (and V³⁺ probably) form α-series compounds. The former series is thought to provide a situation inimical to α-LiAlSi₂O₆ nucleation; the α series furnishes a dense, closely packed environment favorable to α-spodumene structure nucleation.

The following review discusses the types of structures likely to result during crystallization of the various gels and links these with the ability to nucleate α- or β-spodumene.

1. **LiAlSi₂O₆ Gels**

In the Al₂O₃-H₂O system metastable formation of boehmite in the diaspor stability field has often been observed in short duration runs because of its comparative ease of nucleation (e.g., Fyfe and Godwin, 1962), and this accords with our observations. For gels in the Li₂O-Al₂O₃-SiO₂-H₂O system an amorphous Al(OH)₃ formed, probably with octahedrally coordinated Al in an approximately close packed O network (Petz, 1968). Because of the presence of SiO₂ this Al(OH)₃ may have remained amorphous (Caillere and Henin, 1962; Krleza, Stanicic, and Ruzdic, 1968). Formation of bayerite is inhibited by the presence of Li (Torkar and Bertsch, 1961), so that in our gels (at pH around 8 to 9) gibbsite is more stable than bayerite, and at temperatures as low as 60° the precursor of boehmite will begin to form (Ginsberg, Hultig, and Stiehl, 1962). Similarly, Milligan (1951) found that hydrous γ-AlO(OH) forms readily when alumina is precipitated from a nitrate solution; but was unable to prepare bayerite uncontaminated by gibbsite. Formation of diaspor is therefore un-
likely in the gels prepared in our experiments, and the hydrothermal dehydration from diaspor to α-Al₂O₃ (Lima-de-Faria, 1963) cannot take place. It is possible to form α-Al₂O₃ hydrothermally from boehmite at 460° (Cooke and Haresnapke, 1947), but this seems to occur by a solution mechanism (Yamaguchi and Yanagida, 1963; Yamaguchi, Yanagida, and Fujimaru, 1965) and is inhibited by the presence of lithium (Yamaguchi et al., 1965).

The environment throughout gel crystallization thus involves formation of the less dense structural modifications, inhibiting nucleation of α-spodumene. In all experiments β-spodumene (or petalite if excess silica) has formed in the stability field of α-spodumene.

2. LiCrSi₂O₆ Gels

Milligan (1951) showed Cr(OH)₃ precipitated from Cr³⁺ salt solution dries to a bayerite-like material, α-Cr(OH)₃, hydrous chromic hydroxide, that is isostructural with α-Al(OH)₃. The denser hexagonal-close-packed lattice with Cr in 6-fold coordination is preserved during hydrothermal recrystallization in his experiments and ours. Laswick (1962) showed HCrO₂ is more stable than, and does form in preference to, γ-CrO(OH). Eskolaite, α-Cr₂O₃, forms readily during hydrothermal dehydation. α-LiCrSi₂O₆ was easily nucleated and crystallized in these gels because of the favorable structural environment existing throughout gel preparation and crystallization.

3. LiFeSi₂O₆ Gels

During gel formation Fe³⁺ may be expected to form amorphous Fe(OH)₃. Unlike Al, however, Fe³⁺ tends strongly to form the stable α-series compounds during preparations (see Brauer, 1965), where it enters into 6-fold coordination in densest hexagonally close packed O lattices. The α-series minerals form readily during hydrothermal crystallization; Wefers (1966) has shown the γ form of FeOOH to be unstable relative to α at more than 25°C under hydrothermal conditions. So strong is this tendency that during coprecipitation and hydrothermal crystallization of Al-Fe hydroxide gels the hexagonal close packed O lattices set up about Fe may force Al³⁺ to assume α-type structures; Maurel (1967) synthesized haematite + diaspor from Al₂O₃ + Fe₂O₃ + H₂O at 425°C under 2.5 kbar P H₂O, and Montel (1960) found Fe(OH)₃ orienting the crystallization of Al(OH)₃ toward bayerite in amorphous coprecipitates of Fe(OH)₃-Al(OH)₃. On hydrothermal dehydration α-FeOOH converts topotactically to haematite (Lima-de-Faria, 1963). An environment predisposed to nucleation of densest hexagonally-close-packed O structures exists throughout the preparation and crystallization history. Accordingly, α-LiFeSi₂O₆ was easily synthesized.

4. LiVSi₂O₆ Gels

The natural V oxide hydrate, montroseite, (V,Fe)OOH has the diaspor structure (Evans and Block, 1953). It is likely that the model for formation and crystallization of these gels is similar to that for gels with Fe and Cr. That is, a stable, dense, closest-packed O network with V³⁺ in 6-fold coordination forms more readily than, and is more stable than, the γ lattice, and this provides a situation suitable for nucleation of α-spodumene structure.

It is not known why the large In and Sc ions favor spodumene formation and the smaller Ga does not.
Acknowledgments

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References


LIMA-de-FARIA, J. (1963) Dehydration of goethite and diaspore. Z. Kristallogr. 119, 176-203.


NEUHAUS, A., and H. J. MAYER (1965) Behaviour of eucryptite (α LiAlSiO₄) and other oxide phases at high pressures. Naturwissenschaften, 52, 639-640.


SHORYGIN, V. A. (1962) To check the hypothesis that the state of Al in solution influences the character of solid phases. Geochemistry, 548-549.


D. J. DRYSDALE


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