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Hydrothermal Synthesis of Various Spodumenes

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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 Kuznetzov, Shternberg, and Ivanova (1970) using aqueous LiCl solution + Al_2O_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 In these, aluminum has been replaced by iron, chromium, vanadium, and scandium (*e.g.*, Brown, 1971), and these substitutions, together with gallium and manganese, have been observed in natural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-$LiAlSi_2O_6$ 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-$LiAlSi_2O_6$ 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

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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_2O-Al_2O_3-SiO_2-H_2O system (Drysdale, 1971). For Sc, In, and Ga, the starting solution was the chloride.

Results

(a) Synthetic Products

(i) *Aluminum spodumene.* Gels of $LiAlSi_2O_6$ 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 $Al(NO_3)_3 \cdot H_2O + LiOH + NH_4OH$ (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 pegmatite 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 $LiOH + NH_4OH$ to $Fe(NO_3)_3 \cdot 9H_2O$ 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-$LiCrSi_2O_6$, forms from gels of ideal composition.

A hydrated Cr oxide, $Cr(OH)_3 \cdot nH_2O$, was formed from $Cr(NO_3)_3 \cdot 9H_2O + LiOH + NH_4OH$ and at 440°C hydrothermally crystallized to CrO(OH). At 500°C under $P_{H_2O} = 2{,}000$ bars this forms Cr_2O_3, eskolaite, with corundum structure.

(iv) *Vanadium spodumene.* Gels of $Li_2O \cdot V_2O_3 \cdot 4SiO_2$ 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), and V_2O_3 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 ($a_0 = 5.5969 \pm 0.005$ Å).

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

TABLE 1. Hydrothermal Experiments

Bulk Composition	Li added as	Temperature	Product
Li_2O Al_2O_3 $4SiO_2$	carbonate	300	Bikitaite
"	hydroxide	300	Zeolite A
"	carbonate	400-600	β spodumene
do. + excess SiO_2	"	300	Bikitaite + quartz
"	"	400-550	Petalite or petalite + quartz
$Al(OH)_3$	-	440	Boehmite
Li_2O Fe_2O_3 $4SiO_2$*	hydroxide or carbonate	400-500	α-spodumene
do. + excess SiO_2	carbonate	440-520	α-spodumene + quartz
$Fe(OH)_3$	-	440	Haematite
Li_2O Cr_2O_3 $4SiO_2$	carbonate	440-700	α-spodumene
$Cr(OH)_3$	-	440	$HCrO_2$ grimaldiite
"	-	500	Cr_2O_3 eskolaite
Li_2O V_2O_3 $4SiO_2$**	carbonate	600	α-spodumene
Li_2O Sc_2O_3 $4SiO_2$	"	500	α-spodumene
Li_2O In_2O_3 $4SiO_2$	"	500	α-spodumene
Li_2O Ga_2O_3 $4SiO_2$	"	500	unidentified

* *Excess Li_2O does not affect the product.*

** *Synthesised in 4% hydrazine solution.*

TABLE 2. Cell Sizes of Synthesized α-Spodumene

Compound	a Å	b Å	c Å	β°	Volume Å³	Ionic* Radius Å Metal ion
Aluminium spodumene (natural)	9.48 ± .01 (9.449 ± 003)	8.38 ± 0.01 (8.386 ± 001)	5.24 ± 0.01 (5.215 ± 002)	109.5 ± 0.2 (110°6.0' ± 1.7')	392.5	.54
Chromium spodumene	9.60 ± 0.01	8.63 ± 0.01	5.23 ± 0.01	110.2 ± 0.2	406.8	.615
Iron spodumene	9.81 ± 0.02 (9.665 ± .002)	8.64 ± 0.02 (8.669 ± .001)	5.27 ± 0.01 (5.294 ± .001)	110.3 ± 0.1 (110°9.0' ± 1.1')	419.0	.64
Vanadium spodumene	9.78 ± 0.02	8.65 ± 0.03	5.29 ± 0.01	110.0 ± 0.2	420.5	.64
Scandium spodumene	9.78 ± .01	8.91 ± .01	5.27 ± .01	109.9 ± .1	431.8	.75
Indium spodumene	9.70 ± .03	8.95 ± .02	5.24 ± .01	109.1 ± .4	429.9	.80

* *Metal in 3^+ state and with six coordination based on $r(\mathrm{VI}\ O^{2-}) = 1.40$Å (Shannon and Prewitt (1969)). Bracketed data for cell sizes are from Appleman and Stewart (1966).*

and consequently a significantly larger unit cell volume.

Discussion

The syntheses reported show that the α-spodumene structure readily nucleates and grows if Al^{3+} is excluded and its place taken by Fe^{3+}, Cr^{3+}, and V^{3+}. Synthesis of α-$LiAlSi_2O_6$ 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 Al^{3+} stems from the formation of hydroxides, oxyhydroxides, and oxides with Al^{3+} 6-coordinated in relatively open, less dense structures with defective cubic close packing, whereas Fe^{3+}, Cr^{3+}, and V^{3+} tend to form hydroxides, oxyhydroxides, and oxides with Fe^{3+}, Cr^{3+}, and V^{3+} 6-coordinated in more dense structures with hexagonal close packing.

Thus Al^{3+} forms γ series compounds gibbsite, boehmite, and γ-Al_2O_3 rather than bayerite, diaspore, and corundum, while Fe^{3+}, Cr^{3+} (and V^{3+} probably) form α-series compounds. The former series is thought to provide a situation inimical to α-$LiAlSi_2O_6$ 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. $LiAlSi_2O_6$ Gels

In the Al_2O_3-H_2O system metastable formation of boehmite in the diaspore 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 Li_2O-Al_2O_3-SiO_2-H_2O 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 SiO_2 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, Hueltig, 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 diaspore is therefore unlikely in the gels prepared in our experiments, and the hydrothermal dehydration from diaspore to α-Al_2O_3 (Lima-de-Faria, 1963) cannot take place. It *is* possible to form α-Al_2O_3 hydrothermally from boehmite at 460° (Cooke and Haresnape, 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. *$LiCrSi_2O_6$ Gels*

Milligan (1951) showed $Cr(OH)_3$ precipitated from Cr^{3+} 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 $HCrO_2$ is more stable than, and does form in preference to, γ-$CrO(OH)$. Eskolaite, α-Cr_2O_3, forms readily during hydrothermal dehydration. α-$LiCrSi_2O_6$ was easily nucleated and crystallized in these gels because of the favorable structural environment existing throughout gel preparation and crystallization.

TABLE 3. Hydroxide, Oxyhydroxide, and Oxide Structures Possible in Gel Crystallization

M^{3+} in 6-fold Coordination	
Hexagonal Close Packed O Network	Defective Close Packed O Network
$M^{3+} = Al^{3+}$	
α $Al(OH)_3$ Bayerite (Frequently inverts to gibbsite)	γ $Al(OH)_3$ Gibbsite (Forms readily)
α AlOOH Diaspore d 3.2-3.5 (Difficult to synthesize)	γ AlO(OH) Boehmite d 3.0 (Forms readily)
α Al_2O_3 (corundum structure)	γ Al_2O_3 (distorted defect spinel structure)
$M^{3+} = Cr^{3+}$	
α $Cr(OH)_3$ (Bayerite structure)	
α CrOOH Bracewellite d 4.3	γ CrO(OH) d ≈ 4.0
CrOOH Guyanaite d 4.6	
$HCrO_2$ Grimaldiite (readily prepared) d 4.1	
α Cr_2O_3 Eskolaite (corundum structure)	γ Cr_2O_3 (spinel structure)
$M^{3+} = Fe^{3+}$	
α $Fe(OH)_3$ (Bayerite structure)	
α FeOOH Goethite d 4.3 (Diaspore structure - forms readily).	γ FeO(OH) Lepidocrocite d 4.09 (Difficult to prepare; inverts readily to α form).
α Fe_2O_3 Haematite (corundum structure - forms readily)	γ Fe_2O_3 Maghemite (Derived spinel structure - Difficult to prepare; readily inverts to α form).
$M^{3+} = V^{3+}$	
α VOOH Montroseite d 4.0 (diaspore structure)	
α V_2O_3 (corundum structure)	

Data on the chromium oxy-hydroxides is very sparse.

3. *$LiFeSi_2O_6$ Gels*

During gel formation Fe^{3+} may be expected to form amorphous $Fe(OH)_3$. Unlike Al, however, Fe^{3+} 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 Al^{3+} to assume α-type structures; Maurel (1967) synthesized haematite + diaspore from $Al_2O_3 + Fe_2O_3 + H_2O$ at 425°C under 2.5 kbar P_{H_2O}, 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-$LiFeSi_2O_6$ was easily synthesized.

4. *$LiVSi_2O_6$ Gels*

The natural V oxide hydrate, montroseite, (V,Fe)OOH has the diaspore 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 V^{3+} 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.

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