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Effect of the Substitution of Boron for Aluminium in the β-Eucryptite $LiAlSiO_4$ Structure

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Abstract

The substitution of B for Al in the β-eucryptite structure was examined along the compositional series described by the stoichiometry $LiAl_{(1-x)}B_xSiO_4$ *with* x *ranging from 0 to 1. These samples were prepared according to a sol–gel route which employs prehydrolysed tetraethylorthosilicate (TEOS), Al and Li nitrates and boric acid in aqueous solution. Two different monophasic fields were found with the β-eucryptite and the β-spodumene structure, respectively, with* $0 \leq x \leq 0.40$ *and* $0.60 \leq x \leq 0.80$*; their relative stability is discussed in terms of averaged ionic radius of B, Al and Si ions and of lithium content.*

Die Substitution von Al durch B in der β-Eucryptit-Struktur, entlang der Zusammensetzung, die durch die Stöchiometrie $LiAl_{(1-x)}B_xSiO_4$ *beschrieben wird, wobei* x *zwischen 0 und 0.1 liegt, wurde untersucht. Die Herstellung der Proben erfolgte mittels der Sol–Gel-Methode unter Verwendung von vorhydrolysiertem Tetraethylorthosilikat (TEOS), Al- und, Li-Nitraten und Borsäure in wässriger Lösung. Es zeigten sich zwei verschiedene monophasige Gebiete mit β-Eucryptit- und β-Spodumen-Struktur mit* $0 \leq x \leq 0.40$ *beziehungsweise* $0.60 \leq x \leq 0.80$*. Ihre relative Stabilität wird bezüglich des durchschnittlichen Ionenradiuses von B, Al, Si und des Lithiumgehalts diskutiert.*

Nous avons étudié la substitution d'Al par B au sein de la structure de l'eucryptite β, ceci pour différentes stoechiométries x *du composé* $LiAl_{(1-x)}B_xSiO_4$ *(où* $0 \leq x \leq 1$*). Ces échantillons ont été préparés par un procédé sol–gel utilisant de l'orthosilicate de tetraéthyl hydrolysé au préalable, des nitrates de aluminium et de lithium et de l'acide borique en solution aqueuse. Deux domaines monophases ont été mis en évidence, l'un correspondant à une structure de type eucryptite β, l'autre à une structure de type spodumène β, pour* $0 \leq x \leq 0.40$ *et* $0.60 \leq x \leq 0.80$ *respectivement; leurs stabilités relatives sont interprétées en termes des rayons ioniques moyens de B, Al, Si et du contenu en lithium.*

1 Introduction

In a previous paper[1] the preparation, by a sol–gel route, of some amorphous xerogels was discussed, with the composition described as $Li_2O \cdot Al_2O_3 \cdot nSiO_2$ (n=2 to 4).

These xerogels were shown to exhibit a transition to a crystalline structure of the β-eucryptite type at about 600°C. In this paper we refer to the effect of the substitution of B for Al in the β-eucryptite (n = 2) examining the compositions described by the stoichiometry $LiAl_{(1-x)}B_xSiO_4$ with x ranging from 0 to 1. These compositions are prepared by a sol–gel technique, by means of the preliminary formation of an amorphous solid (xerogel). The preparative route employs prehydrolysed silicon alcoxide, Li and Al nitrates and boric acid and takes place in aqueous solution under slightly basic conditions.

The so-prepared xerogels display a nearly atomic mixing level which permits crystalline phases to be obtained quickly by heat treatment at relatively low temperatures. This fact is of fundamental importance, as both unreacted Li_2O and B_2O_3 show a not negligible vapour pressure at temperatures higher than 1100°C. If the crystalline phases are prepared by conventional solid state reaction, a method which requires very long heating at high temperatures, Li_2O and B_2O_3 partially sublimate before completion of the reaction and the compositional stoichiometry is no longer assured.

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2 Experimental

2.1 Preparation

A measured volume of tetraethylorthosilicate (TEOS) is added to an equal volume of ethanol (95%) and half a volume of distilled water. The pH of the aqueous alcoholic phase is adjusted to 0.5–1.0 with a few drops of 1 M HNO_3. In this way a clear solution is quickly obtained after a few minutes of stirring at room temperature. The *r* factor (water moles/TEOS moles) reaches a value of about 7.

Under these conditions TEOS is first partially hydrolysed to silanol[2] monomers. An aqueous solution of aluminium and lithium nitrates and boric acid in proper amounts is then added to the stoichiometric quantity of the above solution. The clear solution thus obtained is then treated with excess aqueous ammonia (10 wt%) . Condensation and crosslinking of the silanols and gelation of the solution occurs, whilst aluminium hydroxide precipitates in the form of an amorphous gel. The basic (pH = 10) gel obtained is first cautiously dried at 105°C and then gradually heated up to 400 °C, thus removing water and gaseous products formed by the decomposition of nitrates, leaving a white crispy oxide powder. The solids obtained by this procedure are found to be amorphous when examined by X-ray diffraction; they are hereinafter referred to as B*xx*, *xx* indicating the atomic percentage of aluminium substitution.

The xerogels obtained at 400°C were submitted to DTA in a Netzsch 414 differential calorimeter with a heating rate of 10°C/min using Pt crucibles and about 50 mg of powder. The DTA curves are all characterized by two marked endothermic peaks, the first beginning at about 200°C and the second beginning at about 400°C with a maximum at 500°C (see Fig.1 for example). Both these phenomena are accompanied by a simultaneous weight loss, as evidenced by the thermogravimetry, and are due, in the authors' opinion to the loss of the physically and chemically adsorbed water (first peak) and to the loss of surface hydroxyls with simultaneous decrease in surface area (second peak).

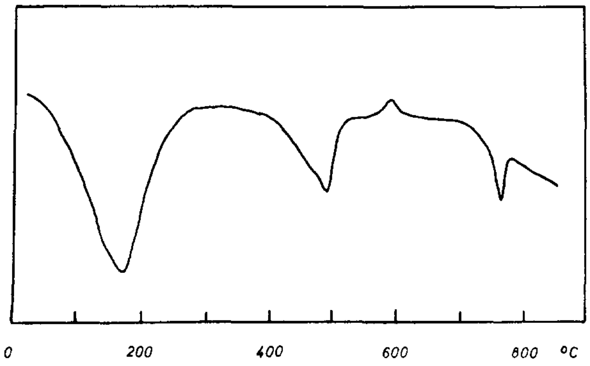

Fig. 1. Differential thermoanalysis (DTA) curve for B60 sample.

Indeed the xerogels develop a high surface area: preliminary results obtained by nitrogen adsorption at 78K show values of specific areas ranging from 191 to 25 m^2/g with a progressive and regular decrement along with the boron increase from $x = 0$ to $x = 1$ compositions.

In a higher temperature range (600–700°C) an exothermic peak occurs; the XRD analysis performed on samples heat treated at temperatures preceding and following these exotherms allowed them to be assigned to a crystallization process. The same XRD analysis allowed the crystallization products to be structurally characterized.

The powder diffraction analysis was performed with computer-aided Philips PW 1710 equipment (Cu K_α radiation, graphite monochromator). The analysis was carried out at room temperature on samples obtained from amorphous xerogels, directly heat treated in air at the indicated temperatures for 30 min, unless stated otherwise.

3 Results and Discussion

3.1 Compositions B0, B20 and B40

The amorphous samples with a boron content comprised between 0 and 40 were each heated

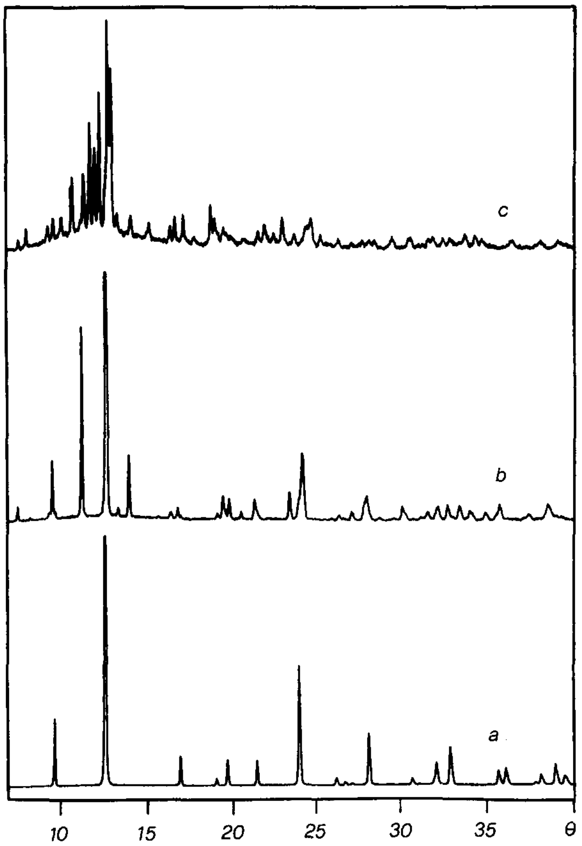

Fig. 2. X-ray powder patterns of: (a) B40 sample, 1200°C (β-eucryptite structure); (b) B60 sample, 800°C (β-spodumene structure); (c) B90 sample, 700°C (polyphasic sample with amorphous material).

above the crystallization transition at three different temperatures (800, 1000 and 1200°C). The relative XRD patterns showed in every case the formation of a crystalline structure, with slightly more broadened peaks at the lowest (800°C) temperature. The reflections were indexable according to a hexagonal structure of the stuffed β–quartz type. In this structure the mode of linking of the silicon tetrahedra typical of the quartz structure is retained, while some of the Si atoms are replaced by Al or B, and Li cations are accommodated in the interstices of the structure in order to maintain the charge balance.

For the compositions B20 and B40, the XRD peaks (Fig. 2) were all indexable on the basis of a simple β-quartz structure, whilst for the B0 sample ($LiAlSiO_4$), as referred to in a previous paper,[1] evidence was found of additional diffraction peaks requiring a doubling of the c_0 cell parameter. This fact was shown to be related to the mutual Si–Al ordering in the tetrahedral framework of the phase $LiAlSiO_4$ (B0) and to a contemporary ordering of lithium along the positions in the framework channels, as first proposed by Pillars & Peacor.[3]

A complete disorder between Al and Si atoms would make all the tetrahedral interchannel positions equivalent and hence imply an order → disorder transition for the lithium atoms too; superstructure XRD reflections of the c-type would decrease to zero intensity, therefore halving c_0.

Among the different samples examined only B0 displays a superstructure along the c_0 axis, and therefore some degree of Si–Al ordering, in contrast to the samples B20 and B40.

In order to confirm the B–Al substitution over the same crystallographic positions and to show the influence of the substitution on all the interatomic distances, the two compositions B20 and B40, heated at 1200°C, were submitted to a measure of the diffracted X-ray peak intensities (Cu–K_α radiation). The data were computer-collected (step scan interval $2\Theta = 0.005$, count time = 2 s) and further elaborated for background subtraction, net intensity evaluation, Lorentz and polarization correction. Overlapping peaks were deconvoluted using a Lorentzian curve fitting. The peaks used ranged from 10 to 80 degrees 2Θ . The independent coordinates and the occupation factors for the Li, Al and Si atoms were refined on the basis of the XRD net intensities using a full-matrix least-squares procedure, starting from the high temperature β-eucryptite structure in the space group $P6_222$ (no. 180). The results of this refinement are collected in Table 1.

A marked variation in the unit cell parameters, as shown in Fig.3, was measured; noteworthily, the B substitution affects to a much greater extent the c_0 cell parameter in respect to a_0. This fact could be explained by the stuffed β-quartz structure of these phases: the helix of the SiO_4 tetrahedra, formed by the interconnection of opposite corners, is evidently largely affected in this 'repetitive interval' by the foreign elements (Al, B) which substitute for Si into the oxygen tetrahedra. This effect is caused by the difference in ionic size of Si,

Table 1. Results of the XRD intensities refinements

Position	*x/a*	*y/b*	*z/c*	*Occupation (%)*	*Thermal factor (isotropic)*
B0, $LiAlSiO_4$ (a_0 = 0.5267 nm, c_0 = 1.115 nm), space group = $P6_222$ (No. 180)[a]					
Si (3*c*)	1/2	0	0	100	0.5
Al (3*d*)	1/2	0	1/2	100	0.5
Li (3*a*)	0	0	0	31 ± 8	0.5
Li (3*b*)	0	0	1/2	19 ± 8	0·5
O (12*k*)	0.233 (4)	0.399 (3)	0.747 (4)	100	0.5
R = 0.0605					
B20, $LiAl_{0.8}B_{0.2}SiO_4$ (a_0 = 0.5257 nm, c_0 = 0.5519 nm), space group = $P6_222$ (No. 180), number of reflections = 29					
Si (3*c*)	1/2	0	0	50	0.5
Al (3*c*)	1/2	0	0	40	0.5
B (3*c*)	1/2	0	0	10	0.5
Li (3*a*)	0	0	0	50	0·5
O (6*j*)	0.203 (2)	0.406 (4)	1/2	100	2.0 (2)
R = 0.0648					
B40, $LiAl_{0.6}B_{0.4}SiO_4$ (a_0 = 0.5246 nm, c_0 = 0.5469 nm), space group = $P6_222$ (No. 180), number of reflections = 29					
Si (3*c*)	1/2	0	0	50	0.5
Al (3*c*)	1/2	0	0	40	0.5
B (3*c*)	1/2	0	0	10	0.5
Li (3*a*)	0	0	0	50	0·5
O (6*j*)	0.203 (2)	0.406 (4)	1/2	100	4.2 (2)
R = 0.0532					

[a] Values taken from Ref. 1.

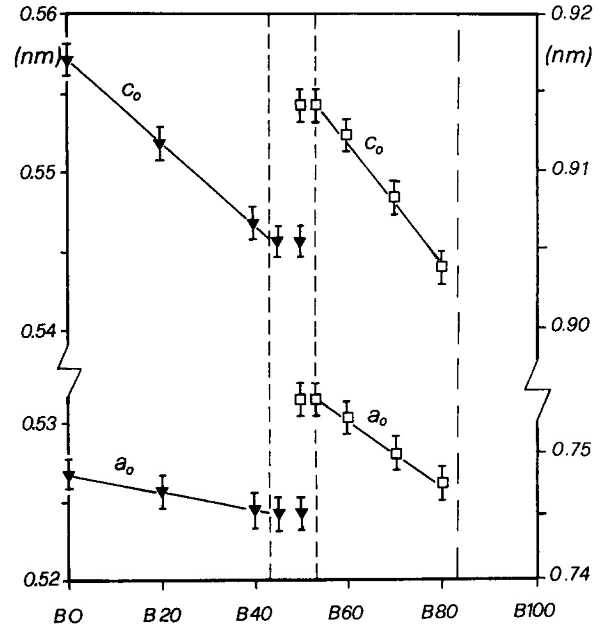

Fig. 3. Unit cell parameters of the B0–B100 series (silicon used as internal standard, a_0 = 5.43088 Å).

Al and B (Si^{4+}=26 pm, Al^{3+}=39 pm, B^{3+}=12 pm in four-fold coordination.[4]) Consequently it can be argued that the average Me–O distance (Me=Si, Al, B in tetrahedral coordination) decreases with an increase in the B for Al substitution therefore affecting the packing characteristics of the MeO_4 tetrahedra in the helix.

The high thermal factor which results for the oxygen atom in the refinement for the B20 structure (2.0) and particularly for the B40 structure (4.2) is most probably a consequence of the multifold occupation of the 3*c* position by elements of such different ionic radii as Si, Al and B. This fact forces local displacements in the oxygen positions, simulating an abnormally high thermal factor for the same atom during the refinement of its position.

3.2 Compositions B45 and B50

These two compositions show, after the crystallization, the presence of two phases: the β-eucryptite solid solution and a second phase, whose diffraction peaks can be indexed as a β-spodumene solid solution.

3.3 Compositions B60, B70 and B80

These compositions when heated at 800°C show the presence of a single structure, of the β-spodumene type (Fig.2). XRD patterns of samples heated at lower temperature (700°C) show evidence of the $Li_2B_4O_7$ phase: however this phase disappears completely between 700 and 800°C, this transformation being probably connected to the endotherm DTA peak shown at 760°C (Fig.1). The β-spodumene structure has a tetragonal symmetry, space group $P4_32_12$, and was first proposed for the $LiAlSi_2O_6$ compound by Li and Peacor.[5]

Table 2. Interatomic distances

Sample	*Distance*	*Calculated from structural refinement (pm)*	*Calculated from ionic radii (pm)*[4]
B0	S–O	164	161
	Al–O	171	174
B20	Me–O	166	165
	Li–O	206	209
B40	Me–O	164	162
	Li–O	206	209

The same authors showed that it may be considered as a stuffed derivative of the keatite (a high-pressure modification of SiO_2). This structure is characterized by a three-dimensional aluminosilicate framework in whose interstices the Li^+ cations lie. These atoms were found to be coordinated to four oxygen atoms, while the distribution of Si and Al in the tetrahedra is random. This structure is dominated by the interlocking of five-membered rings of $(Si,Al)O_4$ tetrahedra, which are located approximately parallel to the *xy* plane and are arranged so as to create zeolite-like channels (Fig.4) (indeed $LiAlSi_2O_6$ was shown to possess ion exchange properties) . In one unit cell of this structure, with *Z*=4, are contained four lithium atoms, which result located on an eight-fold site, being however distributed among four sets of paired sites of the eight-fold positions.

Each Li atom in $LiAlSi_2O_6$ occupies either of the two sites in each pair, the distance between the two sites in each pair (133 pm)being too short for a simultaneous occupation of both sites. The average (Al,Si)–O distance in this structure is 164.5 pm, whilst the same increases to 167.5 pm in the β-eucryptite form of $LiAlSiO_4$. The former structural type is therefore stabilized through the occupation of tetrahedral sites by ions with a shorter average ionic radius. This structural stabilization finds a match in the silica polymorphs: high pressures shorten the average Si–O bonds and therefore simulate a Si substitution by smaller

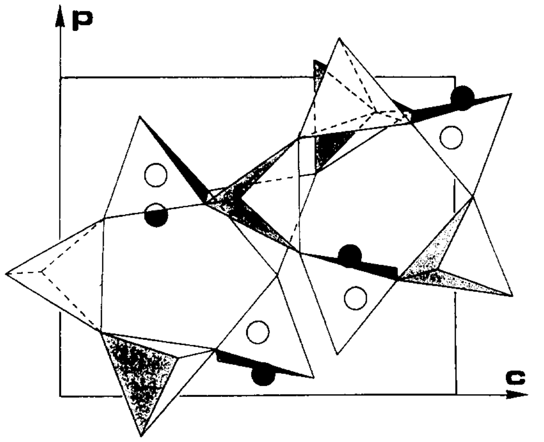

Fig. 4. Interlocking of five-membered rings in the β-spodumene structure (○, lithium atoms).

cations; keatite indeed results stabilized by higher pressures and therefore by shorter Si–O bonds with respect to quartz.

These experiments show that along the compositions $LiAl_{1-x}B_xSiO_4$ the same effect has to be found, the averaged ionic radius of the cation being varied according to the degree of boron for aluminum substitution. Indeed these compositions crystallize:

(a) with a β-eucryptite structure when the average Me–O distance ranges from 167.5 to 162 pm (B0 to B40) (Me=Si,Al,B; values calculated according to Shannon,[4] oxygen in twofold coordination);
(b) in a biphasic admixture of β-eucryptite and β-spodumene solid solution with an average Me–O distance from 161.5 to 160 pm (B45 and B50);
(c) with a β-spodumene structure with an average Me–O distance of 159.4 to 156.7 pm (B60, B70 and B80).

The transition from one crystallization form to the other occurs however with Me–O distance shorter than that found for the $LiAlSiO_4$ to $LiAlSi_2O_6$ transition. This difference can be explained, in the authors' opinion, by the higher lithium content of the solid solutions examined here (one Li atom over two MeO_4 units) with respect to $LiAlSi_2O_6$ (one Li over three MeO_4 units). This fact should indeed hinder the crystallization of the boron-containing β-spodumene solid solution, in the unit cell of which 6 Li atoms are contained, with the contemporary forced occupation of two paired sites; therefore shorter Me–O distances have to be reached in order to allow this form of crystallization.

3.4 Compositions B90 and B100

The crystalline phases arising from the amorphous B90 composition at 700°C are the β-spodumene solid solution limit term, with an approximate composition B80 as estimated from the unit cell parameters, $Li_2Si_2O_5$ and $Li_2B_4O_7$.

Moreover a broadened XRD peak centred around 12Θ is indicative of the presence of still-amorphous material. Heat treatments higher than 700°C yielded a bulky glassy mass, difficult to crystallize and to characterize. From the evidence of the ternary phase diagram $Li_2O–B_2O_3–SiO_2$[6] the amorphous material should be constituted mainly by SiO_2, which cannot evolve at such low temperatures into a crystalline form. This situation is apparently reversed for the B100 composition ($LiBSiO_4$). This sample, heated at 700 or 800°C seems to originate as a crystalline phase with only some α(low)-quartz (XRD evidence) while the presence of a large and broadened background peak is undoubtedly indicative of still-amorphous material, in this case mainly borosilicates.

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