

Boron for Aluminium Substitution in the KAlSi_2O_6 Leucite Structure

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Abstract

Boron for aluminium substitution in the leucite structure (ANA-type zeolitic framework) has been examined by sol-gel preparation of different samples along the compositional junction $\text{KAl}_{(1-x)}\text{B}_x\text{Si}_2\text{O}_6$ with $0 \leq x \leq 1$. By increasing the x value from 0 to 1 the samples crystallize, in a temperature range from 900 to 1250°C, with tetragonal ($0 \leq x \leq 0.25$), cubic ($0.50 \leq x \leq 0.80$) and again tetragonal ($0.90 \leq x \leq 1.00$) symmetry. This result for the end member with $x=1$ (KBSi_2O_6) conflicts with earlier determinations. The apparent cubic symmetry, evidenced by previous data in the literature on this phase, is discussed in terms of K, B, Si imbalance in the preparations. The samples along the above junction were examined with XRD (room and high temperature), DTA, FTIR, Dilatometry; the results indicate that all the phases derive from a cubic high-temperature form by means of a displacive transition. © 1997 Elsevier Science Limited.

Introduction

The leucite structure, showing the ANA-type of zeolitic framework, has been the subject of extensive research, due to its displacive tetragonal to cubic transition, the ordering of Al and Si on the T-sites and its ferroelastic and dielectric properties.^{1,2} The structure itself is quite compliant toward substitution of the trivalent ion in the tetrahedral (T) sites; indeed Al can be replaced by another trivalent element like Fe,³ B^{4,5} or even by an equimolar mixture of Si and a bivalent element like Mg, Zn or Cd.⁶ A phase referred to as KBSi_2O_6 was first prepared by Bayer and Florke⁷ through solid-state reaction and later by Ihara and Kamei⁴ from glass of the same composition in the form of single crystals grown in KCl flux.

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Both workers obtained an apparently cubic phase, whose structure was solved by Ihara in the I43d space group.

Recently, the hydrothermal synthesis of a fully B-substituted K-leucite was attempted by Millini *et al.*⁸ They operated at 150°C for time intervals varying between 5 and 10 days, starting from gel compositions having a $\text{SiO}_2/\text{B}_2\text{O}_3$ molar ratio of two and a KOH/SiO_2 ratio between 0.65 and 0.9. In some of their preparations a tetrapropyl- or tetraethylammonium bromide or choline chloride template was used. The final products were often accompanied by an amorphous phase; the chemical analyses of samples free from the amorphous phase showed compositions with an ANA structure but imbalance in both the Si/B and K/B atomic ratios; indeed, the Si/B ratio was between 2.2 and 2.45 and the K/B ratio between 1.02 and 1.18. The above authors found an apparent cubic symmetry ($a_0 = 12.64 \text{ \AA}$) and refined the structure in the space group Ia3d, different from that used by Ihara, from a powder X-ray diffraction profile fitting.

Finally, F. Di Renzo and co-workers (pers. commun.) very recently obtained, under mild hydrothermal conditions and with Si/B ratios in the starting gel composition ranging from 2.35 to 4.25, the borosilicates of rubidium and cesium with the leucite structure. In the presence of potassium, however, these preparative conditions led to K-danburite (KBSi_3O_8).

The aim of this work was to study the solids originating from the gradual substitution of B for Al in the leucite stoichiometry, which can be represented by the general formula $\text{KAl}_{(1-x)}\text{B}_x\text{Si}_2\text{O}_6$, and to reconsider critically the end member having $x = 1$.

Experimental

Different compositions with formula $\text{KAl}_{(1-x)}\text{B}_x\text{Si}_2\text{O}_6$ were synthesized with a sol-gel technique

through an amorphous xerogel precursor. This preparative route leads to higher homogeneity of the precursor (nanostructured precursor), which then lowers the crystallization temperature of the amorphous mass and consequently avoids any possible loss of B_2O_3 or K_2O at the elevated temperatures necessary for conventional methods of solid-state reaction, thus preventing undesired compositional changes of the crystalline products.

The sol-gel technique employs an organosilicon precursor (tetraethoxysilane, TEOS), boric acid and K, Al nitrates. TEOS is first hydrolysed in acidic HNO_3 environment ($pH \approx 1$) yielding a clear aqueous solution of silanol monomers,⁹ to which is then added the stoichiometric amount of H_3BO_3 , $Al(NO_3)_3 \cdot 9H_2O$ and KNO_3 . It is then rapidly hydrolysed by addition of concentrated ammonia solution. The mass obtained is cautiously heated to $400^\circ C$; during this treatment the nitrates and organic residues decompose. The resulting xerogels are amorphous by X-ray diffraction.

Each amorphous composition is first submitted to simultaneous DTA and TG analyses. All thermographs are characterized by two endotherms coupled with weight losses, which are centred around 120 and $600^\circ C$ respectively, and which can be accounted for in terms of two kinds of water loss: the former endotherm is due to physically absorbed water and the latter to chemically bound water (OH groups) in the xerogel mass. The second weight loss is particular evident in boron-rich samples where it can account for up to 15%, while it corresponds to only 2–3% in the pure Al-leucite sample.

A marked exotherm occurs at higher temperatures, with no associated weight loss. This can be related to crystallization of the amorphous xerogel mass. Peak temperatures listed in Table 1 are strongly affected by boron content. Hereafter, the composition is indicated with the notation B_{xx} , where xx denotes the atomic percentage of aluminum substitution in Al-leucite.

Table 1. Crystallization temperatures of the different xerogels measured at the peak (heating rate 10 K/min in fluxed chromatographic air)

| Composition | Cryst. temp. ($^\circ C$) |
|-------------|-----------------------------|
| B00 | 1250 |
| B12 | 995 |
| B25 | 920 |
| B33 | 910 |
| B40 | 885 |
| B50 | 890 |
| B60 | 875 |
| B70 | 875 |
| B80 | 870 |
| B90 | 780 |
| B100 | 675 |

The amorphous xerogels were all crystallized in air at $1000^\circ C$ for 60 min, except for B00 which was crystallized at $1250^\circ C$ for 30 min; further characterizations were conducted on these samples.

XRD, TG-DTA dilatometry characterization

The X-ray powder diffraction patterns (Cu K_α radiation, graphite monochromator on the diffracted beam, sample spinner, variable divergence slit, room temperature) of the crystallized samples show the presence of only one phase or, in some cases (B33 and B40), the simultaneous presence of two. The monophasic samples are easily indexable on the basis of a cubic or a tetragonal leucite framework, while the biphasic ones clearly show the simultaneous presence of both structures. Prolonged heating at the preparation temperature did not affect the initial patterns.

Samples B00, B12 and B25 are tetragonal and no lines in conflict with the $I4_1/a$ symmetry of pure Al-leucite (B00) were found; the two unit cell parameters a_0 and c_0 are about 0.6 \AA apart, which gives a tetragonal deformation of about 5%. The B33 and B40 samples are biphasic (cubic + tetragonal with $\approx 5\%$ deformation), the B50, B60, B70 and B80 samples are cubic, while B90 and B100 are tetragonal, characterized by a unit cell with the two parameters only 0.1 \AA apart. Figure 1 and Table 2 show the a_0 and c_0 lattice parameters corresponding to the different compositions, measured with Si as internal standard ($a_0 = 5.43088 \text{ \AA}$). The interplanar distances, the indices of the hkl

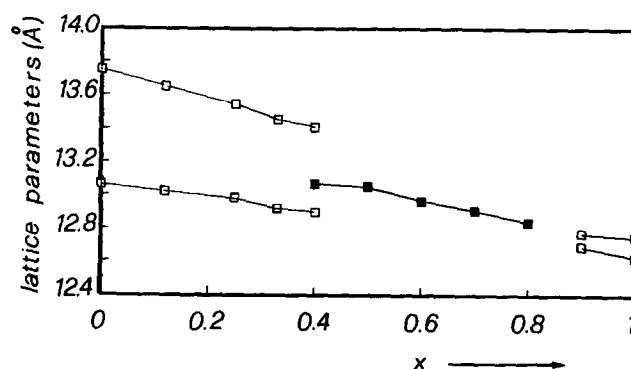


Fig. 1. Lattice parameters for the different compositions.

Table 2. a_0 and c_0 lattice parameters for the monophasic compositions

| Composition | a_0 (\AA) | c_0 (\AA) |
|-------------|------------------------|------------------------|
| B00 | 13.06 | 13.75 |
| B12 | 13.02 | 13.65 |
| B25 | 12.98 | 13.54 |
| B50 | 13.05 | — |
| B60 | 12.97 | — |
| B70 | 12.91 | — |
| B80 | 12.84 | — |
| B90 | 12.69 | 12.77 |
| B100 | 12.626 | 12.745 |

Table 3. Interplanar distances (d_{hkl} , Å), indices of the hkl reflections and relative observed intensities (I_{obs}) for $KBSi_2O_6$ (B100). (Radiation: Cu $K\alpha = 1.54178$ Å, Si standard, $a_0 = 5.43088$ Å)

| d_{hkl} | hkl | I_{obs} |
|-----------|-----------------|-----------|
| 5.1709 | 112 + 211 | 39 |
| 4.4734 | 202 + 220 | 3 |
| 3.3840 | 213 + 312 + 321 | 8 |
| 3.1861 | 004 | 48 |
| 3.1574 | 400 | 100 |
| 2.8447 | 204 | 2 |
| 2.8263 | 402 + 420 | 4 |
| 2.6995 | 323 + 332 | 45 |
| 2.4872 | 314 + 413 | 6 |
| 2.4766 | 510 + 431 | 3 |
| 2.2424 | 404 | 13 |
| 2.2318 | 440 | 6 |
| 2.0660 | 116 | 1 |
| 2.0606 | 325 | 4 |
| 2.0513 | 523 + 532 + 611 | 11 |
| 1.7621 | 406 | 2 |
| 1.7558 | 604 | 3 |
| 1.7508 | 640 | 2 |
| 1.7287 | 336 | 2 |
| 1.7199 | 633 + 712 + 552 | 5 |
| 1.6122 | 516 | 7 |
| 1.6042 | 732 + 651 | 14 |
| 1.5928 | 008 | 3 |
| 1.5784 | 800 | 5 |
| 1.5647 | 417 | 1 |
| 1.4792 | 318 | 1 |

reflections and the observed intensities from XRD powder pattern of B100 are listed in Table 3.

All tetragonal phases derive from a high temperature cubic structure, through a displacive transition, as demonstrated by thermal analyses, high temperature XRD and dilatometry. For Al-leucite, this transition was reported to occur at about 650°C ¹⁰ and was shown to consist of two steps, one, at the lowest temperature, from tetragonal $I4_1/a$ to tetragonal $I4_1/acd$ (645°C) closely followed by a second (665°C) to cubic $Ia3d$. DTA traces of the B00 crystallized sample showed two endotherms on heating, one broad and the second sharper, as already reported by Faust;¹¹ both peaks were fully reversible on cooling.

For the B12 composition, the DTA pattern showed a single broad peak, centred around 480°C ; however, for the B25 sample the peak was either non-existent or so broad that it could not be separated from the baseline. The B100 composition also showed a cubic to tetragonal transition over a rather wide temperature range from 410 to 515°C , as evidenced by dilatometric measurements. The enthalpy variation associated with this B100 transition is smaller than that of B00 and was therefore not revealed by thermal analyses, i.e. DTA or high sensitivity DSC. This tetragonal-cubic transition in $KBSi_2O_6$ was noticed for the first time here and confirmed by XRD at high

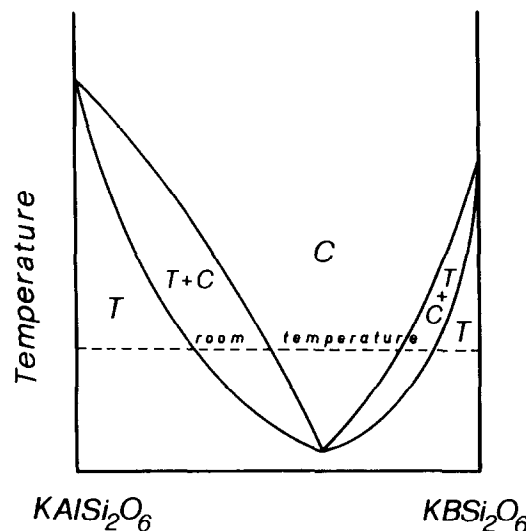


Fig. 2. Proposed phase diagram for the $KAlSi_2O_6$ - $KBSi_2O_6$ system.

temperatures. The XRD patterns at 380 , 500 and 600°C show a gradual convergence of the two tetragonal parameters which is complete by 600°C . The above experimental evidence indicates that all the compositions examined are cubic at the crystallization temperature, and suggests that those which are cubic at room temperature also transform from cubic to tetragonal below 20°C .

The existence of the two biphasic compositions B33 and B40 indicates a region where both cubic and tetragonal solid solutions can coexist. The relative amounts of cubic and tetragonal phase in these samples depend on the composition and also on the cooling rate from crystallization temperature. If the samples are quenched in liquid nitrogen, the cubic-tetragonal transition is very fast and appears to occur in all samples; it is therefore diffusionless. Practically all the high-temperature cubic phases transform into the low-temperature tetragonal, leaving a slight residue of the cubic. On the other hand, slow cooling (e.g. 2 K/min) allows a moderate amount of boron diffusion to occur at the transition temperature and the consequent formation of two phases with different compositions, one cubic and richer in boron, and the other tetragonal and richer in aluminum. The above considerations allow us to trace a tentative subsolidus phase diagram, composed of the stability fields of the cubic and tetragonal phases connected by two biphasic regions as shown in Fig. 2.

IR Characterization

For IR measurements, small amounts of the powders were mixed with an excess of KBr and pelleted in self-supported discs. IR spectra were

taken on a Perkin-Elmer 1760-X spectrophotometer equipped with a TGS detector, at a resolution of 2 cm^{-1} (number of scans 128).

In Figs 3(a) and 3(b) the spectra of samples with different boron contents are shown in the range $1400\text{--}650\text{ cm}^{-1}$. The stretching modes of the TO_4 tetrahedra are observed, i.e. the T-O-T asymmetric stretching modes (complex of bands with a maximum around $1000\text{--}1100\text{ cm}^{-1}$) and the T-O-T symmetric stretching modes (absorptions in the range $820\text{--}650\text{ cm}^{-1}$).

With increasing boron content, the broad and intense absorption attributed to the T-O-T asymmetric stretching modes, which has its maximum at about 980 cm^{-1} in B00 (spectrum 1), shifts to higher frequencies and becomes smoother. For B100 (spectrum 6), this band envelope (maximum at about 1050 cm^{-1}) seems to be once again complex and similar to that observed for B00.

The shift to higher frequencies of the T-O-T asymmetric stretching modes can be interpreted by considering that when boron is incorporated in the structure, it substitutes for aluminum in the

tetrahedral sites; therefore, boron being lighter than aluminum, the frequency of the stretching mode of BO_4 tetrahedra is expected to be higher than that of AlO_4 .

The change in shape of the band envelope from a more complex one at the B00 composition to a smoother one with increasing boron content, and again to a complex one at B100, may be correlated with the change from tetragonal symmetry of B00 to the cubic symmetry of intermediate compositions and finally back to tetragonal symmetry of B100.

No absorption at about 1400 cm^{-1} , attributable to possible threefold coordinated boron,¹² is present in the spectra of the samples containing boron. Instead, a band at 900 cm^{-1} increases in intensity with the increase of the boron content. A band at 880 cm^{-1} was observed in some pollucites containing boron⁵ and was assigned to tetrahedrally coordinated boron, according to previous literature on boron in tetrahedral coordination.¹³ These results confirm that boron is actually located in tetrahedral coordination in the leucite structure, although planar coordination is generally preferred by this element because of its small size.

With the increase in boron content, complex changes are observed in the region of the T-O-T symmetric stretching modes. The quite sharp band at about 700 cm^{-1} shown by the B00 composition disappears in the spectra of the samples containing boron: instead, broad bands appear at higher frequencies. For B100, a definite band is observed at about 780 cm^{-1} . A shift to higher frequencies of the T-O-T symmetric stretching modes with replacement of aluminium by boron is expected on the basis of the mass effect, as indicated above for the T-O-T asymmetric stretching modes.

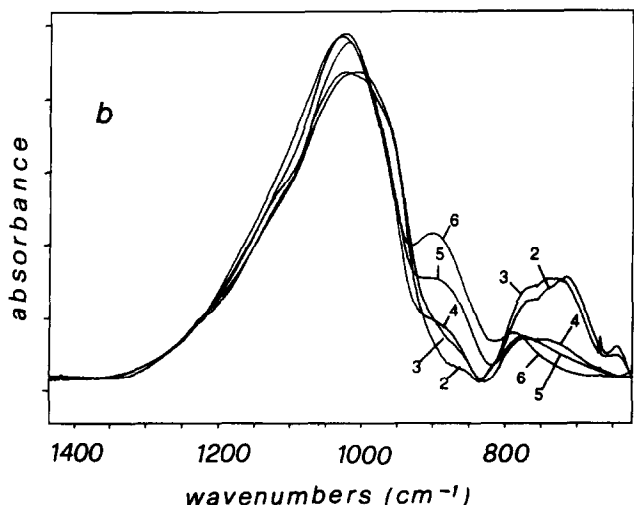
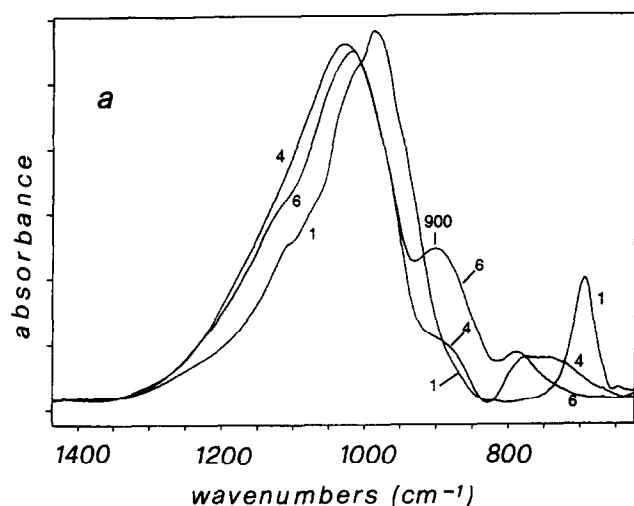


Fig. 3. (a) IR spectra of the samples B00 (1), B50 (4) and B100 (6); (b) IR spectra of the samples B12 (2), B25 (3), B50 (4), B70 (5), B100 (6).

Conclusions

Experimental evidence indicates that, at room temperature, along the $\text{KAlSi}_2\text{O}_6\text{--KBSi}_2\text{O}_6$ junction, three different solid solution fields exist: a tetragonal Al-rich phase ranging from B00 to B25, a cubic intermediate phase ranging from B50 to B80 and finally a tetragonal B-rich phase ranging from B90 to B100. A sensible choice of space groups seems to be $I4_1/a$ (that of tetragonal leucite), $Ia3d$ and $I4_1/a$ again for the tetragonal and cubic modifications on considering that the corresponding XRD patterns can be fully indexed with these assumptions.

These results are not in agreement with some references in the literature concerning KBSi_2O_6 ,^{4,7,8} which assign a cubic symmetry to this phase, with

a_0 equal to 12.60 Å,⁴ 12.645 ± 0.005 Å⁷ and 12.64 Å⁸ respectively.

In our opinion the above results may be explained by a stoichiometry deviation from the starting composition 1:1:4 ($K_2O : B_2O_3 : SiO_2$). This deviation supposedly may arise during some of the preparation routes in the aforementioned routes leading to $KBSi_2O_6$, possibly for the following reasons:

- (1) Excess of both K and B may be present in the Bayer solid state preparation,⁷ possibly caused by unreacted SiO_2 . Indeed, boric acid and potassium carbonate, or other K and B precursors, react rapidly at the preparation temperature (800–1100°C) to form potassium borate, which afterwards slowly reacts in the solid state with silica.
- (2) Excess of K may arise from the large amount of KCl used as flux by Ihara *et al.*⁴ during crystal growth.
- (3) Excess of Si with respect to K and B as indicated by the chemical analyses of the different preparations of Millini *et al.*⁸

The possibility of a coupled substitution of K and B for Si in the leucite framework, which would correspond to the $K_{(1+x)}B_{(1+x)}Si_{(2-x)}O_6$ formula, has been confirmed by us, using the same preparative route employed for the other samples.

Xerogels having $x = 0.1$ ($K_{1.1}B_{1.1}Si_{1.9}O_6$) crystallized at 1000°C for 60 min to produce a single cubic phase, with sharp diffraction peaks, having $a_0 = 12.657$ Å. The extinctions of the XRD pattern ($h, k, l: h + k + l = 2n$ and $h, h, l: 2h + l = 4n$) are compatible with the I43d space group proposed by Ihara for ' $KBSi_2O_6$ ', while the presence of the 307 reflection of the 0, k, l type with $k = 2n + 1$ excludes the Ia3d space group for this phase.

It therefore appears to be confirmed that a substitution of K and B for Si leads to cubic structures, at least for moderate substitution amounts; the bulky K^+ ions in excess can be

accommodated in the large channels of the leucite structure, while the negative charge of the framework is correspondingly increased by the substitution of B for Si. Structural analyses of this non-stoichiometric phase are in progress, together with determination of the substitutional range; the results will be communicated in a further paper.

This substitutional mechanism is not confined only to boron-containing leucite, but, under suitable preparative conditions, applies to Al-leucite as well. Indeed, a recent paper¹⁴ describes the preparation and characterization of a polymorph of $KAlSiO_4$, prepared at 1300°C from an amorphous precursor, having a distorted ANA-type zeolitic framework. This composition represents the end member of the solid solution $K_{(1+x)}Al_{(1+x)}Si_{(2-x)}O_6$ with $x = 0.5$, having 24 K^+ ions per unit cell, instead of 16, presumably located in the channels of the framework.

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