

# On the Substitution of Fe and B for Al in the Pollucite ( $\text{CsAlSi}_2\text{O}_6$ ) Structure

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## Abstract

The partial or total substitution of Fe and B for Al in the pollucite ( $\text{CsAlSi}_2\text{O}_6$ ) structure was examined or re-examined by means of XRD and FTIR. The samples, prepared through a sol-gel technique, showed a complete solid solution series along the join  $\text{CsAlSi}_2\text{O}_6$ - $\text{CsFeSi}_2\text{O}_6$  and along the join  $\text{CsAlSi}_2\text{O}_6$ - $\text{CsBSi}_2\text{O}_6$ , whilst along the join  $\text{CsFeSi}_2\text{O}_6$ - $\text{CsBSi}_2\text{O}_6$  the mutual substitution of boron for iron is no longer complete; indeed a miscibility gap exists, probably due to the large difference between the ionic radii of Fe and B. Along the latter join, XRD intensity measurements on selected samples ( $\text{CsFeSi}_2\text{O}_6$ ,  $\text{Cs}(\text{Fe}_{0.5}\text{B}_{0.5})\text{Si}_2\text{O}_6$  and  $\text{CsBSi}_2\text{O}_6$ ) allowed to carry out their structural analysis in the Space Group Ia3d. © 1997 Elsevier Science Limited.

## 1 Introduction

Pollucite ( $\text{CsAlSi}_2\text{O}_6$ ) is a zeolite-like aluminosilicate with cubic Ia3d symmetry and a tridimensional framework of interconnected (Al,Si) $\text{O}_4$  tetrahedra, in which Al and Si are randomly distributed.<sup>1</sup> This framework is topologically equivalent to that of leucite ( $\text{KAlSi}_2\text{O}_6$ ), both in the low-temperature  $\text{I4}_1/\text{a}$  tetragonal form and in the high-temperature cubic Ia3d form.

Leucite and pollucite can be considered to be 'type structures' of a large family of related compounds, which includes both natural and synthetic varieties. The members of this family can display structural phase transitions related to displacive instabilities, and moreover variable ordering of Si and Al in the tetrahedral sites. This material family might be of technological significance, because the large channel-cations are possible fast-ion conductors;<sup>2</sup> moreover these cations can be easily exchanged with species like  $\text{Ag}^+$  thus obtaining materials with interesting catalytic properties.<sup>3</sup> Pollucite itself has been proposed for the use as

a commercial fluid cracking catalyst and is described in patent literature.<sup>4</sup>

Kopp *et al.*<sup>5</sup> first hydrothermally synthesized a red Fe(III) cubic analogue of pollucite, for which they confirmed, on the basis of precession and Weissenberg photographs, a random distribution of Fe and Si in the tetrahedral sites and cubic space group Ia3d. Kume and Kozumi<sup>6</sup> observed a linear increase, with increasing Fe content, of the lattice constants and of the refractive index of the isomorphous Fe-Al solid solution series, on samples prepared by hydrothermal treatment. The same authors however pointed out that the lattice constants, measured by Kopp *et al.*<sup>5</sup> on the Fe analogue of pollucite, do not match those of the corresponding end member of the series, but are closer to those of the  $\text{Fe}_{0.5}\text{-Al}_{0.5}$  composition. Moreover they assigned to the iron analogue of pollucite an undefined water content, expressed by the unit formula  $(\text{Cs}_2\text{O}.\text{Fe}_2\text{O}_3.4\text{SiO}_2.\text{H}_2\text{O})$ .

The boron analogue of pollucite ( $\text{CsBSi}_2\text{O}_6$ ) was prepared by Torres-Martinez and West<sup>7</sup> by means of the crystallization of a melt of the same composition. These authors stated that this phase possesses cubic Ia3d symmetry and added that it should be thermodynamically stable only above 900°C, while a low-temperature phase, having a distorted pollucite structure, could also be obtained.

The aim of this work is to examine or re-examine the stability and the structural rearrangement in the pollucite framework after the partial or complete substitution of Al with trivalent iron and boron. Indeed the three compositional joins  $\text{CsAlSi}_2\text{O}_6$ - $\text{CsFeSi}_2\text{O}_6$ ,  $\text{CsAlSi}_2\text{O}_6$ - $\text{CsBSi}_2\text{O}_6$  and  $\text{CsFeSi}_2\text{O}_6$ - $\text{CsBSi}_2\text{O}_6$  were examined.

## 2 Experimental

### 2.1 Preparation

The preparation of the different compositions was carried out by a sol-gel technique, by means of the preliminary formation of an amorphous solid

(xerogel). This preparative route employs pre-hydrolysed silicon alkoxide, Cs/Fe/Al nitrates and boric acid; it was devised to overcome some of the problems encountered in the multicomponent alkoxide method, mainly the different hydrolysis rate of silicon and other alkoxides.

A measured volume of tetraethylorthosilicate (TEOS) is added to an equal volume of distilled water and ethyl alcohol. The pH of the aqueous alcoholic phase is then adjusted to 0.5–1.0 with a few drops of 1 M HNO<sub>3</sub>. In this way a clear solution is quickly obtained after a short stirring at room temperature. The 'r' factor (water moles/TEOS moles) reaches a value of about 7.

Under these conditions TEOS is firstly hydrolysed to silanol monomers.<sup>8</sup> An aqueous solution of nitrates and boric acid in stoichiometric amounts is then added to the solution of TEOS. The clear solution thus obtained is subsequently treated with excess aqueous ammonia (10% wt). Condensation and crosslinking of the silanols and gelation of the solution occurs, whilst aluminum and iron hydroxides precipitate. The basic (pH = 10) gel obtained is first dried at 105°C and then gradually heated up to 400°C, thus removing excess water and gaseous products formed by the decomposition of nitrates, leaving a white crispy oxide powder.

The xerogels obtained at 400°C were submitted to simultaneous thermal analysis DTA, TG. All the curves obtained with the different compositions show common features. They are characterized by a first marked endotherm around 140°C and a second broad one in a wider temperature range, from 500 to 700°C, both accompanied by a weight loss (Fig. 1). These transitions have been assigned to the loss of physically absorbed water (first peak) and to the loss of surface hydroxyls (second peak) accompanied by the coalescence of the mass.

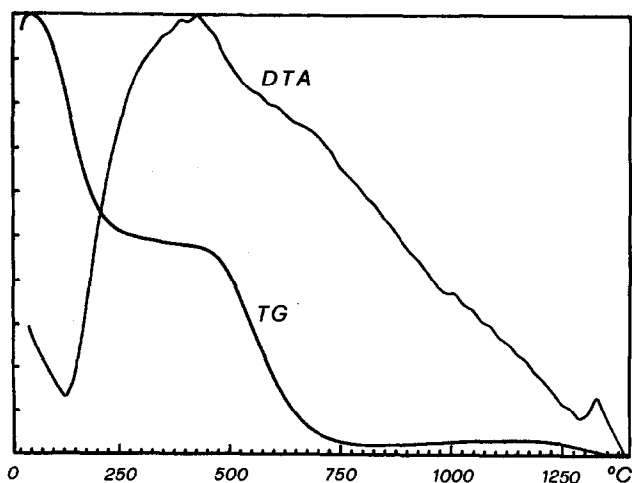


Fig. 1. Thermal analysis (DTA and TG) of the sample Cs<sub>2</sub>AlSi<sub>4</sub>O<sub>12</sub>.

At higher temperatures an exothermic peak occurs, due to the crystallization of the still amorphous mass. CsFeSi<sub>2</sub>O<sub>6</sub> is characterized by a broad crystallization exothermic peak, stretching from 900 to 1100°C; CsAlSi<sub>2</sub>O<sub>6</sub> crystallizes sharply at 1360°C (maximum peak temperature). The boron-containing compositions, CsBSi<sub>2</sub>O<sub>6</sub> and CsFe<sub>0.5</sub>B<sub>0.5</sub>Si<sub>2</sub>O<sub>6</sub> crystallize at 850 and 920°C respectively, temperatures that follow immediately the second weight loss (surface hydroxyls).

To obtain a good crystallization, all xerogels were treated at temperatures consistent with the DTA results: i.e. for 30–120 minutes at 50° above the value of the crystallization peak. The good degree of crystallization was then confirmed by the XRPD analysis. These relatively low crystallization temperatures, warranted by the intimate degree of mixing (nearly at the atomic scale), allowed to obtain crystalline samples with definitely the same composition as the parent sol. Crystallization at higher temperatures could cause the partial sublimation of B<sub>2</sub>O<sub>3</sub> (*p* = 0.11 mm Hg at 1327 K)<sup>9</sup> or possibly of Cs<sub>2</sub>O with consequent compositional variations.

TGA studies on selected crystallized samples, as well as IR evidence on the same samples, assured that no structural water is present in these leucite analogues; a certain amount of water is adsorbed on the surface of the very fine-grained powders and has no structural significance.

## 2.2 IR characterization

Because of its small ionic size, boron is able to assume both three- and fourfold coordination in oxide lattices, simply shifting from the centre to one face of the tetrahedral hole.<sup>10</sup>

IR analysis offers significant information about the boron coordination, in fact in the borosilicates the BO<sub>3</sub> asymmetric stretching is associated with a characteristic peak or doublet centered in the region 1300–1420 cm<sup>-1</sup>,<sup>11,12</sup> whilst BO<sub>4</sub> vibrational modes are observed in the region 850–1100 cm<sup>-1</sup><sup>13</sup> and are generally convoluted with the SiO<sub>4</sub> stretching modes.

The IR pattern of the boron-containing composition CsBSi<sub>2</sub>O<sub>6</sub> (CsI pressed disc, 580–1400 cm<sup>-1</sup>, Fig. 2 — solid line) did not reveal any detectable peak in the BO<sub>3</sub> stretching region, while on the contrary a wide absorption band was found at 880 cm<sup>-1</sup> which was completely absent in the IR spectrum of CsAlSi<sub>2</sub>O<sub>6</sub> (Fig. 2 — dashed line). According to the preceding literature data on boron in tetrahedral coordination,<sup>13,14</sup> this latter band was assigned to tetrahedral coordinated boron.

On the basis of these results fourfold coordination of boron in the structure and the complete

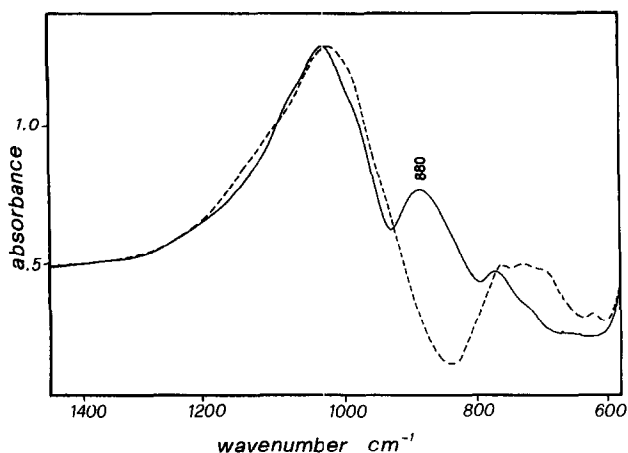


Fig. 2. FTIR spectra of  $\text{CsAlSi}_2\text{O}_6$  (dashed line) and  $\text{CsBSi}_2\text{O}_6$  (solid line).

substitution of silicon by boron in the tetrahedral sites was assumed.

### 2.3 XRD characterization

The X-ray powder diffraction patterns of the crystallized samples were recorded with  $\text{Cu } K_\alpha$  radiation, graphite monochromator on the diffracted beam, sample spinner, variable divergence slit, room temperature. The three compositional joins examined show that:

(1) along the join  $\text{CsAlSi}_2\text{O}_6$ – $\text{CsFeSi}_2\text{O}_6$  all the samples ( $x = 0, 0.25, 0.50, 0.75, 1.0$ ) are monophasic and share the cubic symmetry of the two

end members (Figs 3A and 3B). The  $\text{Ia}3d$  symmetry of the two end members is apparently common to all intermediate terms; no peaks conflicting with the extinction rules were detected. A linear variation of the cell parameter  $a_0$  with the composition is shown in Fig. 4 and in Table 1.

(2) along the join  $\text{CsAlSi}_2\text{O}_6$ – $\text{CsBSi}_2\text{O}_6$  all the samples ( $x = 0, 0.25, 0.50, 0.75, 1.0$ ) are monophasic and share the cubic symmetry of the two end members (Figs 3B and 3C). A linear variation of the lattice parameters is also observed and described in Table 1. It is to be noticed that intermediate compositions show an apparent slight broadening of the diffraction lines, which could be related to smaller crystallite size or to a higher degree of lattice defects.

(3) along the join  $\text{CsFeSi}_2\text{O}_6$ – $\text{CsBSi}_2\text{O}_6$  the mutual substitution of boron for iron is no longer complete; indeed a miscibility gap exists, probably due to the large difference between the ionic radii of Fe and B (B–O and Fe–O distances sum to 1.36 and 1.98 Å, according to Shannon and Prewitt,<sup>16</sup> for Fe and B in tetrahedral coordination and O in twofold coordination). When crystallized at 1000°C, the compositions having  $0.7 < x < 0.8$  are biphasic, being constituted by the two limit terms with approximate compositions  $x = 0.7$  and  $x = 0.8$ . In the ranges  $0 \leq x \leq 0.7$  and  $0.8 \leq x \leq 1.0$ , however, a complete solid solution exists. Intermediate compositions show an appreciable peak enlargement; in some cases a still noticeable amorphous halo even after crystallization,

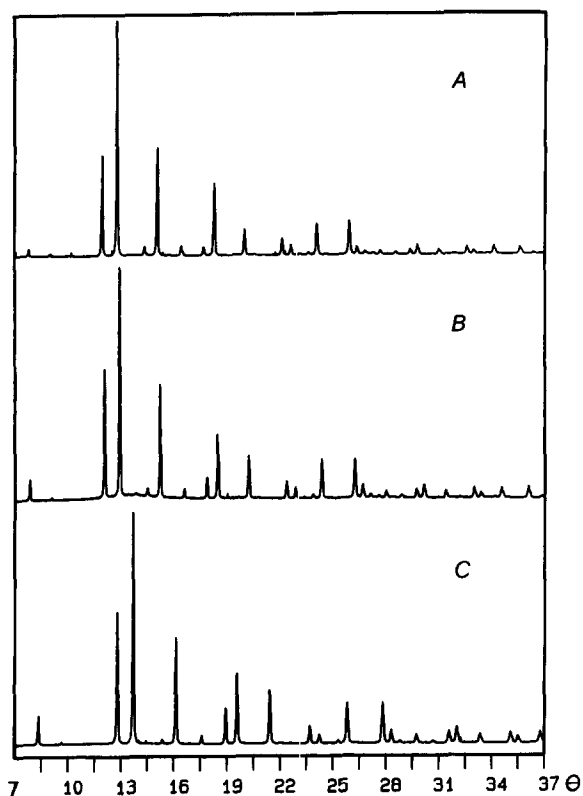


Fig. 3. XR powder diffraction patterns for (A)  $\text{CsFeSi}_2\text{O}_6$ ; (B)  $\text{CsAlSi}_2\text{O}_6$ ; (C)  $\text{CsBSi}_2\text{O}_6$ .

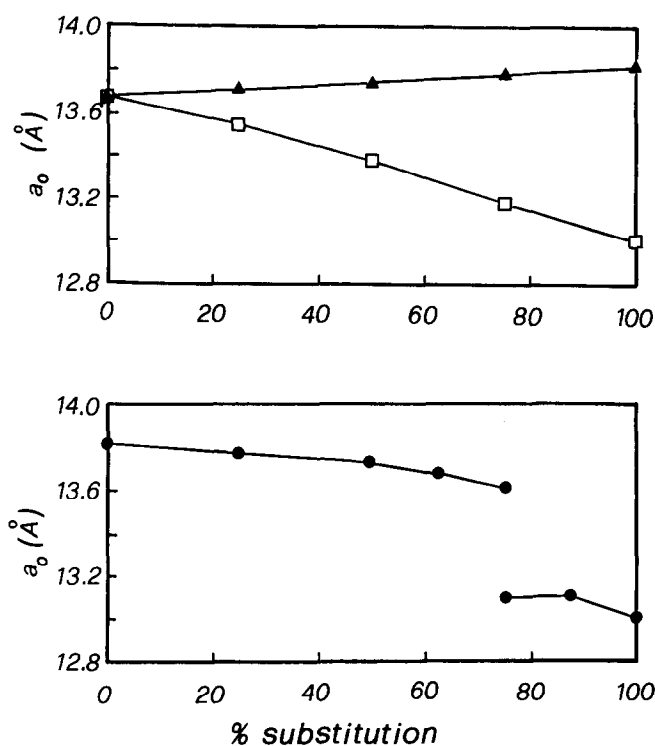


Fig. 4. Unit cell parameter (Å) for the three solid solutions:  $\text{CsAl}_{(1-x)}\text{Fe}_x\text{Si}_2\text{O}_6$  (triangle);  $\text{CsAl}_{(1-x)}\text{B}_x\text{Si}_2\text{O}_6$  (square);  $\text{CsFe}_{(1-x)}\text{B}_x\text{Si}_2\text{O}_6$  (circle).

Table 1. Unit cell parameter  $a_0$  (Å) for the several solid solution terms

x	$a_0$ ( $\text{CsFe}_{1-x}\text{B}_x\text{Si}_2\text{O}_6$ )	$a_0$ ( $\text{CsAl}_{1-x}\text{B}_x\text{Si}_2\text{O}_6$ )	$a_0$ ( $\text{CsAl}_{1-x}\text{Fe}_x\text{Si}_2\text{O}_6$ )
0	13.82 (13.66 <sup>a</sup> )	13.67 (13.674 <sup>c</sup> )	13.67 (13.653 <sup>d</sup> )
0.25	13.77	13.54	13.71 (13.696 <sup>d</sup> )
0.5	13.73	13.38	13.74 (13.737 <sup>d</sup> )
0.625	13.68	—	—
0.75	13.61 + 13.10 <sup>e</sup>	13.18	13.78 (13.768 <sup>d</sup> )
0.875	13.11	—	—
1	13.01 (12.9905 <sup>b</sup> )	13.01 (12.9905 <sup>b</sup> )	13.82 (13.82 <sup>d</sup> )

<sup>a</sup>Ref. 5.<sup>b</sup>Ref. 9.<sup>c</sup>Ref. 15.<sup>d</sup>Ref. 6.<sup>e</sup>Biphasic sample.

centred around  $\theta = 12^\circ$  which required further heat treatment to gradually disappear. The  $a_0$  variation along the Fe-B solid solution shows a marked deviation from linearity, possibly caused by the strong difference in ionic radii of the two substituents. Three samples along this interesting join of solid solution, namely  $\text{CsFeSi}_2\text{O}_6$  (CFS),  $\text{Cs}(\text{Fe}_{0.5}\text{B}_{0.5})\text{Si}_2\text{O}_6$  (CFBS) and  $\text{CsBSi}_2\text{O}_6$  (CBS) were submitted to structural analysis.\* To this end the XR diffraction patterns were recorded with the equipment previously described in the  $5\text{--}50^\circ$   $\theta$  range,  $0.01^\circ$   $\theta$  step and 8 s counting time. The background was subtracted from the integrated intensities; the diffraction peaks were deconvoluted by a mixed gaussian-lorenzian peak shape profile. In this way the net intensities were evaluated. The structural parameters of the independent atoms in space group Ia3d (four independent coordinates and three isotropic thermal factors) were then refined on the basis of these net intensities, with standard least square procedures.<sup>17</sup> No peak was detected incompatible with the space group Ia3d.

The goodness of fit was estimated on the basis of the unit weights  $R$  factor ( $R = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum I_{\text{obs}}$ ). The starting parameters for the refinement were in each case the values of Kopp *et al.*<sup>5</sup> for the CFS structure. The results of the refinement and the resulting distances and angles are listed in Table 2. The final  $R$  values for the three structures reached the values 0.075 (CFS), 0.059 (CFBS) and 0.061 (CBS). The thermal factor results are invariably high, except for the oxygen atoms in CBS. This can be an indication of a high statistical disorder, i.e. positional displacement not caused by thermal vibration but by the random arrangement of such different ions as Si, Fe and B in tetrahedral sites.

\*The values of the atomic coordinates for CFS as reported in Ref. 5 were taken from the former structural determination of  $\text{CsAlSi}_2\text{O}_6$  of Naray-Szabo (Die Struktur des Pollucits, *Zeit. Krist.*, 1938, **99**, 277–282) and were not refined.

In CBS the absence of relatively large  $\text{Fe}^{3+}$  ions might explain the low thermal factor for oxygen. In addition, the alkaline cations in the large cavities are subject to large vibrations, in these structural types. On this point we may note that Bell *et al.*<sup>18</sup> found for dry-synthesized leucite-like  $\text{K}_2\text{MgSi}_5\text{O}_{12}$  (Ia3d) thermal factors as high as 12.8 (K), 10.0 (O) and 5.42 (Si, Mg) from the Rietveld refinement of powder pattern.

The oxygen distances of the fourfold and 12-fold coordinated atoms remain nearly unaffected from CFS to CFBS whilst they show an abrupt decrement from CFBS to CBS, a fact to be related with the miscibility gap between the latter two structures (Table 2).

The four T–O distances (T = tetrahedral atom) are different in pairs; the difference resulting in 0.026 and 0.025 Å in CFBS and in CBS respectively, values that are nearly coincident with the corresponding 0.025 value of Beger<sup>1</sup> for  $\text{CsAlSi}_2\text{O}_6$ . The difference is only 0.013 in CFS, a fact that could be related to the  $3d^5$  spherical symmetry of  $\text{Fe}^{3+}$  high spin ions (Table 2).

Cs ions are coordinated to 12 oxygen, of which six share a closer distance and the other six are a little far apart. The difference between the six closer and the six further is 0.119, 0.106 and 0.106 Å for CFS, CFBS and CBS. These differences are slightly less than the corresponding one (0.167 Å) found by Beger in  $\text{CsAlSi}_2\text{O}_6$ .

With the Ia3d space group, the Cs atoms are compelled on the (1/8, 1/8, 1/8) special positions, at the intersection of the three- and two-fold symmetry axes. In order to assess whether the high thermal factor could suggest a positional displacement of these atoms, a refinement of the CBS structure was tried in a subgroup of Ia3d, the I43d space group. The assumption of the latter space group implies that the Cs atoms lie on the (x, x, x) positions and that the oxygen atoms split into two independent sets of positions. Here it may be noted that the space group I43d was assigned by

Table 2. Results of the structural refinements

CFS						
Refined coordinates (e.s.d's are in parentheses):						
		x	y	z	B(iso)	N
Cs	16(b)	0.125	0.125	0.125	3.9(1)	16
Si	48(g)	0.6614(4)	0.5886(4)	0.125	2.9(2)	32
Fe	48(g)	0.6614(4)	0.5886(4)	0.125	2.9(2)	16
O	96(h)	0.1060(9)	0.1352(6)	0.7210(9)	3.7(3)	96
R = 0.0755						
Number of reflections used = 52						
Bond lengths (Å):						
T-O	1.668 × 2;	1.655 × 2				
Cs-O	3.473 × 6;	3.592 × 6				
Bond angles (°):						
O-T-O	109.2 × 2;	112.5 × 2;	106.3;	107.1		
T-O-T	145.4					
CFBS						
Refined coordinates (e.s.d's are in parentheses):						
		x	y	z	B(iso)	N
Cs	16(b)	0.125	0.125	0.125	7.3(1)	16
Si	48(g)	0.6593(6)	0.5907(6)	0.125	2.1(3)	32
Fe	48(g)	0.6593(6)	0.5907(6)	0.125	2.1(3)	8
B	48(g)	0.6593(6)	0.5907(6)	0.125	2.1(3)	8
O	96(h)	0.108(1)	0.1339(7)	0.722(1)	4.2(4)	96
R = 0.0591						
Number of reflections used = 30						
Bond lengths (Å):						
T-O	1.653 × 2;	1.627 × 2				
Cs-O	3.483 × 6;	3.589 × 6				
Bond angles (°):						
O-T-O	108.2 × 2;	111.0 × 2;	107.1;	111.2		
T-O-T	148.1					
CBS						
Refined coordinates (e.s.d's are in parentheses):						
		x	y	z	B(iso)	N
Cs	16(b)	0.125	0.125	0.125	3.5(1)	16
Si	48(g)	0.6606(5)	0.5894(5)	0.125	1.4(2)	32
B	48(g)	0.6606(5)	0.5894(5)	0.125	1.4(2)	16
O	96(h)	0.1070(8)	0.1347(4)	0.7206(6)	0.2(2)	96
R = 0.0614						
Number of reflections used = 43						
Bond lengths (Å):						
T-O	1.566 × 2;	1.541 × 2				
Cs-O	3.264 × 6;	3.370 × 6				
Bond angles (°):						
O-T-O	109.0 × 2;	112.1 × 2;	107.1;	107.7		
T-O-T	146.1					

Ihara *et al.* to the structure of  $\text{KBSi}_2\text{O}_6$ . The refinement (in this space group) yielded a slightly higher  $R$  value, 0.0646, but the coordinates remained practically those from the previous refinement. However it was not possible to refine simultaneously all the parameters, since the thermal factors behave anomalously, hence it may be concluded that the choice of the space group  $\text{Ia}3\text{d}$  is the right one.

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