

# Reinvestigation of the structure of $\text{BaCuSi}_2\text{O}_6$ – evidence for a phase transition at high temperature

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Superstructure reflections have been observed in the room-temperature X-ray diffraction pattern of  $\text{BaCuSi}_2\text{O}_6$ , barium copper disilicate. The tetragonal structure has a fourfold unit-cell volume compared with the original structure determined by Finger *et al.* [(1989), *Am. Mineral.* **74**, 952–955]. At  $T_s = 610$  K  $\text{BaCuSi}_2\text{O}_6$  undergoes a structural phase transition upon which the superstructure reflections disappear. The description of the structure in the larger cell removes the crystal-chemical inconsistencies observed for the original structure.

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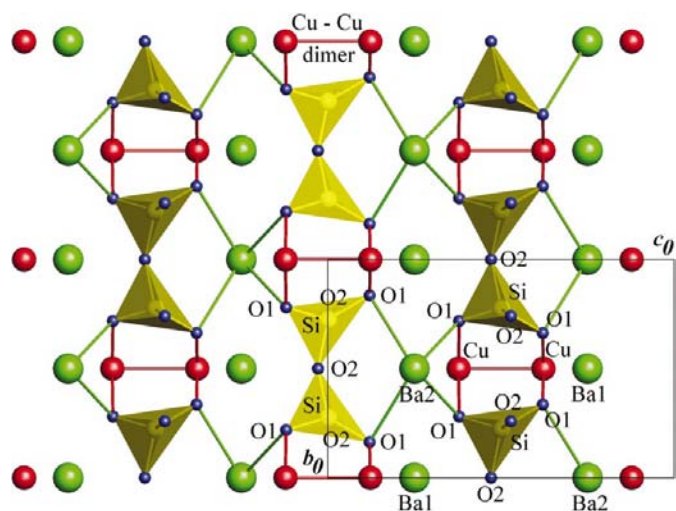
## 1. Introduction

Low-dimensional quantum spin systems with a spin gap and a disordered ground state have been widely studied theoretically and investigated experimentally over the last few decades. Indeed, the study of such strongly correlated electron systems may well be of importance for the understanding of superconductivity in weakly doped high- $T_c$  superconductors. Spin-singlet ground states are usually known to arise in one-dimensional spin ladders (Azuma *et al.*, 1994; Prokofiev *et al.*, 1998) or *via* the dimerization of Heisenberg spin chains, as in spin-Peierls transitions (Bray *et al.*, 1975; Hase *et al.*, 1993; Isobe & Ueda, 1996). However, it was shown that, under certain typological circumstances, two-dimensional spin systems could also exhibit a dimer ground state with a spin gap instead of a long-range magnetically ordered Néel phase (Shastry & Sutherland, 1981; Kageyama *et al.*, 1999).

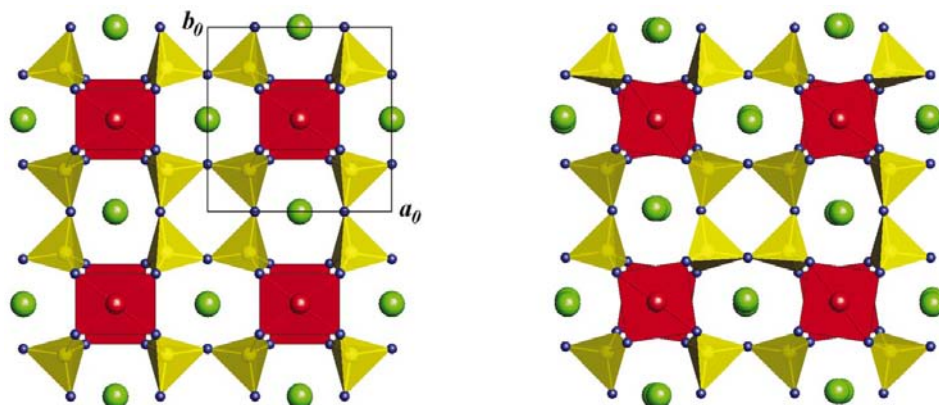
The barium copper cyclosilicate  $\text{BaCuSi}_2\text{O}_6$  is a quasi-two-dimensional antiferromagnetic system having a spin-singlet dimerized quantum ground state, with a spin gap of  $\Delta \simeq 4.5$  meV (Sasago *et al.*, 1997). Its structure consists of  $\text{Cu}_2\text{Si}_4\text{O}_{12}$  layers orthogonal to the  $c$  axis, separated by layers of barium (Finger *et al.*, 1989). Within a  $\text{Cu}_2\text{Si}_4\text{O}_{12}$  layer, the  $\text{Cu}^{2+}$  ions ( $S = 1/2$ ) form a square lattice of  $\text{CuO}_4$ – $\text{CuO}_4$  dimers parallel to the  $c$  axis with antiferromagnetic coupling (Fig. 1).

$\text{BaCuSi}_2\text{O}_6$  is also unusual in being one of the very few silicates containing isolated  $\text{Si}_4\text{O}_{12}$  rings composed of four  $\text{SiO}_4$  tetrahedra. This feature, together with the relatively high symmetry of the compound, has made  $\text{BaCuSi}_2\text{O}_6$  a choice material to study the vibrational modes characteristic of the  $\text{Si}_4\text{O}_{12}$  rings and therefore to obtain a better understanding of the structure of amorphous  $\text{SiO}_2$  (Finger *et al.*, 1989; McKeown & Bell, 1997).

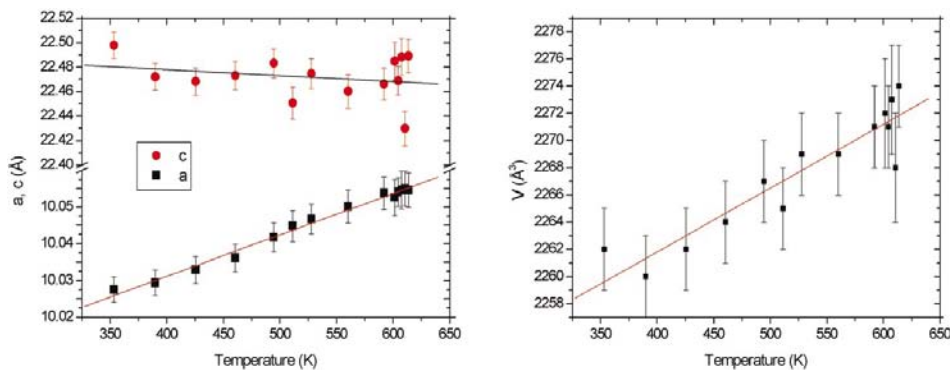
Previous single-crystal X-ray diffraction studies have stated that  $\text{BaCuSi}_2\text{O}_6$  crystallizes at room temperature in a tetragonal body-centered system, with unit-cell parameters  $a_0 = 7.042$  (3),  $c_0 = 11.133$  (3) Å and  $Z = 4$  (Finger *et al.*, 1989;



**Figure 1**  
Room-temperature structure of BaCuSi<sub>2</sub>O<sub>6</sub> in the space group  $I\bar{4}m2$ , according to Finger *et al.* (1989): view along [100].



**Figure 2**  
Comparison between the average model (Finger *et al.*, 1989) and the one taking into account the superstructure: Projection of a Cu<sub>2</sub>Si<sub>4</sub>O<sub>12</sub> layer onto the (a, b) plane. The spheres represent the Ba atoms, the tetrahedra the SiO<sub>4</sub> groups and the planar squares the CuO<sub>4</sub> groups. Left: Average model  $I\bar{4}m2$ . Right: Model in the space group  $I4_1acd$ .



**Figure 3**  
Temperature evolution of the unit-cell parameters and volume between 353 and 610 K. The lines show the linear data fits.

Janczak & Kubiak, 1992). The correct space group, either the noncentrosymmetric  $I\bar{4}m2$  (No. 119) or the centrosymmetric  $I4/mmm$  (No. 139), was a matter of debate. The two models lead to different point symmetries for the Si<sub>4</sub>O<sub>12</sub> rings ( $2mm$  in the noncentrosymmetric model and  $4/mmm$  in the centrosymmetric one) and thus to different interpretations of the Raman spectrum of BaCuSi<sub>2</sub>O<sub>6</sub>. From the Raman results, the model in the space group  $I\bar{4}m2$  was preferred to the centrosymmetric one.

We have studied the structure of BaCuSi<sub>2</sub>O<sub>6</sub> between room temperature and 640 K. We show that the observed superstructure reflections at room temperature lead to a model in the space group  $I4_1acd$  (No. 142) with  $Z = 16$ . At  $T_s = 610$  K, BaCuSi<sub>2</sub>O<sub>6</sub> undergoes a structural phase transition upon which the unit-cell volume is reduced by four. Above  $T_s$  the structure is well described in the space group  $I4/mmm$  with  $Z = 4$ .

## 2. Experimental

Single crystals of BaCuSi<sub>2</sub>O<sub>6</sub> were grown in a mirror furnace by the team of Professor Uchinokura (University of Tokyo, Japan). Single-crystal X-ray diffraction measurements were performed on an imaging plate diffractometer (Stoe-IPDS-I, Mo  $K\alpha$  radiation, pyrolytic graphite monochromator). The diffractometer was equipped with a hot-gas stream-heating stage mounted on a goniometer head (300–653 K, accuracy 2 K).

Two complete data sets were collected at 293 and 640 K. A  $0.17 \times 0.16 \times 0.11$  mm<sup>3</sup> single crystal was measured at 293 K with a crystal–detector distance of 4 cm, a  $\varphi$  oscillation movement between 0 and 300° ( $\Delta\varphi = 0.8^\circ$  for each frame) and a low tube voltage (30 kV, 25 mA) in order to avoid the presence of the  $\lambda/2$  radiation, resulting in 1056 unique reflections. The high-temperature measurement was performed on a  $0.27 \times 0.24 \times 0.17$  mm<sup>3</sup> single crystal with the usual tube setting (50 kV, 25 mA), a crystal–detector distance of 7.5 cm and a  $\varphi$  oscillation move-

**Table 1**  
Experimental and refinement details.

	293 K	640 K
<b>Crystal data</b>		
Chemical formula	CuO <sub>6</sub> Si <sub>2</sub> Ba	CuO <sub>6</sub> Si <sub>2</sub> Ba
<i>M<sub>r</sub></i>	353.06	353.06
Cell setting, space group	Tetragonal, <i>I</i> <sub>4</sub> / <i>acd</i>	Tetragonal, <i>I</i> <sub>4</sub> / <i>mmm</i>
<i>a</i> , <i>c</i> (Å)	10.0091 (16), 22.467 (6)	7.1104 (13), 11.175 (3)
<i>V</i> (Å <sup>3</sup> )	2250.8 (8)	565.0 (2)
<i>Z</i>	16	4
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	4.167	4.151
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	1214	988
$\theta$ range (°)	3.6–32.8	3.4–24.8
$\mu$ (mm <sup>-1</sup> )	11.12	11.08
Temperature (K)	293 (2)	640 (2)
Crystal form, colour	Cuboid, purple	Cuboid, purple
Crystal size (mm)	0.17 × 0.16 × 0.11	0.27 × 0.24 × 0.17
<b>Data collection</b>		
Diffractometer	Stoe IPDS	Stoe IPDS
Data collection method	Rotation method	Rotation method
Absorption correction	Numerical	Numerical
<i>T<sub>min</sub></i>	0.179	0.050
<i>T<sub>max</sub></i>	0.288	0.144
No. of measured, independent and observed reflections	1056, 1056, 523	170, 170, 135
Criterion for observed reflections	<i>I</i> > 2σ( <i>I</i> )	<i>I</i> > 2σ( <i>I</i> )
<i>R<sub>int</sub></i>	0.000	0.000
$\theta_{\max}$ (°)	32.8	24.8
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 ⇒ <i>h</i> ⇒ 15 0 ⇒ <i>k</i> ⇒ 15 0 ⇒ <i>l</i> ⇒ 34	0 ⇒ <i>h</i> ⇒ 8 0 ⇒ <i>k</i> ⇒ 8 0 ⇒ <i>l</i> ⇒ 13
<b>Refinement</b>		
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.028, 0.042, 1.26	0.015, 0.025, 1.02
No. of reflections	1056	170
No. of parameters	48	23
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0P)^2]$ , where $P = (F_o^2 + 2F_c^2)/3$
(Δ/ <i>σ</i> ) <sub>max</sub>	0.001	<0.0001
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	1.12, -2.04	0.53, -0.51
Extinction method	<i>SHELXL</i>	<i>SHELXL</i>
Extinction coefficient	0.000065 (7)	0.0021 (2)

Computer programs used: *STOE X-RED* and *SHELXL97* (Sheldrick, 1997), *ATOMS*, Version 5.1, and *WinGX*, Version 1.64.05 (Farrugia, 1999).

**Table 2**  
Selected geometric parameters for BaCuSi<sub>2</sub>O<sub>6</sub> at room temperature.

Si—O3 <sup>i</sup>	1.61 (1)	O1—Si—O2	105.2 (6)
Si—O1	1.60 (1)	O1—Si—O2 <sup>ii</sup>	109.2 (5)
Si—O2	1.65 (1)	O1—Si—O3 <sup>i</sup>	117.4 (2)
Si—O2 <sup>ii</sup>	1.64 (1)	O2—Si—O2 <sup>ii</sup>	108.0 (3)
O1—O2	2.58 (1)	O2—Si—O3 <sup>i</sup>	110.4 (5)
O1—O2 <sup>ii</sup>	2.64 (1)	O2 <sup>ii</sup> —Si—O3 <sup>i</sup>	106.4 (6)
O1—O3 <sup>i</sup>	2.750 (5)		
O2—O2 <sup>ii</sup>	2.657 (2)		
O2—O3 <sup>i</sup>	2.68 (1)		
O2 <sup>ii</sup> —O3 <sup>i</sup>	2.60 (1)		
Cu—O1 <sup>iii</sup>	1.939 (9)	O1 <sup>iii</sup> —Cu—O3 <sup>iv</sup>	89.1 (6)
Cu—O3 <sup>v</sup>	1.952 (9)	O3 <sup>vi</sup> —Cu—O1 <sup>vi</sup>	90.9 (6)
O1 <sup>iii</sup> —O3 <sup>v</sup>	2.77 (2)	O1 <sup>iii</sup> —Cu—O1 <sup>vi</sup>	176.2 (6)
O1 <sup>iii</sup> —O3 <sup>iv</sup>	2.73 (2)	O3 <sup>v</sup> —Cu—O3 <sup>iv</sup>	179.8 (6)

Symmetry codes: (i)  $-x + \frac{1}{2}, y, -z + 1$ ; (ii)  $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{3}{4}$ ; (iii)  $y - \frac{3}{4}, x + \frac{1}{4}, z - \frac{3}{4}$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (v)  $x - \frac{1}{2}, -y + 1, z$ ; (vi)  $-y + \frac{3}{4}, -x + \frac{1}{4}, z - \frac{3}{4}$ .

ment between 70 and 300.4° ( $\Delta\varphi = 1.2^\circ$  for each frame), resulting in 170 unique reflections.

The temperature *T<sub>s</sub>* of the phase transition was determined, using short data collections at 14 different temperatures, as the temperature at which the superstructure reflections disappear upon heating. These ‘orienting’ collections were performed with a  $\varphi$  oscillation movement between 70 and 100° ( $\Delta\varphi = 2^\circ$  for each frame), resulting in 194 unique reflections per temperature below *T<sub>s</sub>*.

The programs *X-RED* and *X-SHAPE* (Stoe & Cie, 1996) were used for the numerical absorption correction and merging of the reflections, and *SHELXL93* (Sheldrick, 1997) was used for structure refinement.

### 3. Room-temperature structure

The observed superstructure reflections led to a room-temperature unit cell four times larger than that reported previously (Finger *et al.*, 1989; McKeown & Bell, 1997). The relations between the new (**a**, **b**, **c**) and the old (**a**<sub>0</sub>, **b**<sub>0</sub>, **c**<sub>0</sub>) unit-cell vectors are given by **a** = **a**<sub>0</sub> + **b**<sub>0</sub>, **b** = **b**<sub>0</sub> - **a**<sub>0</sub> and **c** = 2**c**<sub>0</sub>. The presence of this superstructure points to a possible structural phase transition above room temperature.

The correct space group to describe the room-temperature structure of BaCuSi<sub>2</sub>O<sub>6</sub> was found to be *I*<sub>4</sub>/*acd* (*Z* = 16). As the intensities of the superstructure reflections are much weaker than those of the main reflections, the weighted *R* value *wR*(*F*<sup>2</sup>) is rather large (Table 1). The weakness of these reflections also has a slight effect on the accuracy of the positions and the atomic displacement parameters of the O atoms (see supplementary material<sup>1</sup>), which are the major contributors to their intensities.

The main difference between the average structure (space group *I* $\bar{4}$ *m*2) in the smaller cell and the structure, taking into account the superstructure reflections, is a tilting of the SiO<sub>4</sub> tetrahedra, as can be seen in Fig. 2. This tilting gives rise to a more satisfactory coordination for the Cu<sup>2+</sup> ions. Rather than highly orthorhombically distorted CuO<sub>4</sub> groups which, since no strong chemical constraints are applied to them, are very

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA5017). Services for accessing these data are described at the back of the journal.

unusual in terms of the well established crystal chemistry of oxo-cuprates, we now have an almost square-planar coordination for the  $\text{Cu}^{2+}$  ions (Table 2). In this new model, the  $\text{Si}_4\text{O}_{12}$  rings possess point symmetry  $2..$  with a twofold rotation axis at  $(0, \frac{1}{4}, z)$ . The Ba atoms are 10-fold coordinated; the Ba—O bond lengths lie between 2.72 (1) and 3.24 (1) Å.

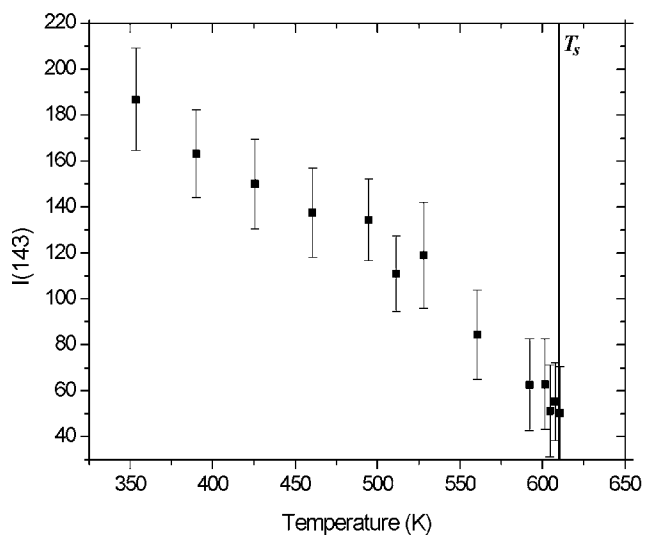
Fig. 3 shows the temperature dependence of the unit-cell parameters  $a$  and  $c$  and the volume  $V$ , between room temperature and  $T_s$ . These parameters were obtained from the ‘orienting’ measurements performed while looking for the temperature of the phase transition. The number of reflections used to refine the unit-cell parameters for this type of measurement is much smaller than for the whole data set: The absolute  $a$  and  $c$  values are different from those obtained from a complete measurement. However, this does not affect the temperature dependence of the unit-cell parameters thus obtained. While  $a$  increases linearly with temperature [the linear thermal expansion coefficient along  $a$  is  $(1/a) \Delta a/\Delta T = 1.13 (3) \times 10^{-5} \text{ K}^{-1}$ ],  $c$  slightly decreases but its linear thermal expansion coefficient is zero to within one standard deviation.

#### 4. High-temperature structure

The temperature of the phase transition, at which the superstructure reflections disappear upon heating, was found to be  $T_s = 610 \text{ K}$ , as shown by the temperature dependence of the (143) superstructure reflection (Fig. 4) obtained from the 14 ‘orienting’ measurements.

The high-temperature structure was measured at 640 K on the same single crystal. The detector had to be moved further away from the sample because of the heating device, resulting in a reduced  $\theta$  range and reduced data/parameter ratio (Table 1).

We found that above  $T_s$ ,  $\text{BaCuSi}_2\text{O}_6$  crystallizes in the space group  $I4/mmm$  ( $Z = 4$ ). The structural model (deposited material) is very similar to the centrosymmetric model



**Figure 4** Temperature dependence of the intensity of the (143) superstructure reflection between 353 K and  $T_s$ .

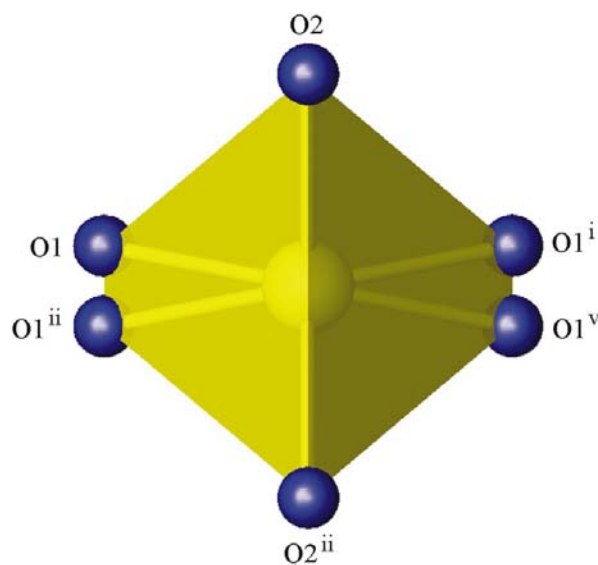
**Table 3** Selected geometric parameters for  $\text{BaCuSi}_2\text{O}_6$  at 640 K.

Si—O1	1.636 (4)	O1—Si—O1 <sup>i</sup>	105.2 (7)
Si—O2	1.593 (5)	O1—Si—O1 <sup>ii</sup>	108.4 (7)
O1—O1 <sup>i</sup>	2.60 (1)	O1—Si—O2	99.9 (7)
O1—O1 <sup>ii</sup>	2.65 (2)	O1 <sup>iii</sup> —Si—O2	116.6 (6)
O1—O2	2.47 (1)	O2—Si—O2 <sup>iii</sup>	116.0 (4)
O1 <sup>iii</sup> —O2	2.75 (1)		
O2—O2 <sup>iii</sup>	2.701 (9)		
Cu—O2	1.927 (5)	O2—Cu—O2 <sup>iv</sup>	90
O2—O2 <sup>iv</sup>	2.725 (7)	O2—Cu—O2 <sup>v</sup>	178.3 (3)

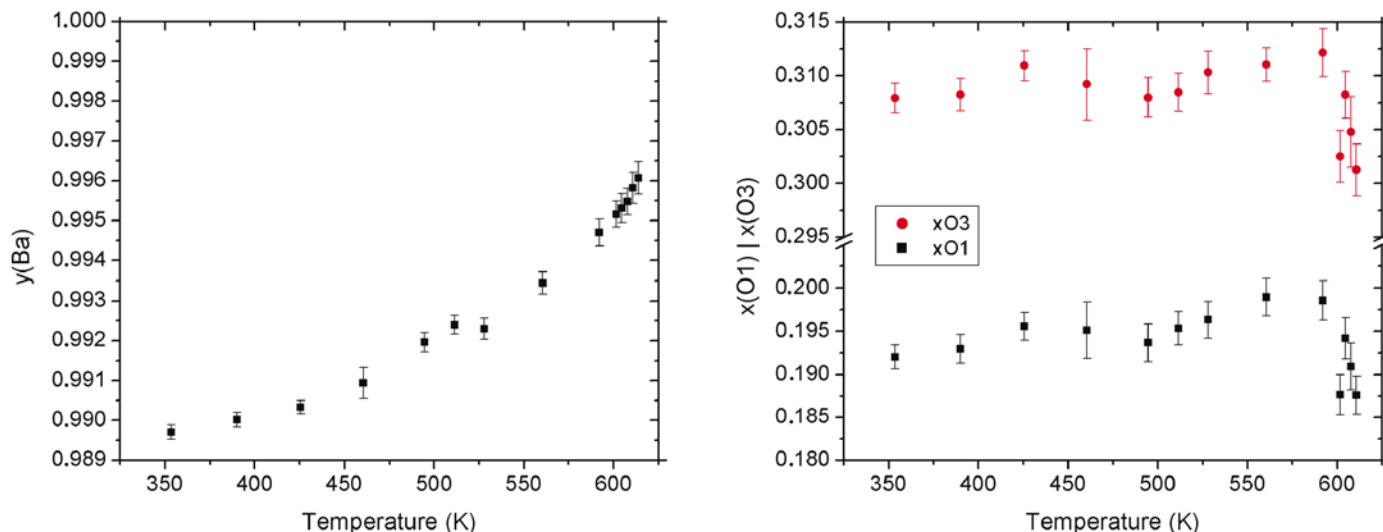
Symmetry codes: (i)  $1 - y, x, z$ ; (ii)  $1 - y, x, -z$ ; (iii)  $x, y, -z$ ; (iv)  $y, -x, z$ ; (v)  $-x, -y, z$ . The occupancy of the O1 site is 50% (Fig. 5).

proposed earlier for the room-temperature structure (Finger *et al.*, 1989; Janczak & Kubiak, 1992), although the thermal parameters were not published in the first paper because of the values for the O atoms which were too high. Our first refinement with  $z = 0$  for the O1 atom also led to very high values of the thermal displacement parameters and an extremely elongated thermal ellipsoid along the  $c$  axis. The introduction of a split position for the O1 atom with an occupancy of 50% above and below the plane  $z = 0$  reduced the anisotropy of its thermal ellipsoid along the  $c$  axis and halved its equivalent isotropic thermal parameter. The distance between the two potential minima for the O1 atom is 0.53 (4) Å; this atom does not coordinate the Cu atom, but the Ba and Si atoms instead (Fig. 5). Obviously, the high-temperature structure is a disordered average structure in time and/or space.

The coordination of the  $\text{Cu}^{2+}$  ions is quasi-ideal, the only deviation being that the Cu atom is at a distance of 0.028 (6) Å from the perfect square plane formed by the O2 atoms (Table 3). In both the average structure and the model with a split



**Figure 5** The split position of the O1 atom: environment of the Si atom. Symmetry codes: (i)  $1 - y, x, z$ ; (ii)  $x, y, -z$ ; (v)  $1 - y, x, -z$ .

**Figure 6**

Atomic coordinates  $y(\text{Ba})$ ,  $x(\text{O1})$  and  $x(\text{O3})$  as a function of temperature between 353 and 610 K.

position for the O1 atom, the  $\text{Si}_4\text{O}_{10}$  rings possess  $4/mmm$  point symmetry. The Ba atoms are tenfold coordinated; the Ba–O1 bond length is 3.06 (2) Å and the Ba–O2 bond length 2.958 (2) Å.

The data from the ‘orienting’ measurements were used to refine the crystal structure of  $\text{BaCuSi}_2\text{O}_6$  between 353 and 610 K. Although the accuracy of the atomic parameters is rather poor because of the small number of measured reflections, we can observe that the Ba atoms seem to move continuously until  $T_s$ , while the positions of the O1 and O3 atoms change abruptly just below  $T_s$  (Fig. 6). In fact, if the high-temperature structure were described in the low-temperature space group, the  $y$  coordinate of the Ba atom would be exactly 1 (or 0); since its value is 0.9961 (4) just below  $T_s$ , it must exhibit a slight jump in its temperature-dependent behaviour. Therefore, the discontinuous change in the unit-cell volume, the intensities of the superstructure reflections and the atom coordinates are all in accordance with the assumption of a first-order phase transition in  $\text{BaCuSi}_2\text{O}_6$  at 610 K.

## 5. Conclusion

The structure of  $\text{BaCuSi}_2\text{O}_6$  has been re-investigated by single-crystal X-ray diffraction measurements. The observed superstructure and the related symmetry reduction at room temperature also calls for a re-evaluation of the Raman results (McKeown & Bell, 1997) for this prototypic silicate with four-membered rings.

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