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The correct symmetry of the sixfold twin in $\beta\text{-Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$

Massimo Nespolo^{1,*}

¹Université de Lorraine, CNRS, CRM2, F-54000 Nancy, France

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Abstract. A recently reported sixfold twin in $\beta\text{-Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$ was interpreted as a transformation twin obtained during cooling of a hypothetical hexagonal high temperature phase. The suggested dichromatic symmetry of the twin is incorrect because 1) a sixfold twin cannot be represented by a dichromatic twin point group but by a hexachromatic group; 2) the reported dichromatic group does not exist. The correct hexachromatic twin point group is reported here.

Introduction

In a recent article [1], an interesting case of multiple twinning in the borosilicate $\beta\text{-Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$ has been presented, where unfortunately the description of twinning is partially incorrect. $\beta\text{-Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$ and the closely related mineral spurrite, $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$, were interpreted as derivative structures of $\beta\text{-Ca}_2\text{SiO}_4$, which is commonly found in ordinary portland cement.

$\beta\text{-Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$ and spurrite crystallize in the same type of space group (No. 14), with similar cell parameters: $P12_1/c1$, $a = 14.059$, $b = 6.834$, $c = 10.597$ Å, $\beta = 100.735^\circ$, $V = 1000.333$ Å³ for the former [1], $P12_1/a1$, $a = 10.484$, $b = 6.712$, $c = 14.156$ Å, $\beta = 101.27^\circ$, $V = 976.930$ Å³ for the latter [2]. If we ignore the small numerical differences, we can convert one unit cell to the other by a change of basis vectors $\mathbf{c}, -\mathbf{b}, \mathbf{a}$, which also converts the two settings of the space group, $P12_1/c1$ and $P12_1/a1$. Both structures are derivatives of the $\beta\text{-Ca}_2\text{SiO}_4$, obtained by partially substituting SiO_4 with BO_3 or CO_3 respectively [3].

The possibility of interpreting the structure of both $\beta\text{-Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$ and spurrite as derivative of that of $\beta\text{-Ca}_2\text{SiO}_4$ and the fact the latter is obtained through a phase transformation from the hexagonal polymorph $\alpha\text{-Ca}_2\text{SiO}_4$ has led the authors [1] to hypothesize a similar hexagonal aristotype for derivatives of $\beta\text{-Ca}_2\text{SiO}_4$. Unfortunately, the proposed transformations are incorrect and incompatible with the corresponding space groups.

The cell parameters of $\beta\text{-Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$ and spurrite can be obtained from those of $\alpha\text{-Ca}_2\text{SiO}_4$ by the change of basis vectors $2\mathbf{a}-\mathbf{b}, -\mathbf{c}, \mathbf{a}+2\mathbf{b}$ and $\mathbf{a}+2\mathbf{b}, \mathbf{c}, 2\mathbf{a}-\mathbf{b}$ respectively (Fig. 10 in [1]); these two transformations are related by a change of basis vectors $\mathbf{c}, -\mathbf{b}, \mathbf{a}$. The results are $a = 14.620$, $b = 7.307$, $c = 9.571$ Å, $\beta = 109.11^\circ$, $V = 1022.517$ Å³ (with a and c exchanged for the second transformation). The closeness of the computed and experimental parameters simply shows the existence of a metric relation, but does not guarantee at all the existence of a group-subgroup relation. Indeed, the corresponding transformation matrices have determinant 5, which means that the metric relation implies an enlargement of the unit cell by a factor 5. The reported basis transformations show that the hexagonal c axis becomes the monoclinic unique axis, so that one should expect a group-subgroup relation in which $6_3/m$ becomes the monoclinic $2_1/c$ with a cell enlargement of 5 in the hexagonal (0001) plane, *i.e.* the monoclinic (010) plane. The maximal subgroup of $P6_3/mmc$ in which the 6_3 screw rotation is transformed to a 2_1 screw rotation is of type $Cmcm$, whose full symbol is $C2/m2/c2_1/m$.

*Correspondence author (e-mail: massimo.nespolo@univ-lorraine.fr)

To obtain a subgroup in which $2_1/m$ becomes $2_1/c$ (in the b -unique setting) one needs at least doubling of the area in the (010) plane, but 2 is not a factor of 5.

Moreover, the symmetry of the twin is incorrectly described by a hypothetical dichromatic group $6'/mm'm'$ which does not exist. If we take the index 2 achromatic subgroup of a dichromatic group by removing the chromatic operations we should get the symmetry of the untwinned crystals. $6'/m$ can be obtained by adding a chromatic twofold rotation to either $\bar{3}$ or $\bar{6}$; because in the hypothetical dichromatic group the mirror reflection normal to [001] is not primed, it must be a symmetry operation of the crystal, ruling out $\bar{3}$. Further, if the mirror reflection normal to both $\langle 100 \rangle$ and $\langle 1\bar{1}0 \rangle$ are chromatic, because the inversion is also chromatic (being absent from $\bar{6}$), then the twofold rotations along the same directions must be achromatic, leading to $\bar{6}22$, which is not a crystallographic point-group type. The twin reported in [1] must actually be described by a hexachromatic group, due to the presence of six twinned individuals. Because of the relative rarity of this type of multiple twinning, we think it is useful to show how to correctly describe this type of twin. Details about how to describe twinning are available in [4] and [5].

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The twin operations are described in Table 2 in [1], although they are incorrectly called “twin elements”. These are given as 1, 2_z , 3^+_y , 2_{x-z} , 3^-_y and 2_{xz} . The first operation is the identity and not a twin operation; the other five operations map the orientation of an individual taken as reference to the orientation of the other five individuals. The 3-fold rotations about [010] and the three twofold rotations about directions in the (010) plane show that the hexagonal twin lattice is described in an unconventional b -unique setting adopted to comply with the $12/m1$ monoclinic setting of the individual taken as reference. The construction of the twin point group is straightforward if we adopt the conventional c -unique setting of the hexagonal twin lattice, although this means to describe the reference individual in the c -unique monoclinic setting $112/m$. The twin lattice can be obtained by the following transformations:

1) **c,-a-c,-b** from $P12_1/c1$ (b -unique) to $P112_1/a$ (c -unique) with cell parameters $a = 10.597$, $b = 15.952$, $c = 6.834$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120.010^\circ$;

2) **3a,2b,c** from the above setting, leading to $a = 31.791$, $b = 31.903$, $c = 6.834$ Å, $\alpha = \beta = 90$; $\gamma = 120.01^\circ$. This is very close to the hexagonal unit cell obtained from the data collection in [1], *i.e.* $a = 31.819$, $c = 6.833$ Å,

The global transformation from the basis vector of $P12_1/c1$ to those of the twin lattice is **3c,-2a-2c,-b**. In this setting, the twin operations are $3^+_{[001]}$, $3^-_{[001]}$, $2_{[010]}$, $2_{[1\bar{1}0]}$, $2_{[100]}$, and the construction of the twin point group is obtained in the following way:

$$\{1, 2_{[001]}, \bar{1}, m_{[001]}\} \cup 3^+_{[001]}\{1, 2_{[001]}, \bar{1}, m_{[001]}\} \cup 3^-_{[001]}\{1, 2_{[001]}, \bar{1}, m_{[001]}\} \cup 2_{[010]}\{1, 2_{[001]}, \bar{1}, m_{[001]}\} \cup 2_{[1\bar{1}0]}\{1, 2_{[001]}, \bar{1}, m_{[001]}\} \cup 2_{[100]}\{1, 2_{[001]}, \bar{1}, m_{[001]}\} = \{1, 2_{[001]}, \bar{1}, m_{[001]}\} \cup \{3^+_{[001]}, 6^-_{[001]}, \bar{3}^+_{[001]}, \bar{6}^-_{[001]}\} \cup \{3^-_{[001]}, 6^+_{[001]}, \bar{3}^-_{[001]}, \bar{6}^+_{[001]}\} \cup \{2_{[010]}, 2_{[210]}, m_{[010]}, m_{[210]}\} \cup \{2_{[1\bar{1}0]}, 2_{[110]}, m_{[1\bar{1}0]}, m_{[110]}\} \cup \{2_{[100]}, 2_{[120]}, m_{[100]}, m_{[120]}\}.$$

The sixfold rotation about the hexagonal [001] direction exchanges three colours (individuals) and is therefore trichromatic, symbol $6^{(3)}$; the mirror perpendicular to it is a symmetry element for the individuals and is therefore achromatic, as is the inversion centre; all the twofold rotations in the (0001) plane, and the mirror planes normal to it, exchange all the colours in pairs, so that the symbol is $2^{(2)}/m^{(2)}$. The symbol of the hexachromatic twin point group is therefore:

$$\mathcal{K}^{(6)} = \left(\frac{6^{(3)}}{m} \frac{2^{(2)}}{m^{(2)}} \frac{2^{(2)}}{m^{(2)}} \right)^{(6)} \quad (1)$$

Fig. 1 shows the construction of the stereographic projection of the hexachromatic group (1).

If **W** is the matrix representation of a twin operation and **P** the matrix expressing the change of the basis vectors **3c,-2a-2c,-b** from the monoclinic to the hexagonal reference obtained above, the transformation is given by $\mathbf{W}_m = \mathbf{P}\mathbf{W}_h\mathbf{P}^{-1}$, where the subscripts m and h stand for monoclinic and hexagonal, respectively. Table 1 gives the matrix representation of a twin operation in each twin law (coset representative) with respect to the hexagonal basis vectors, and in the monoclinic setting $P12_1/c1$ reported in [1]. The results are the transposed matrices of those published in Table 2 of [1],

showing that the hexachromatic point group (1) is consistent with the structure refinement of the twin reported in [1]. To be noted that the directions of the twin elements given in [1], namely [010] (y), [001] (z), [101] (xz) and [10 $\bar{1}$] (x-z) transform to [001], [100], [010] and [430] respectively; the latter is not a symmetry direction of the hexagonal lattice and is therefore incorrect. The matrix given as 2_{x-z} in [1] corresponds to $2_{[110]}$ in the hexagonal setting but the hexagonal direction [110] corresponds to [20 $\bar{1}$] in the $P12_1/c1$ setting, so that the operation should have been listed as 2_{2x-z} . As we have already emphasized previously [6], the representation of the twin operations in the basis of the individual makes these operations much less easy to read and understand; the representation in the basis of the twin lattice is always to be preferred.

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Table 1. Matrix representation of the twin operations in the hexagonal setting of the twin lattice and in the monoclinic setting of the individual. The latter coincides with the transpose of the representation in [1].

Operation	$\bar{6}_{[001]}/\bar{6}_{[010]}$	$3_{[001]}/3_{[010]}$	$2_{[100]}/2_{[001]}$	$2_{[110]}/2_{[201]}$	$2_{[010]}/2_{[101]}$
Hexagonal representation	$\begin{pmatrix} 0 & 1 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 1 & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \bar{1} & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 & 0 \\ \bar{1} & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$
Monoclinic representation	$\begin{pmatrix} \frac{2}{3} & 0 & \frac{2}{3} \\ 0 & \bar{1} & 0 \\ \frac{7}{6} & 0 & \frac{1}{3} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{3} & 0 & \frac{2}{3} \\ 0 & 1 & 0 \\ \frac{7}{6} & 0 & \frac{2}{3} \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ \frac{1}{2} & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{3} & 0 & \frac{2}{3} \\ 0 & \bar{1} & 0 \\ \frac{4}{3} & 0 & \frac{1}{3} \end{pmatrix}$	$\begin{pmatrix} \frac{2}{3} & 0 & \frac{2}{3} \\ 0 & \bar{1} & 0 \\ \frac{5}{6} & 0 & \frac{2}{3} \end{pmatrix}$

Figure captions.

Figure 1. (a) Stereographic projection of a general form (left) and of the symmetry elements (right) of the point group $6/mmm$. (b) Stereographic projection of a general form (left) and of the symmetry elements (right) of the point group $112/m$. (c) Stereographic projection of a general form (left) and of the symmetry elements (right) of the hexachromatic group isomorphic to $6/mmm$ in (a) obtained as extension of the point group $112/m$ in (b). Left: stereographic poles of faces oriented North and South are differentiated by their size; poles with the same colour belong to the same individual (domain state) and are related by the symmetry (achromatic) operations of the individuals. Poles of different colours belong to different individuals (domains) and are related by the twin (chromatic) operations of the individuals. Along the $[001]$ direction a two-fold symmetry (achromatic) axis (black) is co-axial with a six-fold twin (trichromatic) axis (blue, red, green), which is perpendicular to a symmetry (achromatic) mirror plane (black). Along the six symmetry directions of the hexagonal lattice a twin (dichromatic) two-fold axis perpendicular to a twin (dichromatic) plane occur; twin elements bearing the same colour relate the same pairs of individuals (same colour-exchange code).





