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Twin structure deduced from elastic constants of ferroelastic $BiVO_4$

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Abstract. The domain walls of ferroelastic $BiVO_4$ crystals recently investigated by the nuclear magnetic resonance and x-ray diffraction methods were found to be different from those reported by others. The concept of ferroelasticity is considered in terms of the properties of the elastic constants of materials that undergo ferroelastic phase transitions. The acoustic symmetry character of the elastic behaviour of the tetragonal scheelite structure is shown to be exactly the same as that of the point groups 4/m and 4/mmm. From these results domain walls are derived: $(1p0)$ planes with $p = 0.724$ and $p = 1$. The theoretically deduced angles are consistent with an observed value of 37.4° and another value of 44.5°. We have established that there exist two possible orientations for permissible planar walls that are consistent with experimental observations.

1. Introduction

For bismuth vanadate ($BiVO_4$) it has been found that the structure of the ferroelastic phase belongs to the point group 2/m at room temperature and is 4/m in the para-elastic phase above T_c (David *et al* 1979). Domain structure occurs necessarily in all ferroelastic crystals as a consequence of the reduction in symmetry between the para-elastic and ferroelastic phase. In principle, the domain wall directions can be determined from elastic constants (David 1983a). The elastic constants of the 4/m crystal may be obtained from the values of the velocities of ultrasonic waves (Chung and Li 1971). Scheelite structure crystals have 4/m Laue symmetry and normally their elastic constants are referred to an XYZ axial set in which the Z axis is parallel to the fourfold axis (Farley *et al* 1975). In the studies of oxide scheelites ($CaWO_4$, $CaMoO_4$, $SrMoO_4$ and $PbMoO_4$) the orientation of the acoustic symmetry axes in the Z plane has been determined from data on the elastic constants and related to the atomic arrangement in crystals (Farley *et al* 1973, 1975).

The angle between the [100] crystallographic direction and the domain wall of the non-prominent W′ plane was obtained (Wainer *et al* 1981), and the measured value of 37.4° was claimed to be in agreement with the value of 36° calculated from ferroelastic formulae (Sapriel 1975). Recently, however, the prominent W plane, which has an angle of 44.5° with respect to the [100] axis, was reported in work using the NMR and x-ray diffraction techniques (Moon *et al* 1987). These two planes are shown in figure 1.

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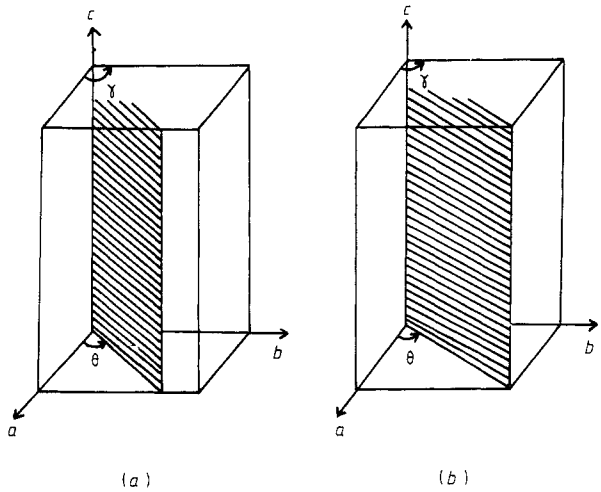

Figure 1. Orientation state of the twin domain walls: (*a*) the non-prominent twin domain wall (a = 5.192 Å, b = 5.088 Å, c = 11.699 Å, γ = 89.62°, θ = 37.4°); (*b*) the prominent twin domain wall (a = 5.196 Å, b = 5.092 Å, c = 11.704 Å, γ = 89.62°, θ = 44.5°).

The present work is a study of the structure of domains in terms of the point group obtained with elastic constants. The choice of the axial set to which the elastic properties are referred is discussed. The angular deviation of the acoustic symmetry axes from the crystallographic axes is also considered.

2. Crystal structure

Ferroelastic $BiVO_4$ crystal is known to undergo a reversible second-order phase transition at T_c (=528 K) between the monoclinic fergusonite and tetragonal scheelite structure (Dudnik *et al* 1979). The ferroelastic phase of $BiVO_4$ has the point group 2/m at room temperature with unit cell dimensions a = 5.1966 Å, b = 5.0921 Å, c = 11.7041 Å and γ = 89.62°. In the para-elastic phase the structure becomes tetragonal with the lattice parameters (determined at 573 K) $a = b$ = 5.1507 Å, c = 11.730 Å and γ = 90.0° (Bierlein and Sleight 1975). It was suggested that the point group is 4/m for $T > T_c$ (Sleight *et al* 1979).

On the basis of symmetry considerations Sapriel (1975) has derived the domain wall orientations in ferroelastic crystals belonging to various crystal classes. According to him the domain walls are classified into W and W′ walls. The orientation of the former is governed only by symmetry, no matter what values the strain components of ferroelastic domains take. Thus it is also known as the commensurate (C) wall. On the other hand, the orientation of the W′ wall is governed by concrete values of strain components and is generally referred to as the incommensurate (IC) wall.

3. Elastic behaviour of tetragonal scheelite structure

It is common practice for the centrosymmetrical elastic stiffness constant tensors (C_{ijkl}) to divide tetragonal crystals into two Laue groups: 4/mmm (TI) and 4/m (TII). In a conventional crystallographic axial system, the higher-symmetry crystals belonging to the TI group (the constituent point groups are 4mm, 422, $\bar{4}$2m and 4/mmm) have six independent elastic stiffness constants. We will use the generally accepted replacement

of pairs of indices of components of the tensor C_{ijkl} by one index such that $11 \rightarrow 1, 22 \rightarrow 2$, $33 \rightarrow 3$, $23(32) \rightarrow 4$, $13(31) \rightarrow 5$ and $12(21) \rightarrow 6$ (Nye 1957), then

$$(C_{ij}) = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}. \tag{1}$$

The reference orthogonal, right-handed, axial set $(+X, +Y, +Z)$ includes the Z axis parallel to the fourfold axis and the X and Y axes are then in the Z plane along the a and b crystallographic axes, respectively. The presence of vertical planes of symmetry or diad axes in the Z plane imposes the condition that C_{16} should be zero. This is not so for crystals of the TII group (the constituent point groups are 4, $\bar{4}$ and 4/m) for which the elastic stiffness constant matrix referred to the frame of the crystallographic axes (a, b, c) is

$$(C_{ij}) = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{11} & C_{13} & 0 & 0 & -C_{16} \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ C_{16} & -C_{16} & 0 & 0 & 0 & C_{66} \end{bmatrix}. \tag{2}$$

The non-zero value of C_{16} in the 4/m (TII) Laue crystals gives rise to apparently more complicated elastic behaviour than is found for the 4/mmm (TI) Laue symmetry. As a special case of tetragonal structure, Khatkevich (1962) and Blanchfield and Saunders (1979) considered that the usual requirement of seven elastic tensor components to describe the elastic behaviour of tetragonal 4/m (TII) crystals could be reduced to six parameters by a suitable choice of reference frame. After a rotation by an angle φ along the Z axis, which transforms the X and Y axes to the pure mode X' and Y' in the Z plane, the components of the elastic stiffness tensor take the form

$$\begin{aligned} C'_{11} &= C'_{22} = \hat{C}_{11} + C\cos 4\varphi + C_{16}\sin 4\varphi \\ C'_{66} &= \hat{C}_{66} - C\cos 4\varphi - C_{16}\sin 4\varphi \\ C'_{12} &= \hat{C}_{12} - C\cos 4\varphi - C_{16}\sin 4\varphi \\ C'_{16} &= -C'_{26} = -C\sin 4\varphi + C_{16}\cos 4\varphi \\ C'_{14} &= -C'_{24} = C'_{56} = C_{14}\cos 3\varphi + C_{25}\sin 3\varphi \\ C'_{25} &= -C'_{15} = C'_{46} = -C_{14}\sin 3\varphi + C_{25}\cos 3\varphi \\ C'_{33} &= C_{33} \qquad C'_{44} = C_{55} = C_{44} \qquad C'_{13} = C'_{23} = C_{13} \\ C'_{34} &= C_{35} = C'_{45} = C'_{36} = 0 \end{aligned} \tag{3}$$

where the coefficients of sin $k\varphi$ and cos $k\varphi$ are zero if $k \neq n$ (where n is the order of the symmetry axis) and

$$\begin{aligned} C &= \tfrac{1}{4}(C_{11} - C_{12} - 2C_{66}) & \hat{C} &= C_{11} - C \\ \hat{C}_{66} &= C_{66} + C & \hat{C}_{12} &= C_{12} + C. \end{aligned} \tag{4}$$

In the particular case of 4/m, the rotation by the angle

$$\varphi_k = \tfrac{1}{4}\tan^{-1}(C_{16}/C) \qquad (\varphi_r = \varphi_\gamma + \pi/2) \tag{5}$$

with k and γ axes of the acoustic symmetry being new X' and Y' axes, respectively, results in the transformed elastic constant C'_{16} becoming equal to zero. Then the number of independent elastic stiffness constants is reduced to six, having the same matrix form as that of (1).

4. Results and analysis

In the tetragonal scheelite structure of $BiVO_4$, the isolated VO_4 tetrahedra have a $\bar{4}$ point symmetry. The fourfold axes of tetrahedra make an angle $\varphi_k = 28.97°$ with respect to the [100] direction. This angle, called the setting angle (David 1983b), has been shown to be related to the components of elastic constants along the k and γ axes of the acoustic symmetry, respectively (Farley *et al* 1975). The transformation of the components of the elastic tensor of the 4/m (TII) crystal due to a rotation about the Z axis through an angle given by equation (5) makes C_{16} equal to zero, and consequently yields a tensor (C'_{ij}) which has the form of 4/mmm (TI) materials. From these results, the elastic properties referred to the acoustic symmetry axes of tetragonal $BiVO_4$ are identical to those of 4/mmm (TI) and 4/m (TII) point group symmetry (Khatkevich 1962, Farley *et al* 1973, 1975).

David and Wood (1983) reported that the $BiVO_4$ crystal belongs to the ferroelastic species 4/mF2/m; the para-elastic and the ferroelastic phases have 4/m and 2/m symmetry, respectively, and F represents the ferroelastic phase. For the ferroelastic species 4/mF2/m, the spontaneous monoclinic distortion takes the following form:

$$\begin{bmatrix} -f & g & 0 \\ g & f & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} (\varepsilon_{11} - \varepsilon_{22})/2 & \varepsilon_{12} & 0 \\ \varepsilon_{12} & -(\varepsilon_{11} - \varepsilon_{22})/2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{6}$$

where ε_{11}, ε_{22} and ε_{12} are determined from the monoclinic (m) and tetragonal (t) lattice parameters measured at temperature T;

$$\begin{aligned} \varepsilon_{11}(T) &= (a_m(T) - a_t(T))/a_m(T) \\ \varepsilon_{22}(T) &= (b_m(T) - b_t(T))/b_m(T) \\ \varepsilon_{12}(T) &= \tan[(\gamma_m - 90°)/2]. \end{aligned} \tag{7}$$

Consequently, the equation of domain walls can be derived as follows (Sapriel 1975)

$$f(x^2 - y^2) - 2gxy = 0. \tag{8}$$

The solution of (8) gives

$$x = py \qquad x = -y/p$$

Table 1. The observed and calculated values of the non-prominent domain wall directions for $BiVO_4$ crystal based on various lattice parameters.

Reference	θ_{ob}	θ_{cal}	Lattice parameter
Manolikas and Amelinckx (1980)	32°	31.4°	$a = 5.20$ Å, $b = 5.09$ Å, $c = 11.14$ Å, $\gamma = 90.63°$
Wainer *et al* (1981)	37.4°	36°	$a = 5.1956$ Å, $b = 5.0935$ Å, $c = 11.7045$ Å, $\gamma = 90.383°$
Masanori *et al* (1982)	39 ± 3°		$a = 5.1966$ Å, $b = 5.0921$ Å, $\gamma = 89.616°$
Mnushkina and Dudnik (1982)		35°	$a = 5.1935$ Å, $b = 5.0898$ Å, $c = 11.6972$ Å, $\gamma = 89.62°$
David and Wood (1983)	37.4°	36°	$a = 5.1966$ Å, $b = 5.0921$ Å, $c = 11.704$ Å, $\gamma = 89.616°$

where

$$p = [g + (f^2 + g^2)^{1/2}]/f. \tag{9}$$

Using the spontaneous strain tensors given by Aizu (1970) and the formulae proposed by Sapriel (1975), we can evaluate the domain wall orientations.

In the case of the transition from 4/mmm to 2/m symmetry, the domain wall orientations are expressed by the following equations (Sapriel 1975):

$$\begin{aligned} &\text{W}' \quad x = py \quad \text{and} \quad x = -y/p \\ &\qquad\quad x = -py \quad \text{and} \quad x = y/p \end{aligned} \tag{10}$$

and

$$\begin{aligned} &\text{W} \quad x = 0 \quad \text{and} \quad y = 0 \\ &\qquad\quad x = y \quad \text{and} \quad x = -y \end{aligned} \tag{11}$$

where p is the same as in (9). These directions lie along crystallographically prominent directions as well as non-prominent ones.

5. Discussion

In $BiVO_4$ the phase transformation from the tetragonal structure with the point group 4/m or 4/mmm to the monoclinic structure with the point group 2/m causes a deformation of the monoclinic crystal into a domain structure. By using the monoclinic axes system, the non-prominent domain walls are the $(1p0)$ planes with p given by (9). The angles of the W′ wall with respect to the [100] axis are summarised in table 1. The calculated angles of the domain wall were obtained by a suitable choice of lattice parameters as indicated. In addition to this wall, the prominent W plane with $x = y$ and $x = -y$ is also permissible. Therefore, another domain wall makes an angle of 45° with respect to the [100] axis.

These theoretically deduced angles between the [100] axis and the domain boundaries are consistent with an observed value of 37.4° (Wainer *et al* 1981, David and Wood 1983) and another one of 44.5° (Moon *et al* 1987). From these results, we can depict the lattice

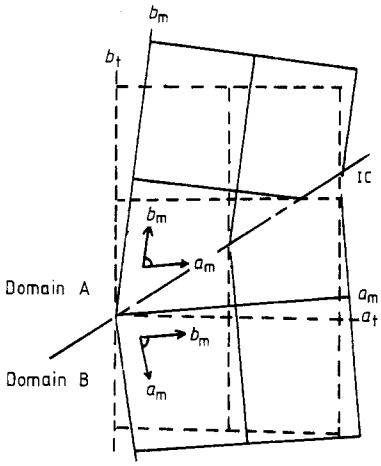

Figure 2. Incommensurate twin domain wall.

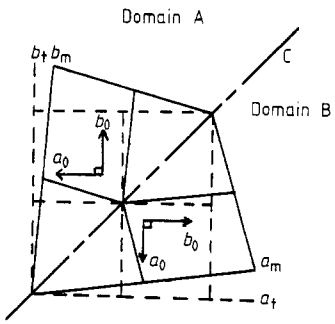

Figure 3. Commensurate twin domain wall.

structure of the domain walls as shown in figures 2 and 3 as the W′ plane and the W plane, respectively. We have established that there exist two possible orientations for permissible planar walls that are consistent with experimental observations.

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