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# Electron microscope study of domains in $PbZrO_3$

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The domains in lead zirconate, $PbZrO_3$, can be classified as two types: The type I domains with the orientation relationship $[001]_A//[001]_B$, $(200)_A//(040)_B$ and the type II domains with the orientation relationship form of $\langle 001\rangle_A//\langle 210\rangle_B$, $\{200\}_A//\{122\}_B$. 

## 1. Introduction

Lead zirconate, $PbZrO_3$, is a typical antiferroelectric material that has an orthorhombic structure of unit cell dimensions $a = 0.5885$ nm $= \sqrt{2}a_0$, $b = 1.1781$ nm $= 2\sqrt{2}a_o$ and $c = 0.8218$ nm $= 2a_o$, where $a_o$ is the cell dimension of its paraelectric-cubic phase [1].

The 90° domain, as well as 120° and 180° domains, which are peculiar to such orthorhombic structure, have been reported in many references [2–4].

Tanaka *et al*. [4] have studied 120° and 90° domains by considering domain configuration on the basis of the pseudo-cubic instead of the orthorhombic cell. They pointed out that some electron microscopy observed fine lines running along the $[100]_o$ direction inside 90° and 60° domains in the electron micrographs were 180° domain walls. They indicated that 180° domains could be formed by displacing to each other. The displacing vectors between domains were determined as $\frac{1}{4}[2\,1\,n]$, $\frac{1}{4}[2\,\bar{1}\,n]$ and $\frac{1}{4}[0\,2\,n]$ ($n = 0$ or 2). However, this characteristic suggested these lines might be stacking faults rather than 180° domain walls. Actually Shen *et al*. [5] have observed 180° domains which can also be explained on the basis of the pseudo-cubic.

A recent electron diffraction study has shown that there are two basic diffraction patterns in the domains of $PbZrO_3$ crystal. After detailed analysis of all the possible orientation relationships in 90°, 120° and 180° domains on the basis of pseudo-cubic, it has been found that there are only two kinds of orientation relationships, which correspond to the two basic diffraction patterns, in the domains of $PbZrO_3$ crystal. They are $[001]_A//[001]_B$, $(200)_A//(040)_B$ and $\langle 001\rangle_A//\langle 210\rangle_B$, $\{200\}_A//\{122\}_B$. This paper will prove that there exist only two types of domains in $PbZrO_3$ crystal. One is type I domain with orientation relationship $[001]_A//[001]_B$, $(200)_A//(040)_B$ and another is type II domains with the orientation relationship form of $\langle 001\rangle_A//\langle 210\rangle_B$, $\{200\}_A//\{112\}_B$.

## 2. Experimental

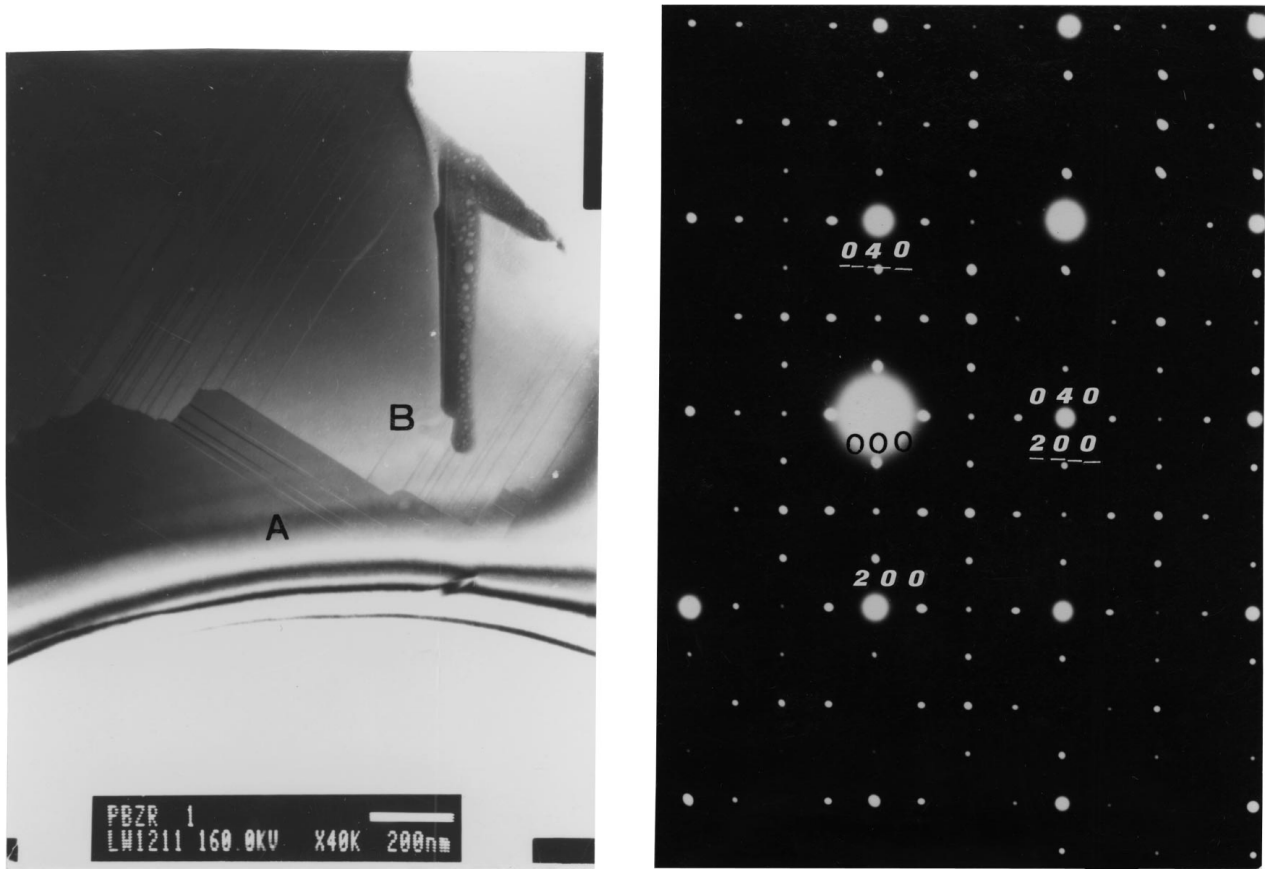
Lead zirconate was synthesized from high purity of PbO and $ZrO_2$ in appropriate proportion using the conventional solid-state technique. Samples for TEM observation were prepared by argon-milling. Slices were cut from the bulk crystals of $PbZrO_3$ and mechanically ground to about 50 $\mu$m thick. They were subsequently mounted on a 3 mm Cu grid and ion milled to electron transparency. TEM observation was carried out by using a JEOL-2000EX TEM at 160 KV.

## 3. Results and discussion

Fig. 1a is a bright field electron micrograph of domains in a $PbZrO_3$ crystal. Some fine lines which are perpendicular to each other in the two domains can be seen clearly. The corresponding selected area diffraction pattern taken from this area is shown in Fig. 1b. It is a composite diffraction pattern which is composed of two $[001]_o$ component patterns rotated by an angle of 90° to each other about the *c*-axis. The electron diffraction patterns are indexed as shown in the Fig. 1b. This indicates the presence of 90° domains with orientation relationship $[001]_A//[001]_B$; $(200)_A//(040)_B$. After correction for rotation between the micrograph and the corresponding diffraction pattern, the fine lines which Tanaka *et al*. regarded as 180° domain walls are shown to be (010) slip plane traces.

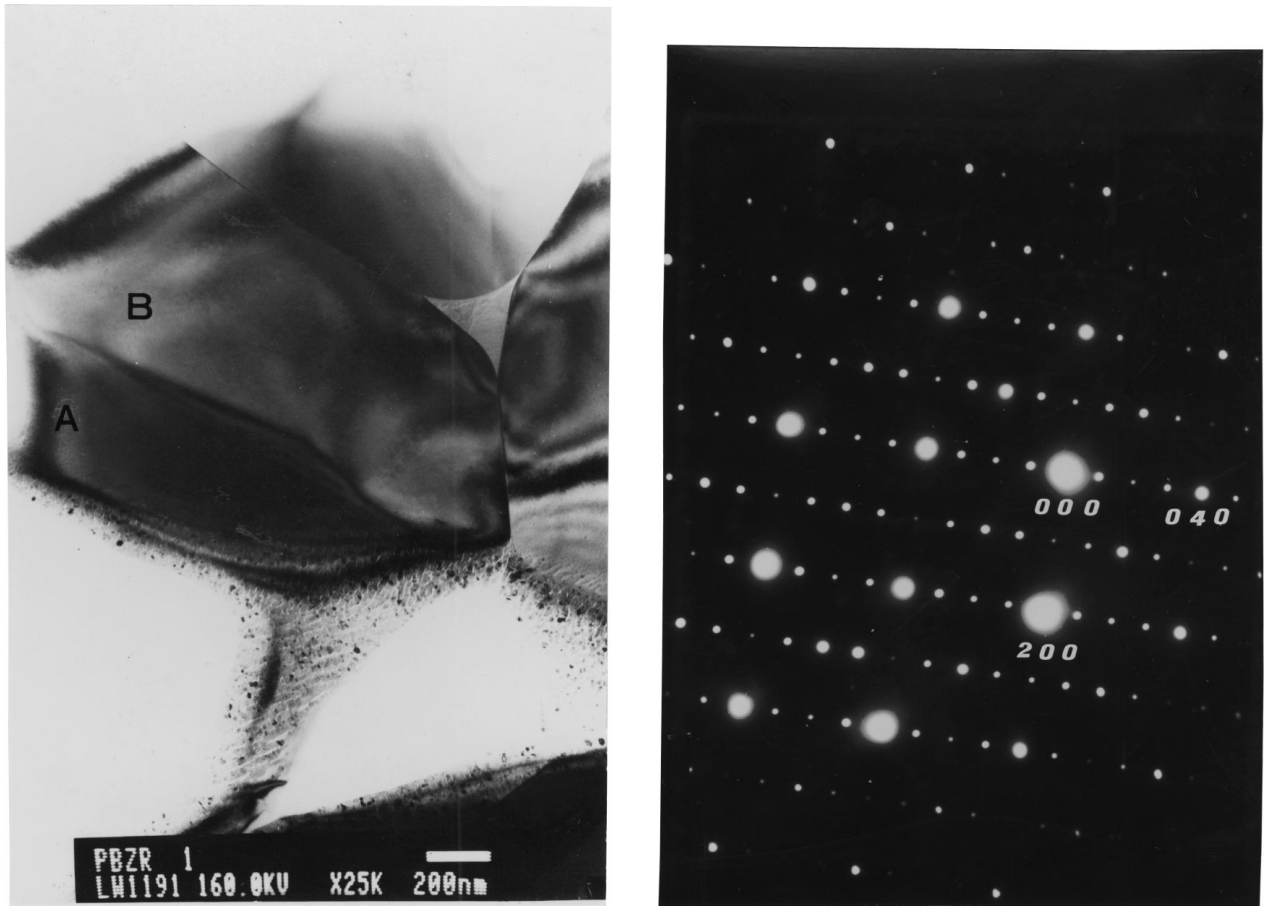
Fig. 2a is a bright field electron micrograph of another type of domain in the crystal. The corresponding diffraction patterns for domains *A* and *B* are shown in Fig. 2b and c respectively. These patterns have been indexed as $[001]_A$ and $[210]_B$. Therefore, the orientation relationship between domain *A* and *B* derived from these diffraction pattern is

$$\begin{matrix}[001]_A//[2\bar{1}0]_B \\ (200)_A//(122)_B\end{matrix} \qquad (1)$$



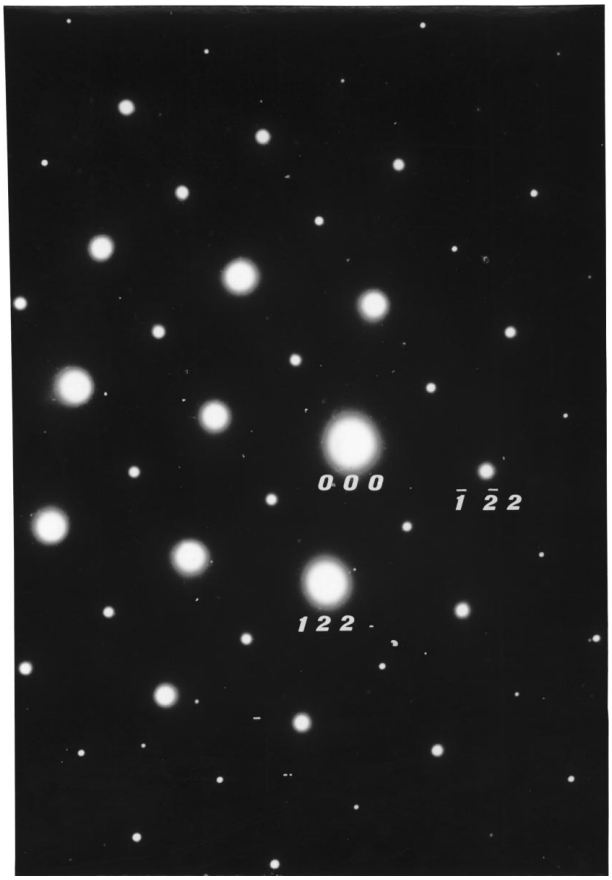

(a) (b)

*Figure 1*




(a) (b)

*Figure 2* (*Continued*)




(c)

*Figure 2* (*Continued*).

If the specimen is tilted to $\langle 201\rangle_o$ (or $\langle 111\rangle_c$) incidence where subscript o and c refer to orthorhombic and cubic unit cell respectively, the *b*-axes in these diffraction patterns would make an angle of 60° to each other about $[201]_o$ axis as indicated by Tanaka *et al*. [4]. This has been regarded as strong evidence for the presence of 120° domains.

However, the indexing of diffraction patterns in Fig. 2b and c are not unique. For example, following orientation relationships also be possible. They can be divided into three groups.

$$\begin{aligned}
&\text{Group 1. } [001]_A//[210]_B\ (200)_A//(1\bar{2}\bar{2})_B;\\
&\qquad [001]_A//[\bar{2}\bar{1}0]_B\ (200)_A//(\bar{1}2\bar{2})_B\\
&\text{Group 2. } [001]_A//[\bar{2}\bar{1}0]_B\ (200)_A//(122)_B;\\
&\qquad [001]_A//[\bar{2}10]_B\ (200)_A//(\bar{1}\bar{2}2)_B\\
&\qquad [001]_A//[2\bar{1}0]_B\ (200)_A//(\bar{1}\bar{2}\bar{2})_B;\\
&\qquad [001]_A//[\bar{2}10]_B\ (200)_A//(12\bar{2})_B\\
&\text{Group 3. } [001]_A//[210]_B(200)_A//(\bar{1}22)_B;\\
&\qquad [001]_A//[\bar{2}\bar{1}0]_B(200)_A//(\bar{1}\bar{2}\bar{2})_B
\end{aligned} \tag{2}$$

Because of the symmetry of the crystal, it is impossible to remove such ambiguity of indexing even by tilting the crystal.

In order to understand the domains in the antiferroelectric $PbZrO_3$, Tanaka *et al*. pointed out that the domain configuration should be considered on the basis of the pseudo-cubic. They have demonstrated that a 120° domain could been constructed by rotating 120° about the $[111]_c$ axis. The relation between the axes of cubic cell in domain *A* and that in domain *B* can be written as following

$$\begin{bmatrix} a_c \\ c_c \\ b_c \end{bmatrix}_B = \mathbf{B} \begin{bmatrix} a_c \\ c_c \\ b_c \end{bmatrix}_A = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} a_c \\ c_c \\ b_c \end{bmatrix}_A \tag{3}$$

Since the transformation of the cubic unit cell to the orthorhombic unit cell of $PbZrO_3$ is given by

$$\begin{bmatrix} a_c \\ b_c \\ c_o \end{bmatrix} = \mathbf{A} \begin{bmatrix} a_c \\ c_c \\ b_c \end{bmatrix} = \begin{bmatrix} 1 & 0 & 1 \\ 2 & 0 & \bar{2} \\ 0 & 2 & 0 \end{bmatrix} \begin{bmatrix} a_c \\ c_c \\ b_c \end{bmatrix} \tag{4}$$

The transformation of indices of a plane, (*hkl*), is given by

$$\begin{bmatrix} h_o \\ k_o \\ l_o \end{bmatrix}_B = \mathbf{ABA^{-1}} \begin{bmatrix} h_o \\ k_o \\ l_o \end{bmatrix}_A = \frac{1}{4} \begin{bmatrix} 2 & \bar{1} & 2 \\ 4 & \bar{2} & \bar{4} \\ 4 & 2 & 0 \end{bmatrix} \begin{bmatrix} h_o \\ k_o \\ l_o \end{bmatrix}_A \tag{5}$$

The indices of a direction, [*u v w*], are transformed from domain *A* to domain *B* by

$$\begin{aligned}
\begin{bmatrix} u_o \\ v_o \\ w_o \end{bmatrix}_B &= \{(\mathbf{ABA^{-1}})^{-1}\}^T \begin{bmatrix} u_o \\ v_o \\ w_o \end{bmatrix}_A \\
&= \frac{1}{4} \begin{bmatrix} 2 & \bar{4} & 4 \\ 1 & \bar{2} & \bar{2} \\ 2 & 4 & 0 \end{bmatrix} \begin{bmatrix} u_o \\ v_o \\ w_o \end{bmatrix}_A
\end{aligned} \tag{6}$$

It can be derived from relations (5) and (6) that $[001]_o$ axis in domain *A* is parallel to $[210]_o$ axis in domain *B* and reflections 2 0 0 in domain *A* and 1 2 2 in domain *B* are superposed. This is actually relation (1) and can successfully explain the experiment result shown in Fig. 2b and c.

Following the same method as described above, 90° domains can be formed by rotating the cubic cell 90° around the $\langle 010\rangle_c$ axis, while 120° (or 60°) domains can be constructed by rotating through an angle of 120° or −120° about the $\langle 111\rangle_c$ axis in the cubic cell. We also can make an 180° domains by rotating through an angle of 180° about $\langle 110\rangle_c$. The possible orientation relationships corresponding to 90°, 120° and 180° domains are listed in the Table I. Because that the domains which are formed by rotating though 180° about $[101]_c$ or $[\bar{1}01]_c$ axes in the cubic cell are actually identical to each other, they are not considered here. It can be found from Table I that there are two basic orientation relationships in domains. Firstly, $[001]_A//[001]_B$, $(200)_A//(040)_B$ which corresponds to diffraction pattern in Fig. 1b, and secondly,

TABLE I All the possible orientation relationships of domains in $PbZrO_3$ crystal

| Rotation axis | Rotation angle | Orientation relationship between $A$ and $B$ domains | |
|---|---|---|---|
| | | $[001]_A$ | $[201]_A$ |
| $[010]_c$ | 90° | $[001]_A//[001]_B$<br>$(200)_A//(040)_B$ | $[20\bar{1}]_A//[0\bar{1}\bar{1}]_B$<br>$(040)_A//(\bar{2}00)_B$ |
| | −90° | $[001]_A//[00\bar{1}]_B$<br>$(200)_A//(0\bar{4}0)_B$ | $[201]_A//[0\bar{1}1]_B$<br>$(040)_A//(200)_B$ |
| $[001]_c$ | 90° | $[001]_A//[\bar{2}\bar{1}0]_B$<br>$(200)_A//(1\bar{2}2)_B$ | $-60$ $[20\bar{1}]_A//[\bar{2}01]_B$<br>$(040)_A//(\bar{1}22)_B$ |
| | −90° | $[001]_A//[2\bar{1}0]_B$<br>$(200)_A//(\bar{1}22)_B$ | 60 $[201]_A//[\bar{2}0\bar{1}]_B$<br>$(040)_A//(\bar{1}\bar{2}2)_B$ |
| $[100]_c$ | 90° | $[001]_A//[\bar{2}10]_B$<br>$(200)_A//(1\bar{2}2)_B$ | $-60$ $[201]_A//[20\bar{1}]_B$<br>$(040)_A//(122)_B$ |
| | −90° | $[001]_A//[\bar{2}10]_B$<br>$(200)_A//(122)_B$ | 60 $[20\bar{1}]_A//[201]_B$<br>$(040)_A//(\bar{1}2\bar{2})_B$ |
| $[111]_c$ | 120° | $[001]_A//[2\bar{1}0]_B$<br>$(200)_A//(122)_B$ | 60 $[201]_A//[\bar{2}01]_B$<br>$(040)_A//(\bar{1}22)_B$ |
| | −120° | $[001]_A//[\bar{2}10]_B$<br>$(200)_A//(1\bar{2}2)_B$ | $-60$ $[201]_A//[20\bar{1}]_B$<br>$(040)_A//(\bar{1}\bar{2}2)_B$ |
| $[\bar{1}11]_c$ | 120° | $[001]_A//[\bar{2}\bar{1}0]_B$<br>$(200)_A//(\bar{1}22)_B$ | $-60$ $[201]_A//[\bar{2}0\bar{1}]_B$<br>$(040)_A//(\bar{1}22)_B$ |
| | −120° | $[001]_A//[2\bar{1}0]_B$<br>$(200)_A//(122)_B$ | $-60$ $[20\bar{1}]_A//[\bar{2}01]_B$<br>$(040)_A//(122)_B$ |
| $[1\bar{1}1]_c$ | 120° | $[001]_A//[\bar{2}\bar{1}0]_B$<br>$(200)_A//(1\bar{2}2)_B$ | 60 $[20\bar{1}]_A//[20\bar{1}]_B$<br>$(040)_A//(\bar{1}\bar{2}2)_B$ |
| | −120° | $[001]_A//[\bar{2}10]_B$<br>$(200)_A//(122)_B$ | $-60$ $[20\bar{1}]_A//[20\bar{1}]_B$<br>$(040)_A//(\bar{1}\bar{2}2)_B$ |
| $[11\bar{1}]_c$ | 120° | $[001]_A//[\bar{2}10]_B$<br>$(200)_A//(1\bar{2}2)_B$ | 60 $[20\bar{1}]_A//[\bar{2}0\bar{1}]_B$<br>$(040)_A//(\bar{1}22)_B$ |
| | −120° | $[001]_A//[\bar{2}10]_B$<br>$(200)_A//(\bar{1}22)_B$ | 60 $[201]_A//[\bar{2}01]_B$<br>$(040)_A//(122)_B$ |
| $[101]_c$ | 180° | $[001]_A//[00\bar{1}]_B$<br>$(200)_A//(200)_B$ | 0 $[201]_A//[20\bar{1}]_B$<br>$(040)_A//(0\bar{4}0)_B$ |
| $[10\bar{1}]_c$ | 180° | $[001]_A//[00\bar{1}]_B$<br>$(200)_A//(\bar{2}00)_B$ | 0 $[201]_A//[\bar{2}0\bar{1}]_B$<br>$(040)_A//(040)_B$ |
| $[011]_c$ | 180° | $[001]_A//[\bar{2}10]_B$<br>$(200)_A//(1\bar{2}2)_B$ | 60 $[20\bar{1}]_A//[\bar{2}01]_B$<br>$(040)_A//(\bar{1}22)_B$ |
| $[01\bar{1}]_c$ | 180° | $[001]_A//[\bar{2}10]_B$<br>$(200)_A//(1\bar{2}2)_B$ | $-60$ $[201]_A//[\bar{2}0\bar{1}]_B$<br>$(040)_A//(\bar{1}22)_B$ |
| $[110]_c$ | 180° | $[001]_A//[2\bar{1}0]_B$<br>$(200)_A//(1\bar{2}2)_B$ | $-60$ $[20\bar{1}]_A//[\bar{2}01]_B$<br>$(040)_A//(\bar{1}\bar{2}2)_B$ |
| $[1\bar{1}0]_c$ | 180° | $[001]_A//[\bar{2}\bar{1}0]_B$<br>$(200)_A//(1\bar{2}2)_B$ | 60 $[201]_A//[\bar{2}0\bar{1}]_B$<br>$(040)_A//(\bar{1}22)_B$ |

$\langle 001\rangle_A//\langle 210\rangle_B$, $\{200\}_A//\{122\}_B$ which correspond to diffraction patterns in Fig. 2b and c. For the second relation, it can be seen that the orientation relationships listed in group 1, group 2 and group 3 in (2) are related to 90°, 120° and 180° domains respectively. That is, the diffraction patterns in Fig. 2b and c can be produced from 90°, 120° or 180° domain.

It may also be seen from fourth column in Table I that if a specimen is tilted to $\langle 201\rangle$c incidence, the *b*-axes of the diffraction patterns could make an angle of 60° to each other in not only 120° domain, but also 90° and 180° domains. The figures "60", "0" and "−60" in front of the orientation relations in this column represent the magnitude of the angle between the *b*-axis of the diffraction pattern of domain *B* and that of domain *A*. Therefore, the *b*-axes forming 60° angle in $\langle 201\rangle_c$ diffraction patterns can not regarded as only criteria to judge 120° domain.

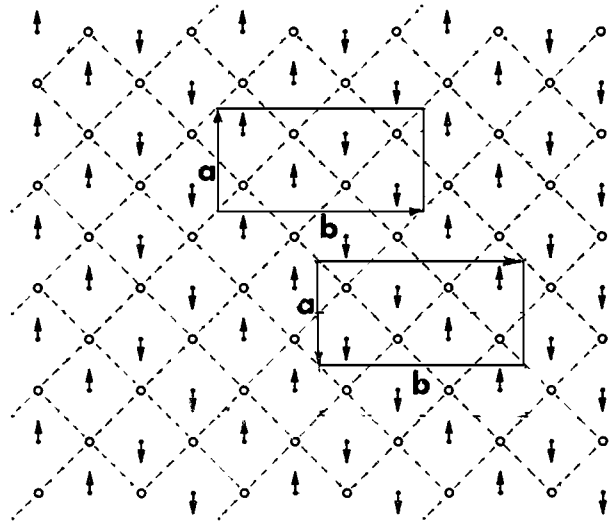



*Figure 3*

It is believed that these domain with orientation relationship form of $\langle 001\rangle_A//\langle 210\rangle_B$, $\{200\}_A//\{122\}_B$ should be equivalent to each other. Therefore, any attempt to distinguish these domains should become meaningless.

The reason that causes such ambiguity is due to the choice of unit cell. In order to illustrate this point, the lead zirconate structure projected along the [001] direction is shown in Fig. 3. It is noted that two possible unit cell can be selected. If an alternative unit cell is chosen, the crystal orientation will change from [001] to $[00\bar{1}]$ or vice versa. Suppose that [001] is replaced by $[00\bar{1}]$ in the relation (1); the change of orientation relationship will result in a change from 120° domain to 90° one, but the atomic configuration will remain the same as before.

From the above analysis, The domains in $PbZrO_3$ should be classified into two types: one with the orientation relationship $[001]_A//[001]_B$, $(200)_A//(040)_B$ is type I domain and another with the orientation relationship form of $\langle 001\rangle_A//\langle 210\rangle_B$, $\{200\}_A//\{122\}_B$ is type II domain.

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