# DOMAIN STRUCTURE AND OXYGEN DISPLACEMENT IN TETRAGONAL ZIRCONIA

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## ABSTRACT

The relation between the domain structure and the displacement of oxygen ions of t-$ZrO_2$ was investigated by TEM observation. The displacement mode of oxygen ions in t-$ZrO_2$ was confirmed by the analysis of electron diffraction patterns. It was revealed that the ideal domain boundary must have a closed surface, while the branching of domain boundaries was also observed. The geometrical meaning of the appearance of forbidden reflections was discussed in relation to the ionic array across the domain boundaries which is regarded as $\pi$-boundary.

## INTRODUCTION

It has been reported that oxygen ions in tetragonal zirconia(t-$ZrO_2$) are slightly displaced alternately towards the direction of c-axis in its fluorite structure as shown in Fig.1.[1,2,3] In the TEM observation of t-$ZrO_2$, forbidden reflections for cubic fluorite structure, which are considered to be caused by the above oxygen ion displacement, appear in the SAD(selected area diffraction) patterns, and a characteristic domain structure is observed in a dark field image of t-$ZrO_2$ by using a forbidden reflection[4]. The domain structure is formed by the diffusionless c-t phase transformation, and the curvilinear feature is thought to be an anti-phase boundary which is associated with the array of oxygen ions.[3,4,5,6] The purpose of this paper is to make a further detailed examination of domain structure.

## EXPERIMENTAL PROCEDURE

Button-shaped specimens were obtained by arc melting using mixed powders of $ZrO_2$-4 and 6 mol% $Y_2O_3$(99.9 wt%, TOSOH Co. Ltd.). The arc melting was performed in Ar gas atmosphere of $6.7 \times 10^4$ Pa. These specimens were sliced by a diamond blade, lapped into a thin foil and finally milled by an Ar ion milling apparatus(Gatan Inc. Model 600). The TEM observation was done using 2000FX(JEOL Ltd.) and H800(HITACHI Ltd.) with an accelerating voltage of 200 kV. The electron diffraction patterns were calculated using the eigen value method of dynamical

diffraction theory in order to simulate the obtained diffraction patterns.[7]

## RESULTS

**TEM observation of t-$ZrO_2$ containing 4 and 6 mol% $Y_2O_3$**

Fig.2 shows a SAD pattern of $ZrO_2$-4mol%$Y_2O_3$. Forbidden reflections are observed in (b) and (d). It is noted that 110 systematic reflections are very weak in Fig.2(b). The 110 reflections are caused by the double reflection which is discussed later. If the structure factors are calculated by assuming the configuration of oxygen ions of Fig.1, it is found that forbidden reflections appear in [110] and [111] SAD patterns but never appear in [101], [100],[010] and [001] SAD patterns. Therefore, the incident beam direction in (b),(c) and (d) are considered to be [110],[101] and [111], respectively. In Fig.2(a), the incident beam direction [001] cannot unambiguously be determined, but the direction is not contradictory to the above extinction rules because no forbidden reflections are observed.

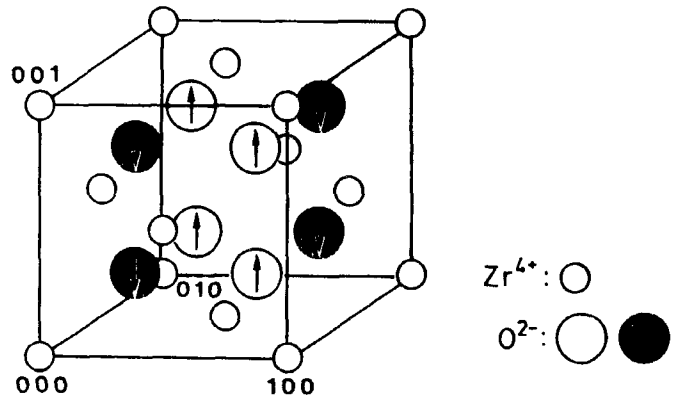


Fig.1 Displacement of oxygen ions in the pseudo fluorite structure of tetragonal zirconia.

Fig.3 shows the diffraction patterns of $ZrO_2$-6mol%$Y_2O_3$. The 110 systematic reflections of Fig.3(b) are stronger than those of Fig.2(b). This is considered that the direction of beam incidence of Fig.3(b) became closer to [110] than that of Fig.2(b) and the effect of double reflection occurred more strongly.

Fig.4 shows a dark field image taken by a 112 forbidden reflection. In general, t-$ZrO_2$ is constituted from three variants. A single 112 reflection is excited from one of the three variants. The tetragonal variant is divided into small regions which are called domains. The domain boundary has a curvilinear feature similar to antiphase domain boundaries in ordered alloys. The contrast of domains in Fig.4 is not uniform. This fact means that the intensity of 112 reflections is also varying, therefore the displacement of oxygen ions is assumed to be varying from place to place.

Fig.5 shows the domain structure in $ZrO_2$-6mol%$Y_2O_3$ annealed for 360 ks at 573 K. The important fact is that there are the domains with a closed boundary. Such domains were generally seen in a sufficiently thin area of specimen. The domains with a closed boundary can be expected from the displacement of oxygen ions in Fig.1 as discussed in the following section.

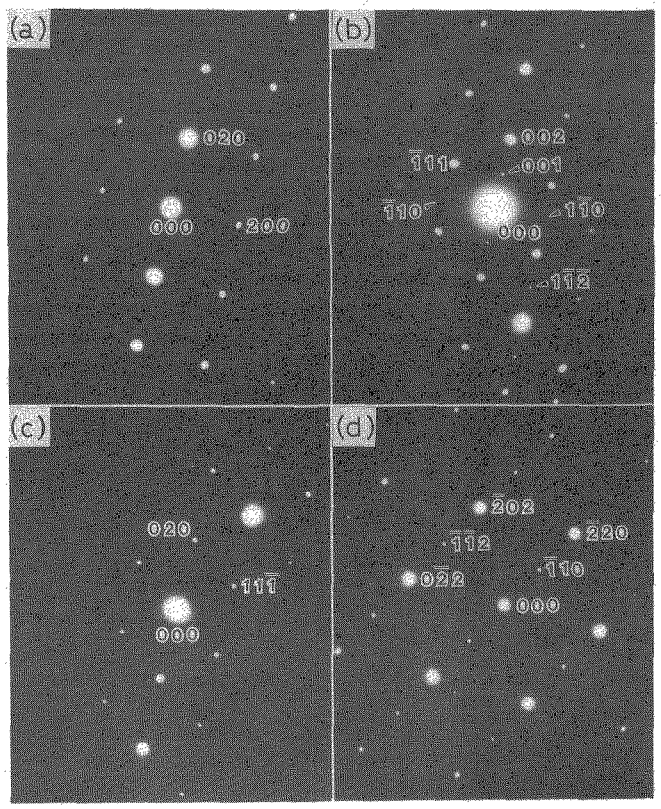


Fig.2 SAD patterns of $ZrO_2$-4mol%$Y_2O_3$.

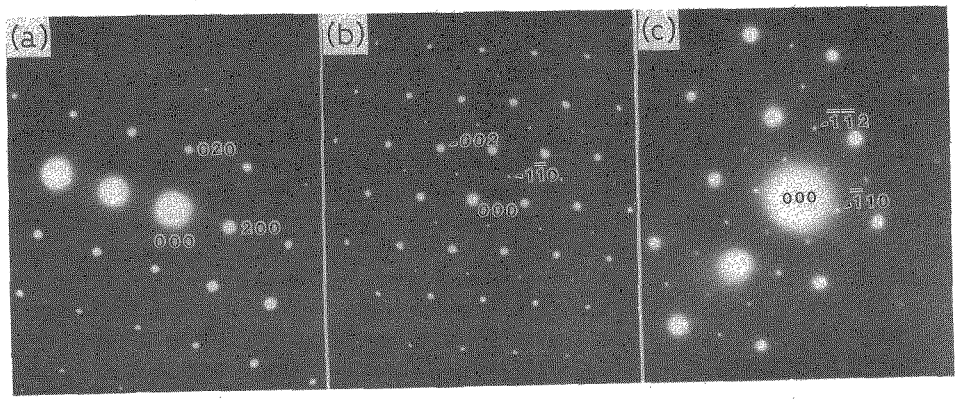


Fig.3 SAD patterns of $ZrO_2$-6mol%$Y_2O_3$. The incident beam directions are (a)[001],(b)[110] and (c)[111],respectively.

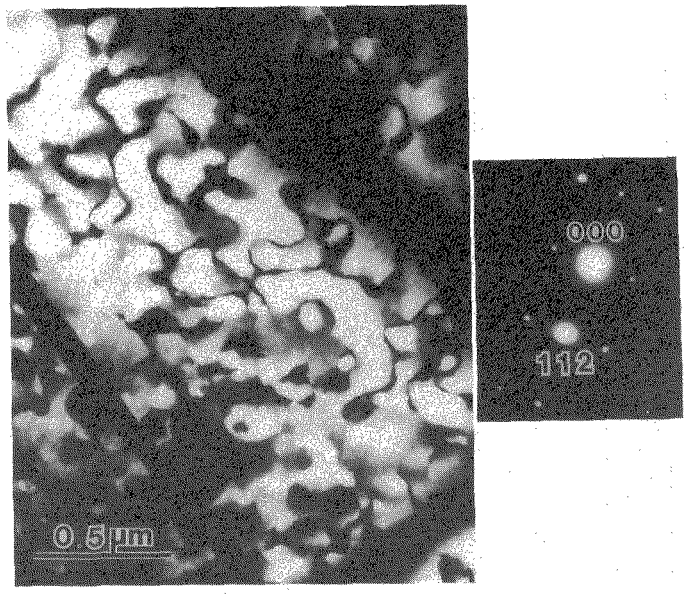


Fig.4 A dark field image of $ZrO_2$-6mol%$Y_2O_3$ taken with a 112 reflection.

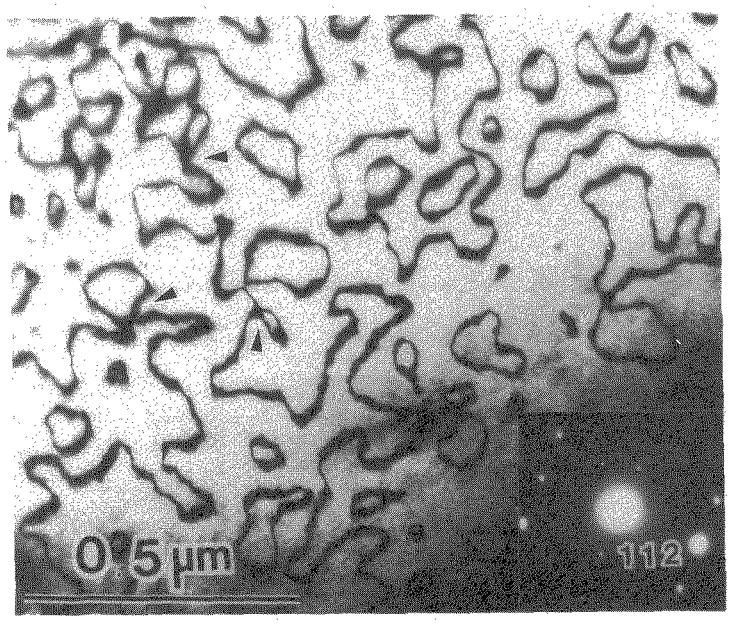


Fig.5 A domain structure of $ZrO_2$-6mol%$Y_2O_3$ annealed at 573 K for 360 ks.

**Calculated diffraction patterns**

Fig.s 6 and 7 are the diffraction patterns(DPs) calculated for t-$ZrO_2$ with a structure of Fig.1 at an acceleration voltage of 200 kV. The total number 81,63,63 and 61 waves was used for the dynamical calculation in the beam

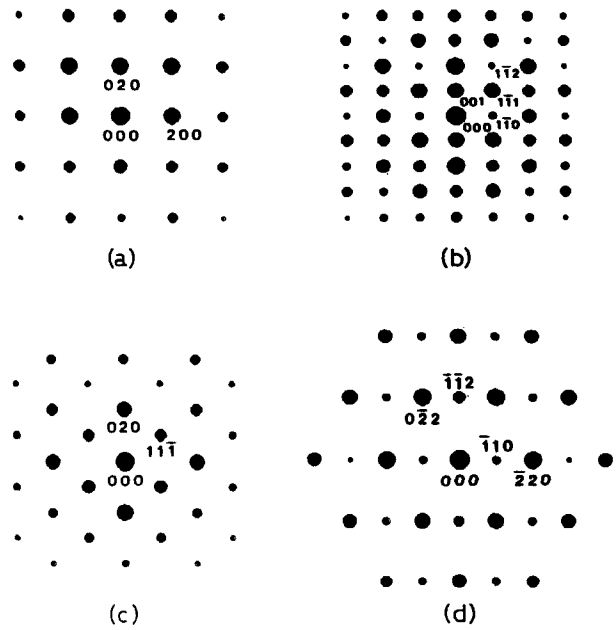


Fig.6 Diffraction patterns calculated for $ZrO_2$-6mol%$Y_2O_3$. Incident beam directions are slightly inclined from (a)[001],(b)[110],(c)[101] and (d)[111] axis, respectively.

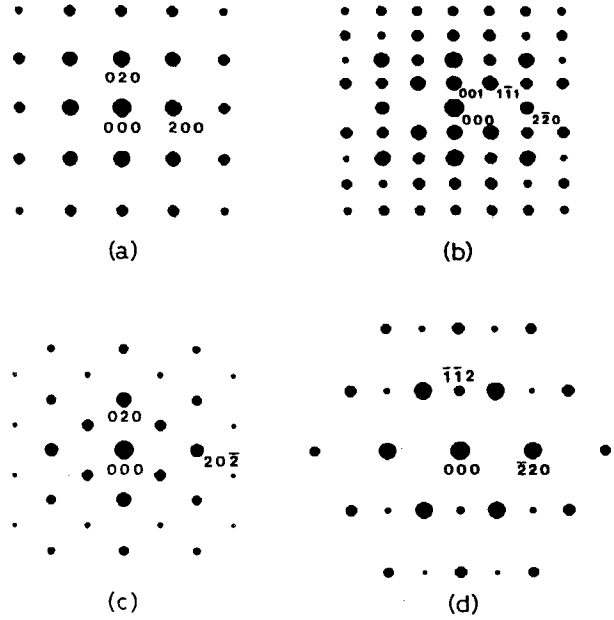


Fig.7 Diffraction patterns calculated for $ZrO_2$-6mol%$Y_2O_3$. Incident beam directions are exactly parallel to (a)[001],(b)[110],(c)[101] and (d)[111] axis,respectively.

direction (a)[001](40nm),(b)[110](80nm), (c)[101](60nm) and (d)[111](80nm), respectively. The numbers in the parentheses indicate the film thickness. The absorption of electrons was ignored. Lattice parameters of $ZrO_2$-6mol%$Y_2O_3$(a=0.5123nm,c=0.5159nm) were used. The [001] displacement of oxygen ions was assumed to be 2% of the unit length of c-axis. The diameter of diffraction spots in Fig.s 6 and 7 is proportional to the logarithmic intensity of electron beam.

In Fig.6, the direction of incident beam is slightly inclined from each zone axis in order to break the symmetry of the deviation parameter.[7] The angles of inclination were 0.1° around [100] axis in [001] DP, 0.05° around [$\bar{1}$10] axis in [110] DP, 0.05° around [10$\bar{1}$] axis in [101] DP and 0.1° around [1$\bar{1}$0] axis in [111] DP. The observed DPs agree with the calculated ones such that the forbidden reflections do not appear in [001] and [101] DPs but appear in [110] and [111] DPs.

In Fig.7, diffraction patterns were calculated for the incident beam directions exactly parallel to the zone axes. It is shown that the forbidden reflections do not appear in [001] and [101] DPs irrespective of beam inclination. It is also noted that forbidden reflections of 110 type are not excited in the exact [110] and [111] DPs, while forbidden reflections of 112 type appear irrespective of the beam inclination.

## DISCUSSIONS

The present results indicate that the diffraction patterns obtained from t-$ZrO_2$ are consistent with the proposed structure of Fig.1. On the basis of this structure, the domain boundary depicted in Fig.8 has been proposed, where the boundary becomes an anti-phase boundary by the

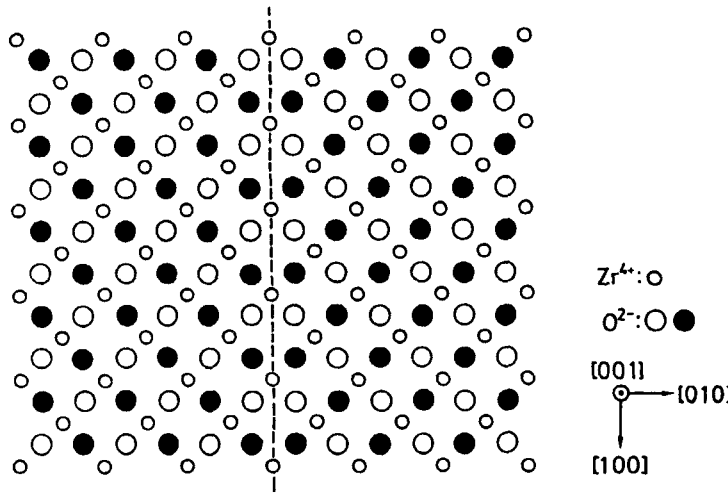


Fig.8 A [001] projection of anti-phase boundary(APB) of t-$ZrO_2$.

reversal of the displacement direction of oxygen ions across the domain boundary.[4] The fact that the domain boundary in t-$ZrO_2$ must be closed as shown in Fig.5 is explained as follows. Let us suppose there are three domains(A,B,C) and the domain boundaries bifurcating as shown in Fig.9, where black and white circles represent the oxygen ions displaced towards the positive and negative directions of c-axis.

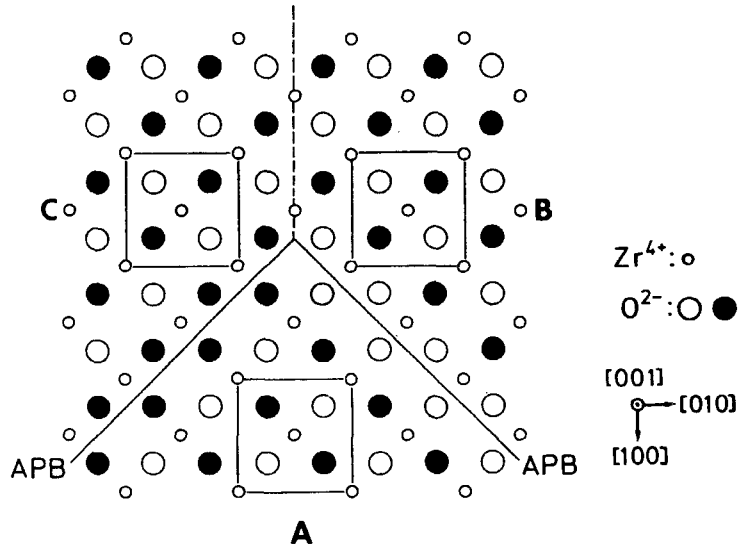


Fig.9 A schematic [001] projection of APB(solid lines).

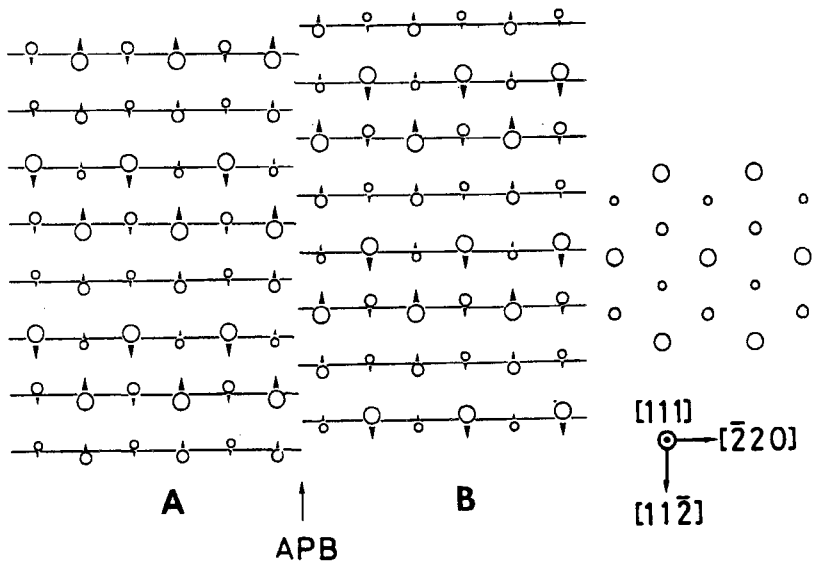


Fig.10 A [111] projection of oxygen ions in t-$ZrO_2$. The arrows show the projected direction of oxygen displacement. The circles with different radii show the oxygen ions belonging to (111) planes of different stacking.

In Fig.9, the domain boundaries appear between A and B domains or A and C domains, but do not appear betweenB and C domains because the phase of oxygen displacement is the same between B and C domains. The situation is the same in three dimensions, so that the domain boundary must be a closed surface. Despite this fact, the branching of a domain boundary is sometimes observed such as indicated by arrows in Fig.5. The branching of domain boundary may be caused by a change in the displacement mode of oxygen ions which was brought about by the interaction of two adjacent domain boundaries, i.e. the intensity of 112 diffraction was weakened between the adjacent domain boundaries. This fact indicates that the change of the direction or magnitude of the oxygen ions' displacement does not occur discontinuously across the domain boundary, but that the change occurs gradually across the boundary. This is important in that the gradual change of oxygen displacement means the accumulation of domain boundary energy.

The geometrical meaning of the domain boundary which is visible by the 112 dark field image is explained in Fig.10. The marks A and B in the figure mean the domains of t-$ZrO_2$, and the arrows show the projected direction of the displacement of oxygen ions in (111) plane. It is found that the (112) planes become distinguishable due to the modulation of (224) interplanar spacing when the oxygen ions are displaced to [112] direction or to the opposite direction. This geometrical fact is corresponding to the appearance of 112 diffraction.

The direction of the oxygen displacement is reversed between domain A and B. As the result, a (112) plane in domain B appear in midway between the two (112) planes of domain A. If **R** is a translation vector of the unit cell of the pseudo fluorite structure and **g** is a diffraction vector expressing 112 reflections, then the relation $\mathbf{g}\cdot\mathbf{R}=1/2$, i.e., $2\pi\mathbf{g}\cdot\mathbf{R}=\pi$ holds. Therefore, the domain boundary is regarded as $\pi$-boundary, and the translation vector is found to be represented by a/2[101]. As written above, the structure factor of 110 reflection becomes zero for the unit cell of Fig.1. This fact means that the appearance of 110 reflection is caused by double reflection. This is further supported by the fact that the 110 forbidden reflection appeared only when the beam direction was inclined slightly from the zone axis [110] or [111] in Fig.6. The absence of the 110 systematic reflections in Fig.7 may be explained as the cancellation of diffracted waves by dynamical effect.[8,9] In the observed DPs, the 110 forbidden reflections usually appeared. This is presumably caused by the asymmetry of diffraction conditions due to the beam divergence or absorption or change of local crystal orientation. The situation may be similar to the appearance of 00·l reflections with odd l values in hexagonal cobalt which was explained by the asymmetry of diffraction condition due to the bending of film, the divergence of beam or the lattice defects.[10]

## CONCLUSIONS

The results on domain structure of t-$ZrO_2$ containing $Y_2O_3$ accompanied by forbidden reflections are summarized as follows.

(1)The oxygen displacement mode of t-$ZrO_2$ was confirmed by the calculation of dynamical diffraction theory.

(2)The ideal domain boundary of t-$ZrO_2$ is considered to have a closed surface, while branching of the domain boundary was observed at the place where the local change of the displacement of oxygen ions was assumed to occur.

(3)The domain boundary was regarded to be a $\pi$-boundary about (112) planes which was caused by the alternate displacement of oxygen ions along the c-axis.

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