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Space group symmetry of $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3$ determined using electron diffraction

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Abstract

An electron diffraction study performed on thin sections of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ ceramics with compositions $x = 0.2$ and 0.5 has revealed diffraction patterns that are inconsistent with currently accepted space group symmetries. Here, the data are presented and alternative models suggested. It is proposed that $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ has the space group $C2/m$ at $x = 0.2$ and the space group $P2_1/m$ across the range $0.2 < x < 0.6$. The sequence of phases across the solid solution is therefore proposed to be

$$Pm\bar{3}m \Rightarrow I4/mcm \Rightarrow C2/m \Rightarrow P2_1/m \Rightarrow Pnma$$

$$x = 0 \quad x < 0.2 \quad x = 0.2 \quad 0.2 < x < 0.6 \quad x > 0.6.$$

1. Introduction

The changes in space group symmetry across the $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ solid solution have been the subject of several recent investigations. Ball *et al* [1] refined structures against synchrotron x-ray diffraction (XRD) data to give the following sequence of space groups and tilt systems:

$$Pnma (1 \geq x \geq 0.6) \Rightarrow Cmcm (0.55 \geq x \geq 0.4)$$

$$a^-b^+a^- \quad a^0b^+c^-$$

$$\Rightarrow I4/mcm (0.35 \geq x \geq 0.1) \Rightarrow Pm\bar{3}m (x \leq 0.05).$$

$$a^0a^0c^- \quad a^0a^0a^0$$

The notation used to describe the octahedral tilt systems was proposed by Glazer [2]. The three characters indicate that the tilting may be resolved as rotations about the three tetrad axes of a simple perovskite. Repetition of a character, e.g. *aaa*, defines the rotations as being of

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equal amplitude. The superscript '0' indicates that no tilting takes place about that particular axis, '-' indicates antiphase tilting and '+' indicates in-phase tilting. Hence the notation $a^0a^0c^-$ defines a structure in which the octahedra are rotated in antiphase about the c axis only. A more detailed description of this notation may be found in the publication by Glazer [2].

Qin *et al* [3] agreed with the sequence of phase transitions suggested by Ball *et al* [1] but their work also contained a graph indicating the $Cmcm-I4/mcm$ and $I4/mcm-Pm\bar{3}m$ phase boundaries as functions of composition and temperature, obtained by differential scanning calorimetry (DSC). However, they were unable to obtain any DSC data relating to the $Pnma-Cmcm$ phase boundary which, according to Howard and Stokes [4], is not a second-order phase transition and should exhibit a DSC peak if it exists. Some studies [5–8] have suggested that the $Cmcm$ phase does not exist and that the $Pnma$ phase extends to at least $x = 0.4$. This is an unsatisfactory conclusion as the apparent discontinuities in lattice parameters [3] are best explained by the presence of at least one phase separating $Pnma$ and $I4/mcm$ space groups.

Using XRD to identify space groups presents two significant problems. Firstly, the diffraction of x-rays by oxygen ions is considerably weaker than the diffraction by the cations and thus diffraction by the oxygen lattice tends to yield peaks that are of such low intensity that they may not be visible. Secondly, structural distortions that lead to split peaks may not be visible if the degree of splitting is small compared to the width of the peaks. The latter is also true of neutron diffraction, which is often used to determine oxygen positions.

In this study, use has been made of electron diffraction to determine tilt systems and space groups. Electrons interact with oxygen ions more strongly than x-rays, allowing clearer evaluation of the octahedral lattice. In addition, reflections present may differ between zone axes of the same general type, providing structural information that may be lost in x-ray or neutron diffraction patterns. A recent publication [9] tabulates the permitted reflections for each tilt system and enables easy identification of the perovskite tilt configurations and symmetries.

2. Experimental details

High purity (>99.95%) $SrCO_3$, $CaCO_3$ and TiO_2 powders were processed using a conventional mixed oxide route to form compounds in the $(Ca_xSr_{1-x})TiO_3$, series. Starting mixtures were wet milled for 16 h, calcined for 4 h at 1150–1350°C in air and re-milled in propan-2-ol with 2 wt% polyethylene glycol binder. 20 mm diameter pellets were uniaxially pressed at 110 MPa into discs and sintered for 4 h at various temperatures in air until the highest density was achieved.

For transmission electron microscopy (TEM), samples of 3 mm diameter were prepared by grinding sections of pellets to $\sim 30 \mu m$ thick on a glass slide, at which point a copper ring was stuck to the sample using epoxy resin. The sample was removed from the slide and excess ceramic material was removed from the outside of the ring using a razor-blade. The sample was then ion beam milled using a Gatan Dual Ion Mill, Model 600, at an angle of 15°, an operating voltage of 6 kV and a total gun current of 0.6 mA until perforation occurred. In our experience, no significant ion beam damage results from using these parameters. Dark field (DF) and bright field (BF) images and zone axis electron diffraction patterns (ZADPs) were obtained using JEOL 3010, FEI Tecnai 20 and Philips 420 microscopes where the smallest selected area aperture has an effective diameter of 450 nm, which was sufficient for obtaining diffraction patterns from single domains. All planes and vectors refer to the simple pseudocubic cell. For information concerning characterization of these samples using SEM and also for a review of their electrical properties the reader is referred to Wise *et al* [10].

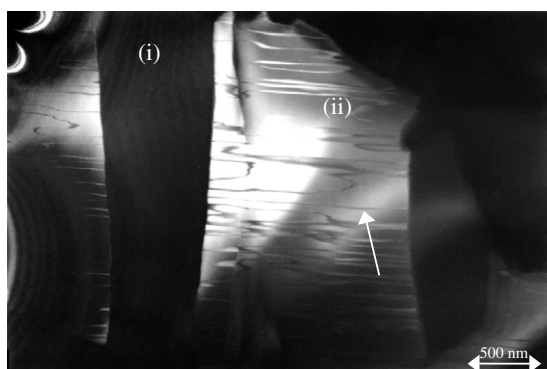


Figure 1. DF image of $x = 0.5$ material obtained using a superstructure reflection of type $\frac{1}{2}\{ooe\}$ and viewed along a $\langle 110 \rangle$ direction. The arrow indicates antiphase domain walls.

3. Results and discussion

3.1. $Ca_{0.5}Sr_{0.5}TiO_3$ ($x = 0.5$)

Figure 1 is a typical DF image of the domain structure encountered in samples with composition $x = 0.5$. Areas labelled (i) and (ii) are both oriented parallel to a direction of type $\langle 110 \rangle$, but area (i) does not contribute $\frac{1}{2}\{ooe\}$ ('o' = an odd Miller index; 'e' = an even Miller index) superstructure reflections that are used to generate the image. The diffraction patterns arising from these areas are shown in figure 2. The illuminated domains in figure 1 contain ribbon-like contrast consistent with the presence of antiphase boundaries (APBs). Since the image is obtained using $\frac{1}{2}\{ooe\}$ reflection as indicated in figure 2(d), these APBs must arise from regions of antiparallel cation displacement [11] that have nucleated out of phase.

Figure 2 shows all single-domain variants associated with [100], [110] and [111] zone axes for $x = 0.5$. Reflections of type $\frac{1}{2}\{ooo\}$, $\frac{1}{2}\{ooe\}$ and $\frac{1}{2}\{oeo\}$ are all clearly present, indicating combined antiphase and in-phase tilting of the TiO_6 octahedra and thus one of the four mixed tilt systems: $a^0b^+c^-$, $a^-b^+c^-$, $a^-b^+a^-$ and $a^+a^+c^-$. According to Woodward and Reaney [9], the distribution of superlattice reflections observed in figures 2(b), (c) and (e) are inconsistent with the $a^+a^+c^-$ tilt system (all reflections of type $\frac{1}{2}\{ooe\}$ should appear in all zones), while in figure 2(d), the coexistence of $\frac{1}{2}\{ooo\}$, $\frac{1}{2}\{ooe\}$ and $\frac{1}{2}\{oeo\}$ in a single variant eliminates the $a^-b^+a^-$ tilt system. This leaves $a^0b^+c^-$ and $a^-b^+c^-$ as the only possible tilt systems. According to Woodward and Reaney [9], the only difference between these systems in terms of scattering from the oxygen sublattice is that $\frac{1}{3}$ of the $\langle 100 \rangle$ ZADPs in the $a^0b^+c^-$ system exhibit no superstructure reflections. In this study, diffraction patterns from at least 10 different domains in several samples were examined and no single diffraction pattern was found matching this description. It is concluded therefore that the tilt system is not $a^0b^+c^-$ and must therefore be $a^-b^+c^-$, corresponding to the monoclinic space group $P2_1/m$.

At this point it is important to re-examine the work of Howard *et al* [7] and Ranjan *et al* [8] who used a similar method to establish the tilt system as $a^-b^+a^-$ for $x = 0.5$. In their study, they dismissed all $\langle 110 \rangle$ ZADPs containing both $\frac{1}{2}\{ooo\}$ and $\frac{1}{2}\{ooe\}$ reflections, believing them to be due to the superposition of diffraction patterns from two different domain variants encountered in the $a^-b^+a^-$ tilt system. However, simply dismissing all $\langle 110 \rangle$ ZADPs containing both $\frac{1}{2}\{ooo\}$ and $\frac{1}{2}\{ooe\}$ ignores completely the possibility of the presence of $a^0b^+c^-$ or $a^-b^+c^-$ tilt systems. These authors also used convergent beam microdiffraction

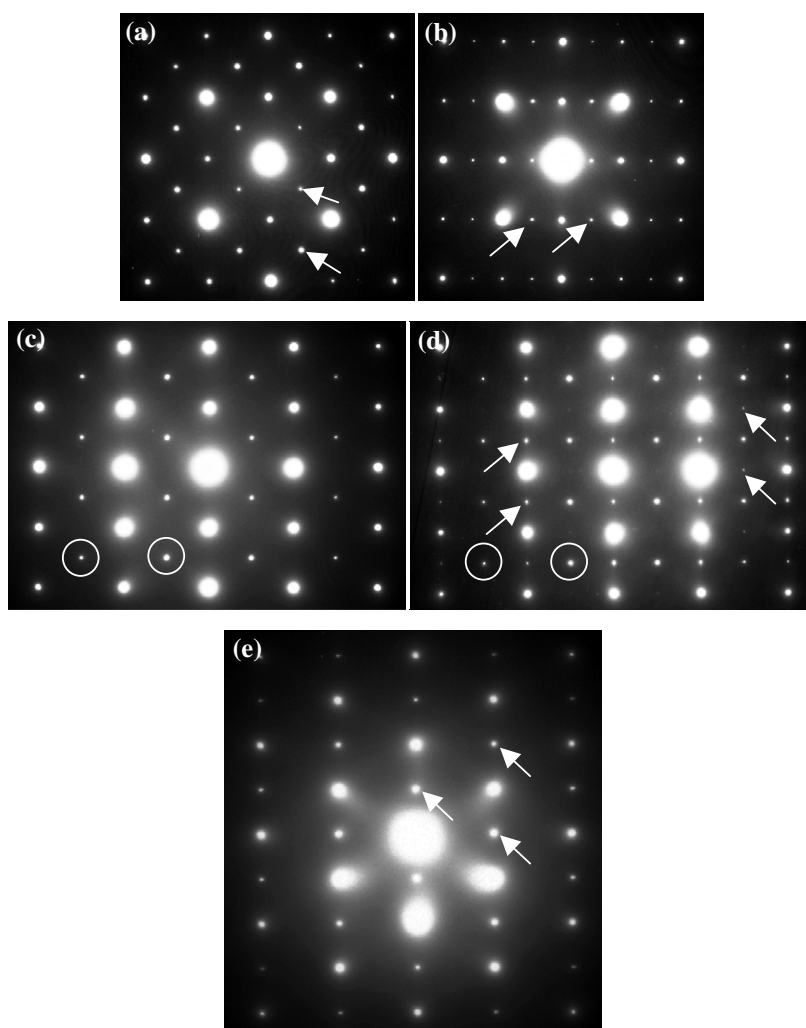


Figure 2. All variants of the principal ZADPs obtained from a sample at $x = 0.5$. (a) $\langle 100 \rangle$ with $\frac{1}{2}\{00c\}$, (b) $\langle 100 \rangle$ with $\frac{1}{2}\{0ec\}$, (c) $\langle 110 \rangle$ with $\frac{1}{2}\{000\}$, (d) $\langle 110 \rangle$ with $\frac{1}{2}\{0ec\}$, $\frac{1}{2}\{0oc\}$ and $\frac{1}{2}\{000\}$ and (e) $\langle 111 \rangle$ with $\frac{1}{2}\{0ee\}$. $\frac{1}{2}\{0ec\}$ superstructure reflections are indicated with right-pointing arrows, $\frac{1}{2}\{0oc\}$ with left-pointing arrows; $\frac{1}{2}\{000\}$ are circled.

to obtain their diffraction patterns: a technique less sensitive to weak reflections than selected aperture diffraction. Consequently, these critical reflections could easily have been too weak to be observed. In the current study, it is evident from the domain structure illustrated in figure 1 that the domain width is easily adequate for obtaining single-domain diffraction data using selected area diffraction and superposition does not explain the observations published here. It is proposed that $x = 0.5$ is at a phase boundary separating $a^-b^+c^-$ tilting from $a^-b^+a^-$. The observations of Howard *et al* [7] and Ranjan *et al* [8] may therefore be attributed to heterogeneity, leading to a small portion of their samples having the tilt system $a^-b^+a^-$, and that their experiments were self-selecting with respect to this tilt configuration.

No other studies have attempted to interpret $x = 0.5$ as having $P2_1/m$ symmetry. It is entirely plausible that this was simply overlooked, possibly due to its scarcity as a space group

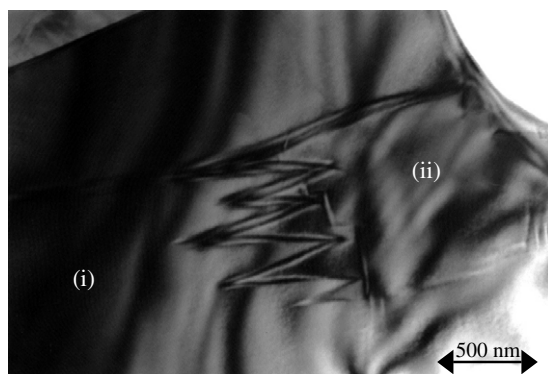


Figure 3. BF TEM image showing a grain in $x = 0.2$ with the electron beam parallel with a (110) zone axis. Areas labelled (i) and (ii) were used to produce the ZADPs in figures 4(b) and (c), respectively.

for perovskite-structured compounds [12] but also because it implies the existence of a low symmetry intermediate monoclinic phase between tetragonal and orthorhombic structures. A phase transition from tilt system $a^0b^+c^-$ (space group $Cmcm$) to tilt system $a^-b^+c^-$ (space group $P2_1/m$) is continuous by nature [4] and the addition of a small antiphase tilt about the a axis leads to small changes in some of the lattice parameters. In an x-ray or neutron diffraction pattern, this leads to weak splitting of a few peaks and the addition of no new peaks. Thus, if the angle of antiphase tilting about a is sufficiently small, it would not be possible to use x-ray or neutron diffraction to distinguish $a^-b^+c^-$ from $a^0b^+c^-$. In addition, the presence of lower symmetry phases at phase boundaries in solid solutions has now been confirmed by several authors [13, 14].

3.2. $Ca_{0.2}Sr_{0.8}TiO_3$ ($x = 0.2$)

Figure 3 shows the typical domain structure observed in a sample of composition $x = 0.2$. Figure 4 illustrates all the domain variants along the $[100]$, $[110]$ and $[111]$ ZADPs. No superlattice reflections are observed in figures 4(a) and (d), indicating that in-phase tilting was not present in this sample. The domains labelled (i) and (ii), however, gave rise to the ZADPs seen in figures 4(b) and (c), respectively. Both ZADPs contain superstructure reflections of type $\frac{1}{2}\{000\}$ (circled), indicating the presence of only antiphase tilting, but those observed in figure 4(c) are significantly weaker than those in figure 4(b). Although it is important in many cases not to attach too much significance to slight intensity variations in electron diffraction patterns, as the variation in sample thickness may give rise to such effects, these two ZADPs were obtained from adjacent domains and any variation in thickness would not be expected to have such a significant effect on the intensity of superstructure reflections. According to the previous studies, samples at this composition should have the tilt system $a^0a^0c^-$, but this does not allow any difference in intensity between the $\frac{1}{2}\{000\}$ reflections. Furthermore, although diffraction patterns were obtained from at least 10 domains in several samples at this composition, no $\langle 110 \rangle$ ZADPs were obtained that did not contain $\frac{1}{2}\{000\}$ reflections, even though $\frac{4}{12}\langle 110 \rangle$ ZADPs in the $a^0a^0c^-$ tilt system do not contain superstructure reflections [8]. Only two tilt systems are consistent with this set of observations; $a^-b^0c^-$ (space group $C2/m$) and $a^-b^-c^-$ (space group $P\bar{1}$). Of these two tilt systems, $a^-b^0c^-$ may be derived from $a^0a^0c^-$ by a second-order phase transition, while $a^-b^-c^-$ may not [4]. It is therefore quite possible

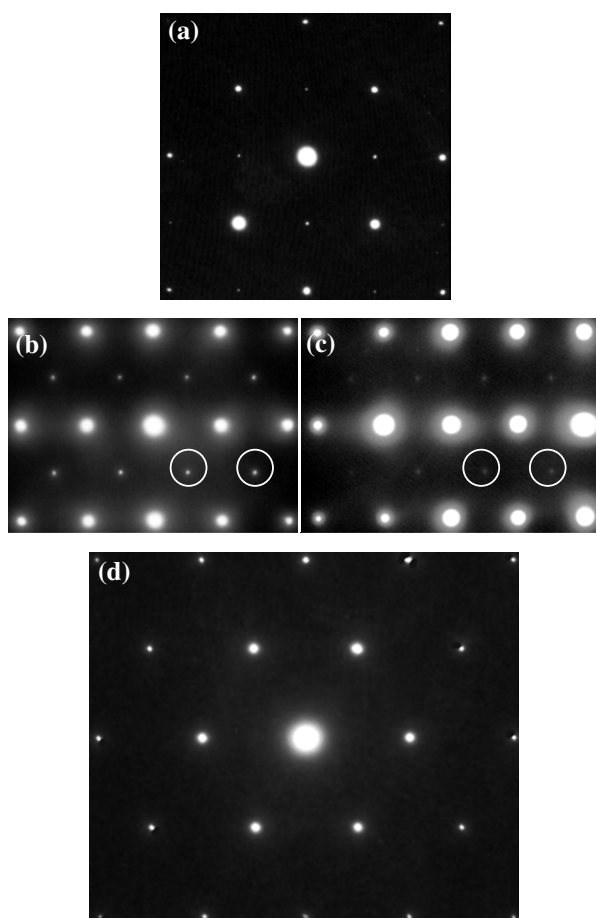


Figure 4. All variants of the principal ZADPs obtained from a sample at $x = 0.2$. (a) $\langle 100 \rangle$ without superstructure, (b) $\langle 110 \rangle$ with strong $\frac{1}{2}\{000\}$, (c) $\langle 110 \rangle$ with weak $\frac{1}{2}\{000\}$ and (d) $\langle 111 \rangle$ without superstructure. $\frac{1}{2}\{000\}$ superstructure reflections are circled. Patterns (b) and (c) are obtained from domains (i) and (ii), respectively, imaged in figure 3.

that $a^-b^0c^-$ could be mistaken for the $a^0a^0c^-$ tilt system if the additional tilt about the a axis was sufficiently small. A small tilt angle around a second orthogonal axis would be extremely difficult to detect by means of XRD as the peak splitting would be slight and no additional peaks would be created.

The additional electron diffraction evidence presented here now allows the proposal of a new sequence of tilt systems and space groups as a function of x that is fully consistent with all observed data:

$$\begin{array}{cccccc}
 Pm\bar{3}m & \Rightarrow & I4/mcm & \Rightarrow & C2/m & \Rightarrow & P2_1/m & \Rightarrow & Pnma \\
 (a^0a^0a^0) & & (a^0a^0c^-) & & (a^-b^0c^-) & & (a^-b^+c^-) & & (a^-b^+a^-) \\
 x = 0 & & x < 0.2 & & x = 0.2 & & 0.2 < x < 0.6 & & x > 0.6.
 \end{array}$$

All phase transitions in this sequence are permitted to be continuous as a function of composition [4]. We suggest that the transitions $Pm\bar{3}m \Rightarrow I4/mcm$ and $C2/m \Rightarrow P2_1/m$ are the transitions responsible for the DSC peaks recorded by Qin *et al* [3] as these are

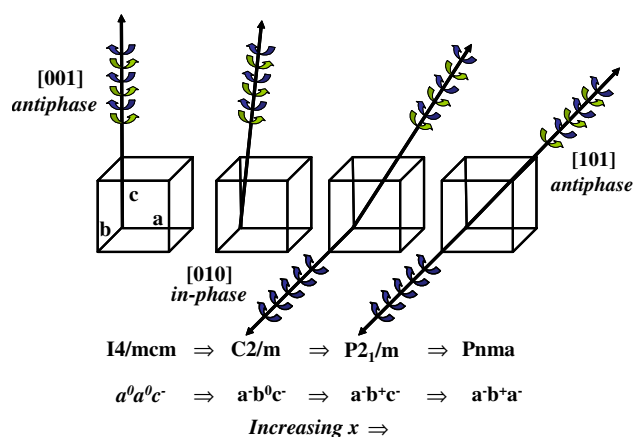


Figure 5. Illustration of the proposed tilt sequence in $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ as a function of x . (This figure is in colour only in the electronic version)

the transitions that are likely to be associated with significant cation displacements, being respectively the onset of antiphase and in-phase tilting.

From a group theoretical approach, such a sequence is initially difficult to rationalize since the transformation from tetragonal to orthorhombic occurs via phases of lower symmetry. However, if the $C2/m$ and $P2_1/m$ phases are viewed as intermediate compounds in which the axis of antiphase tilt is continuously changing from $\langle 001 \rangle$ ($I4/mcm$) to $\langle 101 \rangle$ ($Pnma$) then the transformation sequence has physical significance. The change of antiphase tilt axis away from $\langle 001 \rangle$ toward $\langle 101 \rangle$ occurs as x increases and gives rise to weak $\frac{1}{2}\{000\}$ reflections, forbidden by $I4/mcm$ but allowed by $C2/m$, in which the amplitude of antiphase rotation around c is much greater than that around a . The onset of in-phase tilting ($x \approx 0.5$) occurs before the movement of the antiphase tilt axis from $\langle 001 \rangle$ to $\langle 101 \rangle$ is complete, creating an intermediate $a^-b^+c^-$ tilt system. Previous work by Colla *et al* [15] has suggested that the onset of in-phase tilting is coupled to antiparallel A-site displacements and gives rise to a sharp anomaly in physical properties. As x increases, the amplitudes of antiphase rotation around a and c become equal and the $Pnma$ symmetry becomes stable for $x > 0.6$. This sequence is schematically illustrated in figure 5 where the tilt axes are represented on a pseudocubic cell. One prediction based on the above transformation sequence is that there are only two distinct structural anomalies in the $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3$ system. The first is associated with antiphase rotations and has continuous second-order character. The second results in in-phase rotations of the octahedra, appears discontinuous and is associated with antiparallel A-site cation displacements.

4. Conclusions

Electron diffraction has been used to study the tilt systems of samples of the $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ solid solution with compositions $x = 0.5$ and 0.2 and has demonstrated a distribution of superlattice reflections inconsistent with the current model of phase transitions as a function of composition. According to this study, the most likely tilt system for $x = 0.5$ is $a^-b^+c^-$, corresponding to space group $P2_1/m$, while the most likely tilt system for $x = 0.2$ is $a^-b^0c^-$, corresponding to space group $C2/m$. The following sequence of tilt systems and space groups

as a function of composition is proposed to account for all physical data:

$$\begin{array}{ccccccc}
 Pm\bar{3}m & \Rightarrow & I4/mcm & \Rightarrow & C2/m & \Rightarrow & P2_1/m & \Rightarrow & Pnma \\
 (a^0a^0a^0) & & (a^0a^0c^-) & & (a^-b^0c^-) & & (a^-b^+c^-) & & (a^-b^+a^-) \\
 x = 0 & & x < 0.2 & & x = 0.2 & & 0.2 < x < 0.6 & & x > 0.6
 \end{array}$$

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