

Article

TEM Analysis of Orientational Domain Evolution Triggered by Structural Phase Transition in $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ Ceramics

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Abstract

The structural phase transition and associated orientational domain configurations in perovskite-type $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ ceramics were investigated in this work. A series of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ solid solutions with $x = 0.05, 0.25, 0.33$ were synthesized, and $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ with moderate orthorhombic lattice distortion was selected as the representative sample for systematic TEM characterization. Upon cooling from high temperature, the material undergoes a symmetry-lowering transition from the cubic phase with $\text{Pm}\bar{3}\text{m}$ space group to the orthorhombic phase with Pnma space group. Selected-area electron diffraction (SAED) and bright-field TEM observations reveal the formation of multiple orientational domains, including both 90° and 120° configurations, within individual grains. High-resolution TEM (HRTEM) further confirms the coexistence of three distinct domain orientations at the atomic scale, with well-defined lattice fringes and domain boundaries. The reciprocal-space orientational relationships derived from SAED patterns demonstrate that these domains originate from the symmetry breaking of the parent cubic lattice during the phase transition. These findings provide direct crystallographic insight into the domain structures of BCMO, and such microstructural features are essential for revealing the structural stability and intrinsic functional behaviors of BCMO manganites.

Keywords: BCMO; SAED; orientational domain; structural phase transition

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1. Introduction

Over the past two decades, perovskite manganese oxides $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{Ln} =$ trivalent La, Nd, Pr, Sm, Bi; $\text{A} =$ divalent Ca, Sr, Ba) have attracted tremendous attention because of their wide variety of intriguing physical properties, such as colossal magnetoresistance (CMR) effect, magnetostructural effects, magnetic polarons, and charge ordering (CO). Owing to their diverse correlated electronic phases, perovskite manganites exhibit exceptional application potential in a range of functional devices, such as colossal magnetoresistance for magnetic sensors and spintronics [1–3], electrically tunable dielectric properties for microwave components [4,5], and multiferroic magnetoelectric coupling for multi-state nonvolatile memory and magnetoelectric switching applications [6–8].

The core physical origin of their versatile properties lies in the subtle competitive balance between diverse electronic and magnetic ground states, among which phase-separated states, charge-ordered states and ferromagnetic metallic states constitute the most representative competing phases [9,10]. The incorporation of alkaline-earth cations into rare-earth manganite lattices generates mixed-valent $\text{Mn}^{3+}/\text{Mn}^{4+}$ sites and activates double-exchange interactions, which facilitate the formation of long-range ferromagnetic ordering [11,12]. Meanwhile, lattice distortion originating from cation-size mismatch tends to stabilize localized charge ordering and insulating antiferromagnetic domains [13,14]. The coexistence and dynamic competition between ferromagnetic metallic domains and charge-ordered insulating domains produces electronic phase separation, which directly governs the macroscopic electrical transport and magnetic behaviors of manganite ceramics [15,16]. Revealing the structural evolution of domain configurations under composition modulation is therefore critical to establishing the structure–property relationship of perovskite manganites and guiding the design of novel oxide functional materials.

Among various $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ systems, Bi-substituted CaMnO_3 solid solution $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ is an electron-doped manganite showing some similar structural and physical properties to $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$. On the other hand, the bismuth-based materials also display certain specific behaviors in sharp contrast to $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ materials [17,18]. For instance, FM properties without obvious CMR effects only exist within a narrow Bi doping range $x \leq 0.15$, and the CO phenomenon accompanied by the orbital ordering appears in a broad temperature range from 100 K up to 500 K, i.e., $T_c \approx 335$ K for $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $T_{CO} \approx 500$ K for $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. Recently we prepared a series of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ ceramics with x ranging from 0 to 0.33 [19]. Pure CaMnO_3 adopts an orthorhombic Pnma perovskite structure at room temperature, presenting G-type antiferromagnetic insulating behavior with stable charge ordering at a low temperature. Partial substitution of Ca^{2+} by Bi^{3+} breaks the original cationic charge balance and distorts the MnO_6 octahedral network, inducing reversible structural phase transitions between cubic high-temperature phase and orthorhombic low-temperature phase as Bi content varies. The existing literature has confirmed that increasing Bi doping level continuously modulates the octahedral tilting degree, alters the Néel temperature of antiferromagnetic ordering, and suppresses the long-range charge-ordered state in CaMnO_3 matrix [20]. Previous macroscopic magnetic and electrical measurements have preliminarily reflected the evolution of magnetic and transport properties with Bi concentration, yet most published works only focus on average lattice information obtained by X-ray diffraction, while the microscale domain evolution accompanying structural phase transition remains insufficiently understood. To date, few studies have systematically characterized the orientational domain morphology, domain boundary configuration and phase transition-driven domain rearrangement in $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ ceramics at nanometer scale, limiting the in-depth understanding of the microstructural origin of its competing magnetic and electronic phases.

Transmission electron microscopy (TEM) combined with selected-area electron diffraction (SAED) serves as an indispensable characterization technique to visualize nanoscale domain structures and resolve local crystallographic features. It can provide direct microstructural evidence for analyzing phase transition mechanisms in polycrystalline ceramics and is uniquely suited to clarify the phase-transition-driven domain evolution in Bi-substituted CaMnO_3 . In the present work, polycrystalline $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ ceramics with $x = 0.05, 0.25$ and 0.33 are fabricated via the conventional solid-state reaction route. Considering that moderate Bi substitution ($x = 0.25$) induces prominent orthorhombic structural distortion and obvious domain rearrangement during phase transition, we select $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ as the key research object and conduct systematic TEM and SAED characterizations. We aim to clarify the formation mechanism

of orientational domains triggered by cubic-to-orthorhombic structural phase transition, analyze the crystallographic orientation relationship among adjacent domains, and reveal how octahedral tilting distortion regulates domain evolution behavior. This work provides direct nanoscale microstructural evidence for Bi-doped CaMnO_3 solid solutions, fills the research gap of local domain evolution in the $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ system, and offers new microscopic insights into the competition between charge-ordered and ferromagnetic states in A-site doped perovskite manganites.

2. Experimental

The BCMO solid-solution ceramics with $0 < x \leq 0.33$ investigated in this study were synthesized via conventional solid-state reaction using analytical-grade raw powders ($\geq 99.9\%$ purity, Aladdin Biochemical Technology Co., Ltd., Shanghai, China): CaCO_3 , MnO_2 , and Bi_2O_3 . Significant Bi volatilization occurs during high-temperature sintering; accordingly, an extra 3 mol% excess Bi_2O_3 was added to all precursor mixtures to compensate for bismuth loss, despite which slight Bi deficiency was still detected in the final sintered samples by elemental quantitative analysis. All starting powders were weighed according to the target nominal stoichiometry, mixed uniformly via ethanol ball milling, and fully dried at 353 K. The mixed powders were first calcined at 800 K for 6 h, followed by intermediate grinding and subsequent firing in air at 1320 K for 48 h. The homogenized powders were uniaxially pressed into cylindrical pellets, which received successive thermal treatments ranging from 1320 K to 1470 K with a dwelling time of 24 h. A constant heating rate of 150 K/h was applied for all heating processes, and all specimens were naturally furnace-cooled down to room temperature after sintering.

Powder X-ray diffraction (XRD) measurements were performed with $\text{Cu K}\alpha$ radiation over a full 2θ scanning range of $20\text{--}80^\circ$ to identify crystal phases and lattice evolution. Quantitative Rietveld full-profile refinement was conducted on all full-range XRD datasets using Full Prof Suite software (Version 8.40, Feb 2026). The orthorhombic Pnma perovskite structural model was selected as the initial fitting model, and the pseudo-Voigt function was utilized to simulate diffraction peak profiles. Multiple structural parameters were refined stepwise to guarantee stable convergence, including background polynomial coefficients, scale factor, sample displacement, lattice constants, peak shape parameters, and isotropic thermal vibration factors. The full fitted diffraction patterns, refined lattice parameters, and corresponding refinement reliability factors (R_p , R_{wp} , χ^2) for all compositions are summarized in Figures S1 and S2 and Table S1 within the Supporting Information.

The surface microstructure and actual Bi/Ca/Mn elemental atomic ratios of sintered ceramics were characterized using an XL30 S-FEG scanning electron microscope (FEI Company, Eindhoven, The Netherlands) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector. EDX quantitative analysis was performed on the representative $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ sample, and the elemental distribution mapping and quantified composition data are provided in Figure S3 and Table S2 of Supporting Information. The results verify dense microstructures and homogeneous elemental distribution across all specimens, with consistent Bi volatilization degree among samples prepared under identical sintering schedules.

Transmission electron microscopy (TEM) characterizations, including selected-area electron diffraction (SAED), in situ high-temperature observation and high-resolution TEM (HRTEM), were carried out on two electron microscopes: an F20 microscope (FEI Company, Eindhoven, The Netherlands) operated at 300 kV equipped with a heating sample holder, and a JEM-2010 high-resolution TEM (JEOL Ltd., Tokyo, Japan) operated at 200 kV.

3. Results and Discussion

Figure 1a presents the full-range X-ray diffraction (XRD) patterns ($2\theta = 20\text{--}80^\circ$) of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ solid-solution ceramics with Bi doping contents $x = 0.05, 0.25$ and 0.33 , overlaid with vertical tick marks of the standard ICDD PDF #895424 [21] reference for orthorhombic CaMnO_3 . Clear differences in diffraction profiles are observed with increasing Bi content. The indexed full-range XRD patterns with assigned crystallographic planes are provided in Figure S1 of the Supporting Information, in which all diffraction reflections for the three compositions can be fully indexed to orthorhombic perovskite adopting the Pnma space group. No distinguishable impurity or secondary-phase diffraction signals are detected across the entire scanning range, verifying the high single-phase purity of all synthesized solid solutions. For the low-doping sample $x = 0.05$, the diffraction profile exhibits excellent consistency with the standard CaMnO_3 PDF card, since low-concentration Bi^{3+} substitution barely modifies the lattice framework of the parent phase. The apparent peak splitting and profile distortion at $x = 0.25$ and $x = 0.33$ are not originated from foreign impurity phases, but arise from continuous lattice distortion induced by Bi^{3+} incorporation.

To quantitatively analyze the composition-dependent structural evolution, Rietveld full-profile refinement was performed on all full-range XRD datasets (Figure S2). The refined lattice parameters and fitting reliability factors (R_p , R_{wp} , χ^2) are summarized in Table S1 of Supporting Information. The extracted structural parameters reveal regular lattice evolution behavior: the orthorhombic a and b axes increase monotonically with rising Bi content due to the larger ionic radius of Bi^{3+} relative to Ca^{2+} , while the difference between a and b remains nearly unchanged upon Bi substitution. In contrast, the c -axis parameter shows a prominent non-monotonic trend: it slowly rises at low Bi doping and reaches a maximum near $x = 0.2$, followed by a sharp decrease at higher doping levels. Such nonlinear variation in the c -axis dominates the enhanced peak splitting observed in the XRD patterns, rather than the divergence between a and b . This abnormal structural evolution originates from two competing effects: low-level Bi^{3+} doping causes lattice expansion via cation radius mismatch and elevates the c -axis; at high Bi content, strong Bi–O orbital hybridization suppresses the cooperative tilting and distortion of MnO_6 octahedra, leading to significant contraction of the c -axis lattice parameter. The Rietveld-refined lattice parameters as a function of Bi doping content are plotted in Figure 1b.

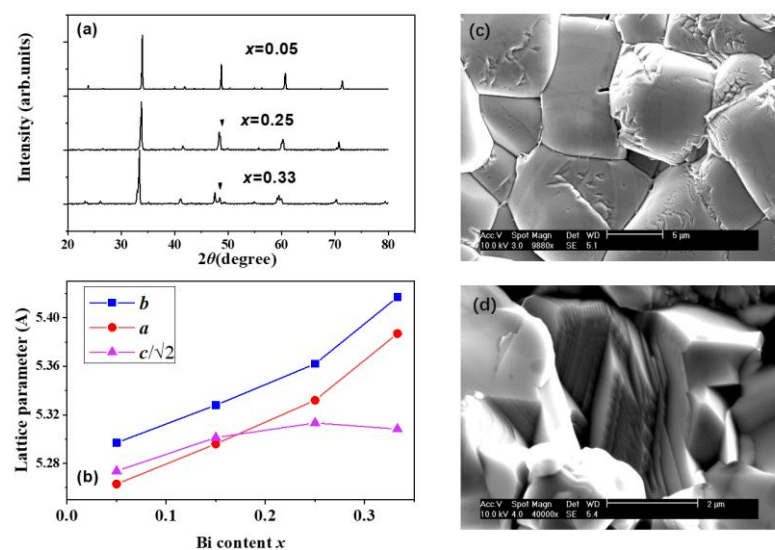


Figure 1. Structural and morphological characterizations of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$. (a) XRD patterns, (b) Rietveld-refined lattice parameters a , b , $c/\sqrt{2}$ as a function of Bi doping content x , and (c,d) SEM micrographs of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ ceramics with Bi contents $x = 0.25$.

Panels (c) and (d) present low- and high-magnification SEM micrographs of the representative $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ ceramic, respectively. The low-magnification image (c) exhibits large, well-faceted crystalline grains with distinct grain boundaries, indicating excellent crystallinity achieved via high-temperature sintering. The high-magnification micrograph (d) clearly captures the typical layered stacking microstructure inherent to distorted perovskite manganites, which arises from cooperative tilting of MnO_6 octahedra triggered by Bi^{3+} substitution and the accompanying orthorhombic lattice distortion. Combined with SEM-EDX results provided in Figure S3 and Table S2 of Supporting Information, uniform elemental distribution across all grains is verified, even though 3 mol% excess Bi_2O_3 was added in the precursor mixture to offset Bi volatilization at high sintering temperatures.

$\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ is a typical perovskite-related solid-solution ceramic, in which Bi and Ca cations occupy the A-site of the ABO_3 perovskite lattice randomly. Among the prepared $x = 0.05, 0.25$ and 0.33 compositions, $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ lies at the critical doping region with moderate orthorhombic lattice distortion, displaying well-resolved and representative orientational domain features that are suitable for systematic TEM characterization; hence, polycrystalline $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ samples were selected as the core research object for microstructural analysis. The crystallographic orientational domains and microstructural evolution of the material were systematically investigated by transmission electron microscopy (TEM). As reported in the literature [17], BCMO exhibits a structural phase transition at approximately 1000 K, where the high-temperature cubic (HTC) phase transforms into the room-temperature orthorhombic (RTO) phase. The perovskite BCMO undergoes a symmetry change from the cubic $\text{Pm}\bar{3}\text{m}$ to the orthorhombic Pnma space group, involving the reduction in both translational symmetry elements and point symmetry operations. Group theory constitutes a fundamental approach to elucidating crystal structures and the full set of orientational variants that may arise during phase transitions driven by symmetry reduction [22,23].

To verify the symmetry analyses associated with the HTC to RTO phase transformation, we conducted in situ experiments by heating samples in the microscope and dynamically observing symmetry changes in diffraction patterns of the crystals. Figure 2 shows the microstructural evolution and corresponding selected-area electron diffraction (SAED) patterns of the crystal in its HTC phase and RTO phase. When the grain is heated to 993 K, the crystal adopts the high-symmetry cubic phase with the $\text{Pm}\bar{3}\text{m}$ space group. The SAED pattern (Figure 2a), recorded along the $[011]$ zone axis, exhibits a regular, well-defined cubic lattice of diffraction spots, consistent with the high crystallographic symmetry of the cubic phase. The corresponding bright-field TEM image (Figure 2b) reveals characteristic contrast features. Upon cooling to room temperature, the crystal undergoes a structural phase transition to the orthorhombic phase with the Pnma space group, which is accompanied by a reduction in crystallographic symmetry. This transition is clearly evidenced by the SAED pattern (Figure 2c) acquired along the $[100]_o$ zone axis. The cubic symmetry of the diffraction spots is broken, resulting in an orthorhombic lattice pattern with distinct spot splitting and the appearance of new reflections (e.g., $(011)_o$) that are forbidden or absent in the parent cubic phase. The corresponding bright-field image (Figure 2d) shows a notable change in microstructure; the distinct domain-like contrast observed in the cubic phase is replaced by a more homogeneous, modulated texture, reflecting the long-range structural distortion associated with the orthorhombic distortion. These observations verify the symmetry-lowering phase transition from cubic $\text{Pm}\bar{3}\text{m}$ to orthorhombic Pnma , which significantly alters both the crystallographic structure and the microstructural features of the BCMO.

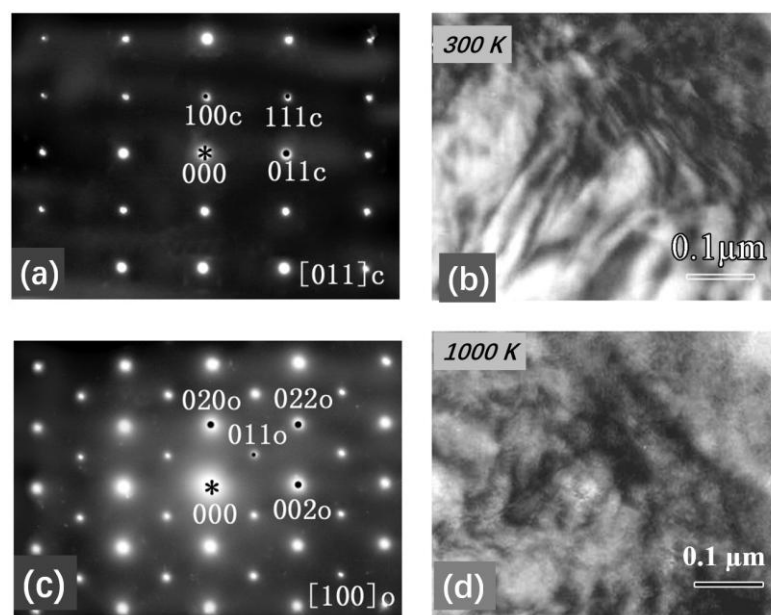


Figure 2. SAED patterns and bright-field TEM images. (a,b) Cubic phase ($Pm\bar{3}m$) at 993 K; (c,d) orthorhombic phase ($Pnma$) at room temperature.

The crystallographic analysis of the BCMO in RTO phase was performed using SAED in TEM, with the corresponding schematic diagrams and experimental patterns presented in Figure 3.

Figure 3a illustrates the real-space crystal lattice of the unit cell, defined by the primitive vectors a_o , b_o , and c_o , with key lattice translation vectors R_1 , R_2 , and R_3 highlighted to show the periodic arrangement of atoms. The reciprocal lattice, derived from the real-space lattice via Fourier transformation, is schematized in Figure 3b. This reciprocal lattice is spanned by the basis vectors a^* , b^* , and c^* , with labeled reciprocal lattice points (e.g., 020, 200, 101) corresponding to crystallographic planes of the real lattice.

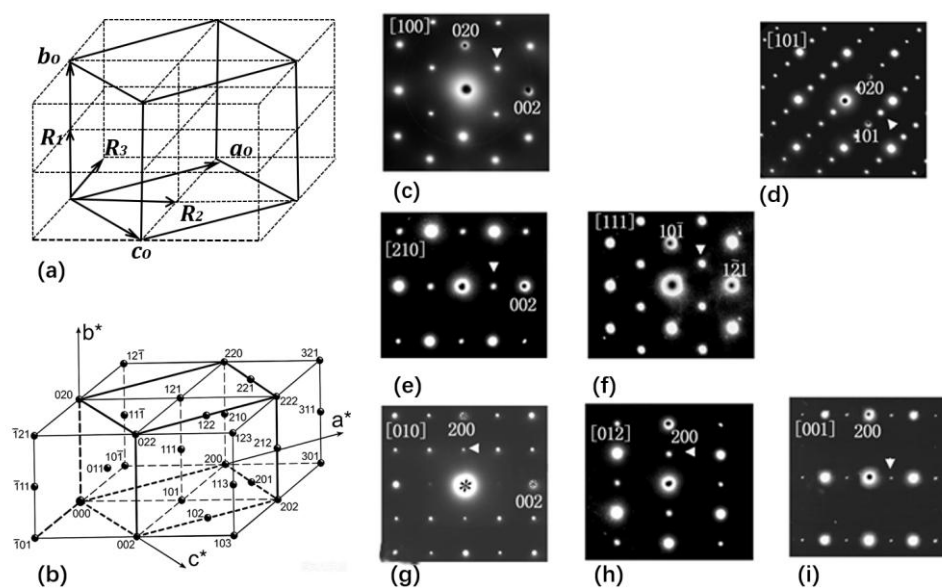


Figure 3. (a) Orthorhombic unit cell distortion relative to the parent cubic lattice. (b) 3D reciprocal lattice of the orthorhombic phase. (c–i) SAED patterns of BCMO along different zone axes, confirming the crystallographic structure and symmetry.

The experimental SAED patterns in Figure 3c–i were acquired along different crystallographic zone axes to verify the crystal structure and orientation. Each pattern exhibits a characteristic arrangement of diffraction spots, which are directly related to the intersection of the Ewald sphere with the reciprocal lattice planes perpendicular to the incident electron beam direction. Specifically, Figure 3c shows the SAED pattern obtained along the [100] zone axis, with indexed reflections including 020 and 002. The pattern along the [101] zone axis (Figure 3d) displays the 020 and 101 reflections, consistent with the reciprocal lattice projections. Additional patterns along [210] (Figure 3e), [111] (Figure 3f), [010] (Figure 3g), [012] (Figure 3h), and [001] (Figure 3i) zone axes further confirm the crystallographic orientation and lattice parameters. The indexing of each pattern, verified against the reciprocal lattice model, demonstrates the single-crystalline nature of the material and provides a comprehensive map of its crystallographic symmetry and orientation.

To understand crystal structure and possible orientational variants formed during a phase transition due to symmetry reduction, the group theory developed by Van Tendeloo and Amelinckx is a fundamental approach [22]. Wang et al. have given a detailed crystallographic analysis of orientational domains in orthorhombic bulk LCMO using the group theory [24]. According to Van Tendeloo and Amelinckx, the number of orientational domains resulting from the loss of point symmetry operations is determined by the ratio of the order of point group of the high-symmetry phase to that of the low-symmetry phase. When lowering the symmetry, the *b*-axis of the low-temperature orthorhombic phase can arbitrarily be chosen along any one of the three $\langle 100 \rangle_c$ cubic axes of the parent cubic phase, yielding three 120° domains. For two domains with a common *b* axis, their *a* and *c* axes can be interchanged, corresponding to two 90° domains.

As shown in the bright-field TEM image (Figure 4), the BCMO crystal exhibits a variety of orientational domain structures during the phase transition. A single grain is found to decompose into at least seven distinct domains (labeled A to F), as well as additional unresolved microdomains, with well-defined domain boundaries clearly observable. This microstructural evolution is a direct consequence of the symmetry-lowering phase transition, where the reduction in crystallographic symmetry allows for multiple equivalent domain orientations to form within the parent grain.

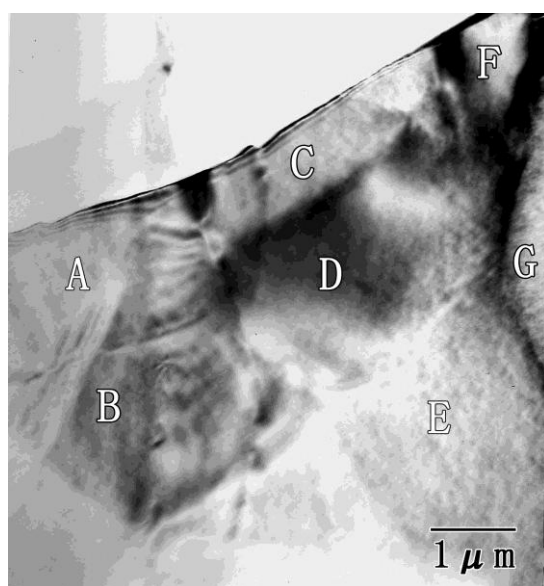


Figure 4. Bright-field transmission electron microscopy (TEM) micrograph of BCMO at room temperature. Labels A–G mark different domain regions with distinct strain-induced contrast. Scale bar: 1 μm .

SAED revealed that the grain was oriented along the $\langle 001 \rangle_c$ direction. Domains A and B were indexed along the $[010]_o$ zone axis, while domains C and D were indexed along the $[101]_o$ zone axis.

Selected-area electron diffraction (SAED) patterns acquired along multiple characteristic zone axes were collected to systematically characterize the reciprocal lattice geometry and crystallographic symmetry of orthorhombic $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$, as presented in Figure 5a–f. SAED pattern (a), taken from domain A alone, shows a single set of reflections corresponding to the $[010]_o$ orientation. In contrast, pattern (b), acquired across the boundary between domains A and B, contains two distinct sets of diffraction spots: one from the $[010]_o$ zone axis and the other from the $[101]_o$ zone axis. The reciprocal-space orientational relationship, as indicated by the arrows, shows that the two domains adopt different $\langle 001 \rangle_o$ axes as their basis vector b_o , which are mutually perpendicular, forming a 120° domain configuration.

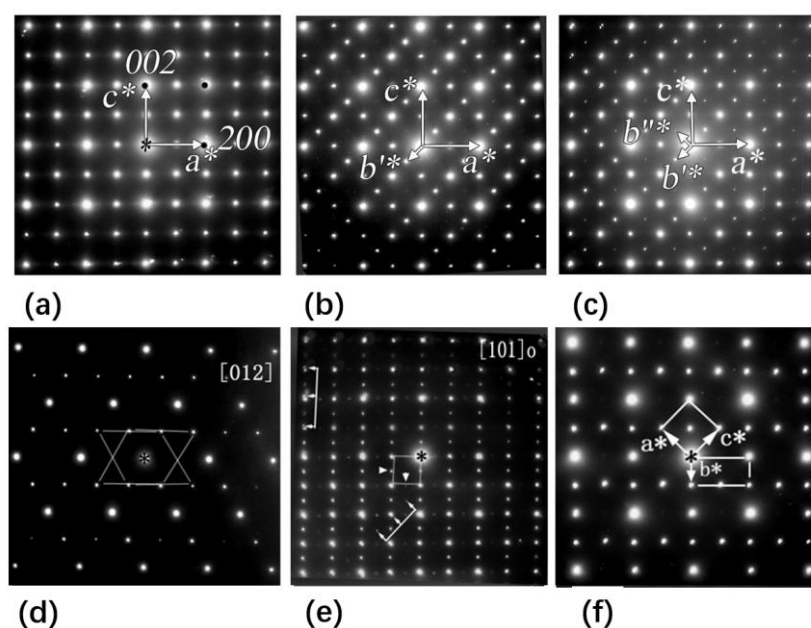


Figure 5. SAED patterns of domain structures in orthorhombic BCMO. (a) Single-domain pattern along $[010]_o$; (b) two-domain pattern along $[101]_o$; (c) superimposed pattern of two 120° domains along $[101]_o$; (d–f) multi-domain patterns showing overlapping reflections from different domain orientations, including 90° and 120° domain configurations.

When SAED was collected over domains A, C, and D simultaneously, pattern (c) exhibited three sets of diffraction spots originating from the three distinct domains. Similarly, SAED from domains B and D (pattern f) also contained two sets of reflections, corresponding to the $[010]_o$ and $[101]_o$ zone axes, confirming them as 120° domains.

Pattern (e), taken across domains C and D, shows the primary reflections of the $[101]_o$ zone axis (marked by the square) together with two sets of orthorhombic superstructure spots (indicated by the white arrows) characteristic of two mutually perpendicular domains, confirming that C and D are 90° domains. A weak additional set of spots (marked by the lower-left arrows), indexed to the $[010]_o$ zone axis, suggests the presence of a microdomain oriented at 120° to domains C and D. The splitting of higher-order reflections (upper-left arrows) further indicates a slight difference between the a_o and c_o lattice parameters. The real-space orientational relationship between domains C and D can be understood as a 90° rotation about the $[101]_o$ axis, with both domains adopting the ac axis as their $[101]_o$ direction during the phase transition.

By tilting the sample to the adjacent $\langle 111 \rangle_c$ orientation, the SAED pattern (f) shows a hexagonal lattice with six-fold rotational symmetry, characteristic of the cubic $[111]_c$ zone axis. At room temperature, the orthorhombic phase exhibits two sets of superstructure reflections originating from the two 120° domains.

The high-resolution transmission electron microscopy (HRTEM) image (Figure 6) clearly reveals the coexistence of three distinct orientational domains (labeled A, B, and C) within a single grain of the orthorhombic BCMO crystal. Domain A exhibits well-defined lattice fringes indexed to the (010) and $(10\bar{1})$ planes, consistent with the $[001]_o$ zone axis. Domain B shows fringes corresponding to the (010) plane, indicating a different crystallographic orientation relative to Domain A. Domain C displays fringes indexed to the (100) and (001) planes, corresponding to the $[010]_o$ zone axis. The sharp boundaries between these domains confirm the formation of distinct orientational domains with different crystallographic axes, resulting from the symmetry-lowering cubic-to-orthorhombic phase transition. The observed domain structure further demonstrates the presence of both 90° and 120° domain configurations, as previously indicated by SAED analysis. The scale bar of 1 nm confirms the high resolution of the lattice fringes, which are consistent with the expected interplanar spacings of the orthorhombic phase.

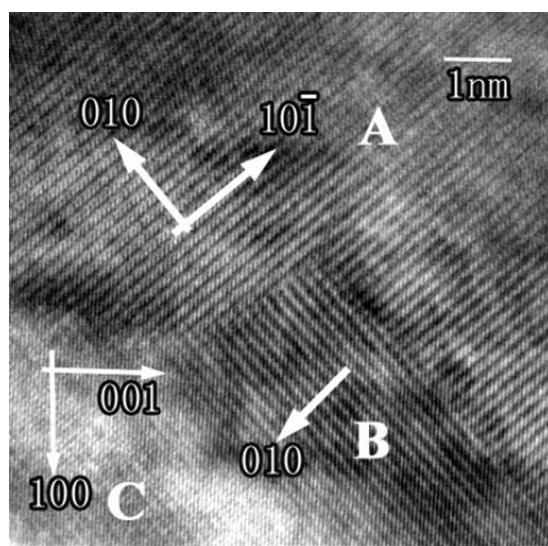


Figure 6. HRTEM image of multi-domain structures in BCMO. Three orientational domains (A, B, C) with distinct lattice fringe orientations are clearly resolved. Scale bar: 1 nm.

4. Conclusions

In this work, the structural phase transition and associated domain structures in $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ crystals have been systematically investigated using transmission electron microscopy. The high-temperature cubic phase with the $\text{Pm}\bar{3}\text{m}$ space group transforms to the room-temperature orthorhombic phase with the Pnma space group, accompanied by a significant reduction in crystallographic symmetry. Selected-area electron diffraction (SAED) studies confirmed the coexistence of multiple orientational domains, including both 90° and 120° configurations, which arise from the symmetry breaking during the cubic-to-orthorhombic transition. High-resolution transmission electron microscopy (HRTEM) further revealed the atomic-scale lattice fringes of three distinct domain orientations within a single grain, providing direct evidence of the domain formation and well-defined domain boundaries. These microstructural features, including domain splitting and the presence of weak superstructure reflections, are closely linked to the lattice distortion and structural ordering of the orthorhombic phase. The results demonstrate that the symmetry-lowering phase transition plays a critical role

in determining the domain configurations and microstructural evolution in BCMO, which are essential for understanding its diverse functional properties.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst16080520/s1>, Figure S1: Full-range XRD patterns ($2\theta = 20\text{--}80^\circ$) of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ solid-solution ceramics with $x = 0.05, 0.25$ and 0.33 ; Figure S2: Rietveld refinement XRD patterns of three samples $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ with $x = 0.05, 0.25$, and 0.33 ; Figure S3: SEM-EDX energy spectrum acquired from the representative $\text{Bi}_{0.25}\text{Ca}_{0.75}\text{MnO}_3$ solid-solution ceramic; Table S1: Rietveld full-profile refinement results of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ solid-solution ceramics; Table S2: Chemical composition verification of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ solid-solution ceramics.

Author Contributions: C.N. designed this study and revised the manuscript. H.W., Z.C., J.W. and Y.L. carried out experiments and data analysis. H.X. sorted data and polished the paper. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare no conflict of interest.

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