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Review

Recent progress on the structural characterizations of domain structures in ferroic and multiferroic perovskite oxides: A review

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Abstract

Multiferroic perovskite oxides have multiple ferroic order parameters simultaneously in the same phase in a certain temperature range, exhibiting an exciting way of coupling between the ferroic order parameters. This provides a possibility for constructing new types of multifunctional devices. Multiferroic domain structures in these materials are considered to be important factors to improve the efficiency and performance of future multiferroic devices. Recent developments in domain characterization techniques, particularly the aberration-corrected transmission electron microscopy (TEM) have enabled one to determine the domain structures at sub-angstrom scale, and the recent development of in-situ TEM techniques allows one to study the dynamic behavior of multiferroic domains under applied fields or stress while the atomic structures are imaged directly. This paper provides a comprehensive review of the recent advances on the structural characterizations of domain structures in ferroic and multiferroic perovskite oxides, which have been achieved by the notable advancement of aberration-corrected TEM.

Keywords: Multiferroics; Perovskite oxides; Domain structures; Characterization techniques

Contents

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1. Introduction

Perovskite oxides exhibit a wide range of functional properties, such as ferroelectricity, piezoelectricity, pyroelectricity, non-linear dielectric behavior, as well as multiferroic properties.[1–4] These properties are indispensable for applications in microelectronic devices. In the perovskite-type ferroelectrics, their physical properties are closely related to the ferroelectric domains and their dynamic behavior under external fields.[5–8] For example, perovskite-type ferroelectrics with engineered domains possess large piezoelectricity, and their fatigue and retention characteristics are closely related to the domain switching process. Therefore, the domain structure characterization plays a crucial role in revealing the underlying mechanisms. On the other hand, perovskite-type manganites exhibit colossal magnetoresistance (CMR) effect (abnormal decrease in the resistivity by an applied magnetic field), which has attracted much attention of researchers.[9,10] Despite intensive researches on the CMR effect, up to date the relationships between the CMR effect and the complex domain structures in the perovskite-type manganites still remain unknown. To shed light on the understanding of the abnormal transport properties (e.g., CMR effect) in the perovskite-type manganites, quantitative magnetic imaging on the complex magnetic domain structures (such as the magnetization distribution, the temperature dependence, and the effect of weak magnetic fields as well as the features of magnetic phase separation between the ferromagnetic and antiferromagnetic phases) in the perovskite-type manganites, is highly required. Recent development of electron holography technique allows one to accurately visualize the complex magnetic domain structures near the Curie temperature and/or Néel temperature in hole-doped perovskite manganites.[11,12] However, in order to reveal these complex and nano-scaled domain structures with sub-angstrom resolution, new developments on the microscopic methods should be sustained.[13]

In recent years multiferroic materials have attracted much interest not only from a fundamental but also a technological point of view because they possess more than one type of ferroic order in the same phase.[14–16] The defining characteristic of a ferroic material is an order parameter (e.g., electric polarization in ferroelectrics, magnetization in ferromagnets, or spontaneous strain in ferroelastics) that has different, energetically equivalent orientations; the orientation of which can be selected by an external field. The ferroic materials may have domains of differently oriented regions, separated by domain walls, coexisting in a sample. Materials that are simultaneously ferroelectric and ferromagnetic are gaining more and more attention within the scientific community because in such magnetoelectric multiferroics either "magnetic control of ferroelectric domains" or "electric control of magnetic domains" is available, which would lead to totally new possibilities in the design of data-storage devices besides revealing the fascinating new basic physics.[17] The ferroelectric and magnetic domain structures in these magnetoelectric multiferroic materials are considered to be important factors to improve the efficiency and performance of future magnetoelectric devices. Therefore, multiferroic domain structures in magnetoelectric multiferroics have been widely investigated. Meanwhile, both the techniques and instruments of transmission electron microscopy (TEM), which is one of the most powerful tools for the domain analysis, have been greatly improved in the last decade. As advances in aberration-corrected TEM have enabled the determination of the three-dimensional structure of materials with sub-angstrom resolution, the recent development of in-*situ* TEM techniques also allows one to study the dynamic behavior of multiferroic domains under applied fields or stress while the atomic structures are imaged directly.[18–20] Therefore, the new generation HRTEM/STEM facility equipped with aberration-correctors will benefit the characterizations of domain structures in the ferroic and multiferroic perovskite oxides. An overview of the state of art in this direction is presented here. First, we introduce the characterization methods for ferroelectric domains in perovskite-type ferroelectrics, and particularly the recent progress on the characterizations of ferroelectric domain structures at atomic-scale achieved by the aberration-corrected TEM, is critically reviewed. Second, the recent progress in the domain structures of perovskite CMR manganites achieved by advanced TEM techniques is also highlighted, which covers the charge-ordered domains in manganites and magnetic domains in the mixed-phase states in manganites. In the third part, recent advances of ferroelastic domain structures are shortly described. Finally, the current progress on multiferroic domain structures in magnetoelectric multiferroics is summarized, and the future challenges of the characterizations of domain structures in multiferroic perovskite oxides are also provided.

2. Ferroelectric domain structures and their characterization techniques

2.1. Ferroelectric domain structures

Ferroelectric crystals are defined by having a spontaneous polarization that can be reoriented by an electric field, where the plot of polarization versus electric field exhibits