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Domain Structures in $La_{0.8}Ca_{0.2}CoO_3$ Perovskite

Miaofang Chi[1], Nigel Browning[1, 2], Nina Orlovskaya[3]

1 University of California-Davis, Dept. of Chemical Engineering and Materials Science, Davis, CA
2 National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.
3 Drexel University, Department of Materials Engineering, 3200 Chestnut St., Philadelphia, PA 19104, USA

Lanthanum cobaltites are of considerable industrial interest due to their high mixed ionic and electrical conductivities (MIEC). This material can be used as a cathode material in solid oxide fuel cells, oxygen permeable membranes and gas sensors. Domains are the dominant microstructure feature of $LaCoO_3$ based perovskites at room temperature. They are formed by the structural transformation from a high symmetry phase at high temperature to a low symmetry phase at low temperature enable stress relieve in the material [1, 2]. Domain behavior relates to the mechanical properties of the materials directly. The purpose of this study is to characterize the microstructure of $La_{0.8}Ca_{0.2}CoO_3$ in particular domains and domain boundaries.

Scanning transmission electron microscopy (STEM) is now established as a powerful tool available for studies of the local microstructure and chemistry for a wide range of materials. Previous work shows that STEM can be applied to study oxygen vacancies and ordering behavior in perovskite materials by combining Z-contrast imaging and Electron Energy Loss Spectroscopy (EELS) [3, 4]. In addition, conventional HRTEM (High Resolution Transmission Electron Microscopy) was used in this work, for imaging domain boundaries by HRTEM and determining domain orientations by selected area electron diffraction (SAED).

A typical domain structure in $La_{0.8}Ca_{0.2}CoO_3$ is shown in Fig.1a, which has domain boundaries in two directions. The HRTEM image in Fig. 2b indicates the origin of a domain with two direction domain boundaries. Domain boundaries are slightly tilted for 1° with respect to the bulk lattice. The spot splitting in the FFT (fast Fourier transformation) (Fig. 1c) shows the existence of domain boundaries in two directions. A different type of domain structure in the material has also been found. As shown in Fig. 2, the crystal has quasi-parallel domains, which reveal contrast in TEM images on zone-axis. The different contrast is due to two types of crystalline structures: the unmodified crystal structure of $La_{0.8}Ca_{0.2}CoO_3$ structure (as seen in Fig. 2a) and a superstructure (as seen in Fig. 2b). Related diffraction patterns confirm the difference in phase. The periodic contrast variation in the HRTEM image in Fig. 2b and the extra spots in diffraction pattern indicate the existence of a superstructure. It is suggested that the formation of superstructure may caused by from oxygen vacancy ordering or Ca ordering. As a result, it may change the overall conductivity of the material. A detailed analysis of the ordered structures and domain boundaries using EELS and Z-contrast imaging will also be presented.

References:
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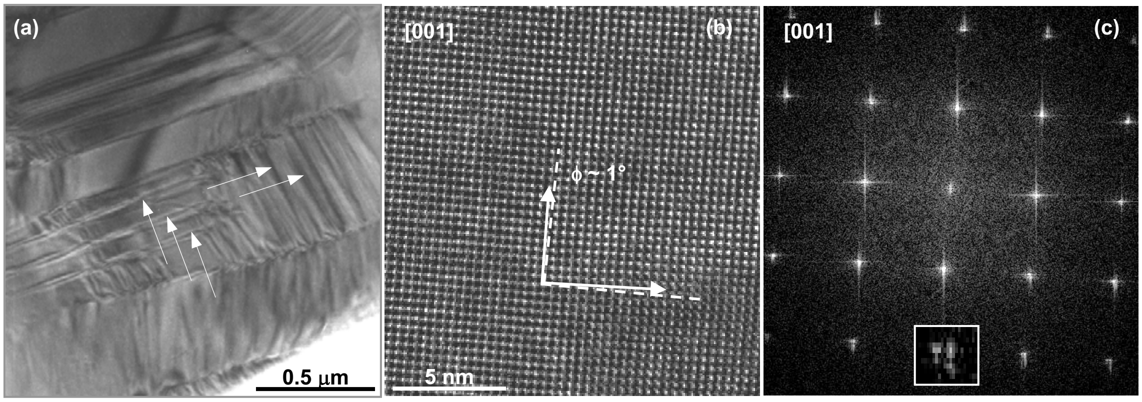

Fig. 1 (a) Bright field TEM image of typical domain structures (see arrows) in $La_{0.8}Ca_{0.2}CoO_3$; (b) HRTEM image of an area with domains in two directions, the arrows and broken lines indicate the tilt of the domains. The tilt angle shown is calculated from diffraction pattern; (c) related FFT of (b), the magnified image of one diffraction spot shows the splitting, which confirms the existence of domains.

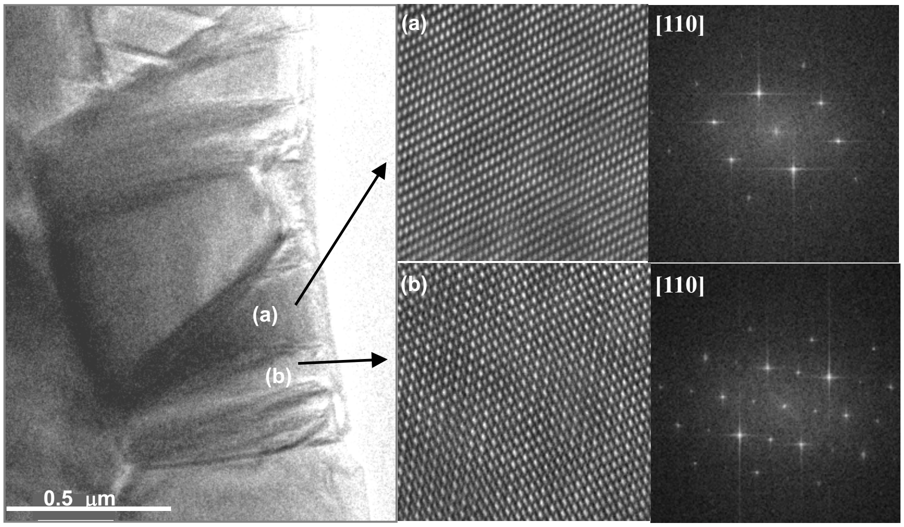

Fig. 2 TEM image of a grain with two types of domains: one with superstructure and the other one with normal structure. The periodic contrast in the HRTEM image and the extra spots in its FFT indicate the existence of the superstructure.