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Determination of Displacive Modulation of Thermoelectric $Ca_3Co_4O_9$ by Simultaneous Acquisitions of HAADF and MAADF Images

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Misfit-layered cobaltates are of great interest due to their unique physical properties controlled by their structural characteristics. A common structure feature of the misfit-layered cobaltates is that they consist of conducting layers and disordered insulating layers. Among them, the calcium cobalt oxides $(Ca_2CoO_3)_{0.62}CoO_2$, often approximated as $Ca_3Co_4O_9$, is particular interesting because it is a model system with a figure of merit value *ZT* above one at high temperatures. It is ideal for structural analysis to understand the enhanced thermoelectric power due to its misfit layered structure with significant lattice displacement that is attributed to the reduced thermal conductivity.

The structure of the $Ca_3Co_4O_9$ has been extensively studied by X-ray, neutron and electron diffractions. The average structure of the compound consists of two interpenetrating subsystems of a CdI_2-type CoO_2 layer and a distorted tri-layered rock-salt-type Ca_2CoO_3 block, being incommensurate along the b-axis. Fig. 1 shows the unrelaxed structure proposed by Miyazaki [1]. Due to the misfit between the two subsystems, it was assumed that the unique thermal power of the material can be explained by one block acting as electron-crystal with high electro-conductivity and the other as phonon liquid with poor thermoconductivity. The determination of the atomic modulation which is essential to the electro- and thermo- conductivity, especially the atomic displacement in the rock-salt subsystem, however, is quite inconclusive due to the absence of the superlattice peaks. Here, we report a new method we developed based on scanning transmission electron microscopy (STEM) to measure the atomic displacement in $Ca_3Co_4O_9$. Unlike the refinements based on the intensities of Bragg reflections in reciprocal space, we directly measure the atomic displacement in real space. Atomically resolved aberration-corrected STEM enables us to measure the atomic displacement independently for each layer in different orientations, in contrast to the diffraction method that refines all the displacements together.

Fig. 2(a) shows the high angle annular dark field (HAADF) and medium angle annular dark field (MAADF) images of the $Ca_3Co_4O_9$ crystal simultaneously acquired using HAADF and MAADF detectors in Hitachi HD2700C STEM [2]. The cations in CoO_2, CoO and CaO layers are clearly visible in both imaging modes when viewed along the [010] direction, though the contrast of CoO layer is quite diffusive along the [100] direction, especially in the MAADF image. The layer intensity decreases in the order of CoO_2, CoO and CaO layer in the HAADF image, which roughly follows the Z-contrast rule as over a period of 2.275 nm along the [010] direction there are 8 Co at CoO_2 layer, 5 Co at CoO layer and 5 Ca at CaO layer. The MAADF image, however, shows atomic column intensity of the CoO layer higher than that of the CoO_2 layer, i.e., a contrast reversal, suggesting that local static and thermal displacement play a significant role in the image intensity. Fig. 2(b) and 2(c) shows the calculated HAADF and MAADF images based on the unrelaxed and relaxed models proposed by Miyazaki [1]. The agreement with experiment was poor, especially for the MAADF images. After extensive structural refinement including both static and thermal displacements for all atoms we derived our structure model (Fig. 2(d)) that agrees well with

experiment (Fig. 2(a)). Our study of the misfit layered $Ca_3Co_4O_9$ provide a fundamental structural base for understanding the origin of the effectively reduced thermoconductivity in this system.

References

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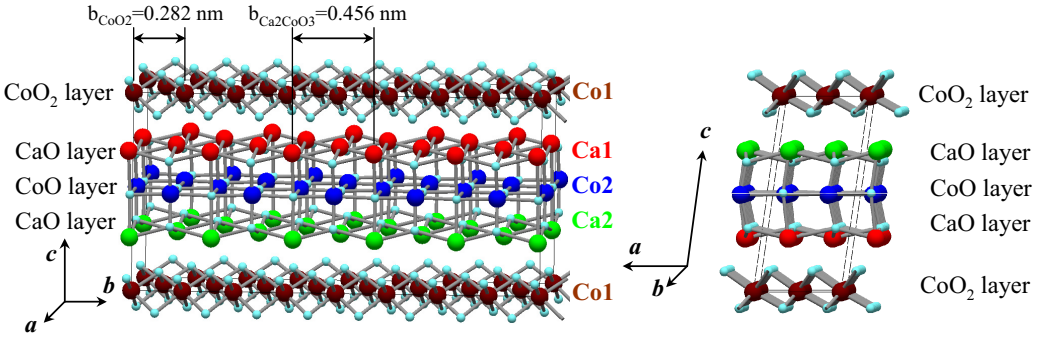

Fig. 1. Structure model of unrelaxed $(Ca_2CoO_3)_{0.62}CoO_2$. The structure consists of two subsystems. Both the subsystems have common ***a***-, ***c***-axes and β-angle with a=0.483 nm, c=1.084 nm and β =98.14º. The ***b***-axis lengths are b_1=0.282 nm for CoO_2 subsystem and b_2=0.456 nm for Ca_2CoO_3 subsystem.

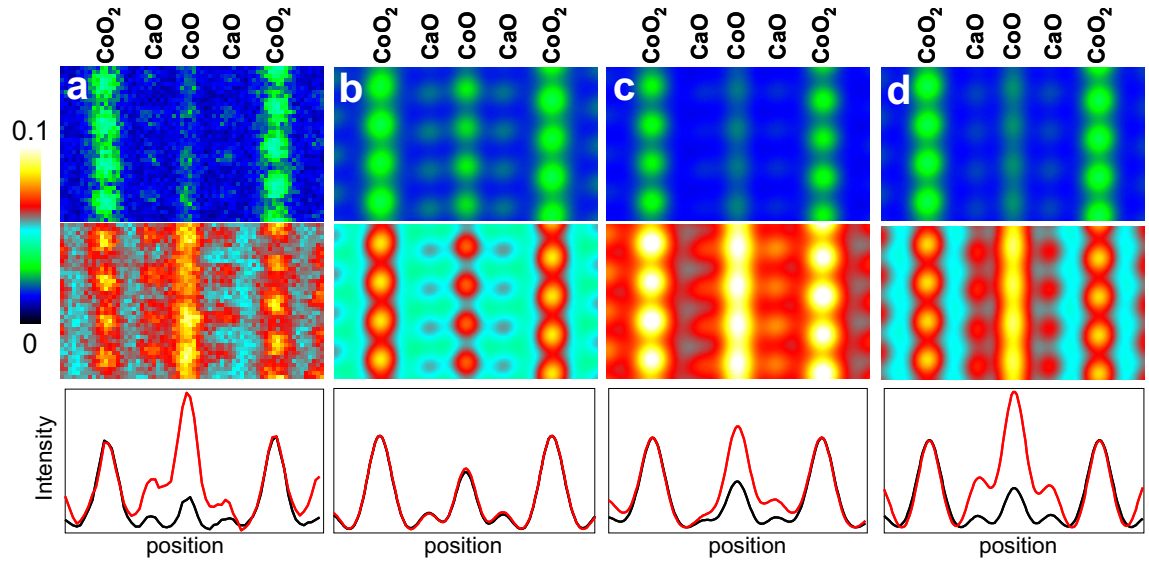

Fig. 2. STEM images viewed along [010] direction. Column (a) experimental images; Column (b-d) Calculated images with Miyazaki's unrelaxed model (b), Miyazaki's relaxed model (c) and our refined structure model (Column d). The image calculations were performed using our own computer codes based on multislice method with frozen phonon approximation. The first and the second rows are the HAADF and MAADF images, respectively. The third row is the profiles of the HAADF (black line) and MAADF (red line) by averaging the intensity along the [100] direction (vertical direction in the figure). The intensity profiles are normalized with the CoO_2 layers (the intensity values as color legend are shown in the left).

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