High-resolution STEM Imaging of Oxide Materials for Thermoelectric Applications

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High-resolution scanning transmission electron microscopy (STEM) with EDS/EELS has become a powerful technique to assess information on the structure and chemical composition of investigated materials on the atomic scale. The STEM images are recorded in a FEG (S)TEM, preferably with a probe Cs corrector. When using HAADF detector, the images are recorded at large inner angles of the annular detector so that thermal diffuse scattering (TDS) becomes the prevailing contribution to the image intensity. Contrary, the ABF images are recorded with the BF detector at small inner and outer angles of the BF detector. In this way light elements can be observed as well. In our work we investigated the structure and the chemical composition of Ruddlesden–Popper[1,2] (RP) type planar faults in doped $Sr(Ti,Nb)O_3$ and inversion boundaries in doped ZnO[3,4] thermoelectric materials. All results were obtained in a Jeol ARM-200F with a CFEG and Cs probe corrector. HAADF imaging was performed at angles from 70 to 175 mrad, while ABF imaging from 11 to 23 mrad. RP faults in doped $Sr(Ti,Nb)O_3$ formed either a 3-D network structures or more or less ordered sequences of polytypic RP phases in the perovskite matrix. While measured intensities of individual Sr atomic columns along a single fault did not scatter significantly, the $(Ti,Nb)O_6$ atom columns exhibited large scatter in measured intensities, thus indicating significant variation in Nb and Ti content within a single mixed atom column. Quantitative analysis of measured HAADF intensities showed that the content of Nb on B sites in perovskite solid solution varied from 5 to 35 at%. In In_2O_3-doped ZnO ceramics, pure indium monolayers were readily observed by HAADF. These basal inversion domain boundaries (IDB's) were parallel to the {0001} ZnO lattice planes and separated domains with different orientation (head-to-head; tail-to-tail). Pyramidal IDB's (p-IDB) were much more clearly resolved by ADF as opposed to basal IDB's (b-IDB) due to an increased contribution of diffraction contrast and/or strain.

1. S.N. Ruddlesden, P. Popper, Acta Cryst., 1958, 11, 54-55.
2. S. Šturm, M. Shiojiri, M. Čeh, J. Mater. Res., 2009, 24(8), 2596-2604.
3. T. Hörlin, G. Svensson, E. Olsson, J. Mater. Chem., 1998, 8(11), 2465-2473.
4. H. Schmidt, E. Okunishi, T. Oikawa, W. Mader, Micron, 2012, 11, 49-56.