Structure determination of nano-precipitates found in La-doped $SrTiO_3$ using 3D precession electron diffraction

Ercin Duran, Feridoon Azough, Alexander Eggeman

University of Manchester, UK

Nanostructured thermoelectric materials have gained attention recently due to their superior thermoelectric properties when compared to the same material produced with the classical synthesis route. The enhanced thermoelectric response is generally attributed to the nano-sized features that are formed during the synthesis and alter the electron scattering rates favourably. Understanding the crystal structure of these features is essential since they have a direct effect on the overall thermoelectric property of the material. Azough et al. recently reported on La-doped $SrTiO_3$ with enhanced thermoelectric response due to this nanostructuring phenomenon [1]. The results indicated that the cores of the grains contain a number of nanoscale precipitates with a different crystal structure which leads to formation of a precipitation free zone around the grain boundaries. However analysis of HRTEM images was unable to discern the atomic arrangement within the precipitates. In this study, the crystal structure of the nano-crystals of La-doped $SrTiO_3$ was investigated by using advanced diffraction techniques in TEM. The reciprocal space of a single crystal was sampled with a precession electron diffraction tilt series. The reconstructed reciprocal lattice indicated the presence of a superstructure coherent with the parent $SrTiO_3$ perovskite.

Individual diffraction patterns of a La-$SrTiO_3$ single crystal were collected while tilting on an arbitrary axis. The tomography data was analysed using the PETS software package which allowed the reciprocal lattice of the material to be reconstructed. By utilising charge-flipping [2] and direct methods [3] approaches, the structure of the supercell was determined as shown in Figure 1. It is conceivable that local variations in the average 10% La doping in Sr sites of $SrTiO_3$ surpass the solubility limit of lanthanum in the strontium titanate matrix, this leads to a transition from random lanthanum positions to an ordered arrangement, these separate as widely as possible in order to minimise the distortion of the remainder of the perovskite structure.

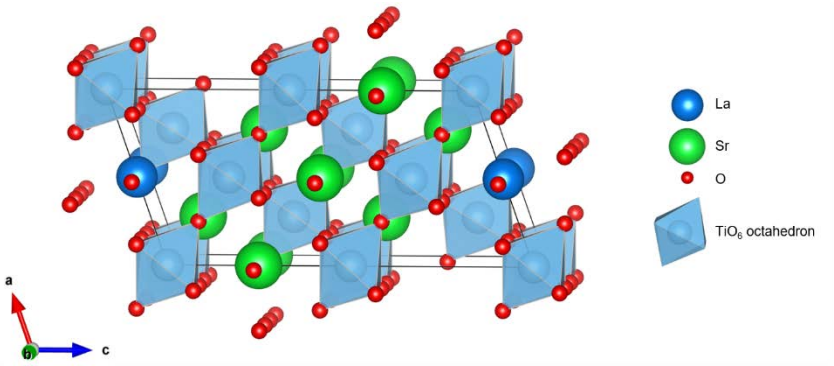

Figure 1. Structure of the as-solved La-$SrTiO_3$ supercell.

[1] F. Azough *et al.*, "Self-Nanostructuring in SrTiO3: A Novel Strategy for Enhancement of Thermoelectric Response in Oxides," *ACS Appl. Mater. Interfaces*, vol. 11, no. 36, pp. 32833–32843, Sep. 2019.

[2] L. Palatinus and G. Chapuis, "SUPERFLIP–a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions," *J. Appl. Crystallogr.*, vol. 40, no. 4, pp. 786–790, 2007.

[3] M. C. Burla *et al.*, "Crystal structure determination and refinement viaSIR2014," *J. Appl. Crystallogr.*, vol. 48, no. 1, pp. 306–309, 2015.