TEM and STEM investigations of Sr(Ti,Nb)O3-δ thermoelectric with the addition of CaO and SrO

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It is known that thermoelectric properties, i.e. figure of merit ZT of oxide-based polycrystalline thermoelectric materials can be improved by introducing planar faults into the microstructure of these materials. It is assumed that in-grown planar faults will reduce thermal conductivity without reducing electrical properties which would consequently increase the ZT value. In order to successfully tailor thermoelectric properties of chosen thermoelectric materials, it is prerequisite to know the structure and chemical composition of introduced planar faults. This is why we used HR TEM and HAADF STEM imaging with EDXS in order to study structure and chemical composition of the Ruddlesden-Popper-type (RP) planar faults[1,2] in $Sr(Ti,Nb)O_{3-d}$ (STNO) thermoelectric material with the addition of SrO and/or CaO. 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 (ADF from 42 to 168 mrad). EDX spectra were acquired using JEOL Centurio Dry SD100GV SDD Detector. TEM bright-field images of pure STNO showed that the STNO solid solution grains contained no planar faults of any kind. Furthermore, the interfaces between the grains were clean with no observable interface phase. However, when SrO and/or CaO were added to the STNO, various nanostructured features were observed. In SrO-doped STNO, one can observe three distinctly different regions, i.e. the STNO solid solution, the regions with ordered SrO faults and the region with a network of random SrO planar faults (Figure 1). In the ordered regions one SrO layer is always followed by two perovskite STNO blocks, which corresponds to the $Sr_3(Ti_{1-x}Nb_x)_2O_7$ RP-type phase in which Nb and Ti occupy the same crystallographic site. While the measured HAADF intensities across Sr atomic columns at the RP fault do not scatter significantly, the mixed $(Ti_{1-x}Nb_x)O_6$ atom columns on the other hand exhibit significant differences in measured intensities thus indicating variation in Nb and Ti content within a single mixed atom column (Figure 2). Semi-quantitative HAADF STEM of the perovskite matrix, i.e. the comparison of measured integrated intensities of the atom columns with the calculated intensities showed that that the Nb content on the Ti sites within the perovskite structure varied from app. X=0.05 to X=0.35 (from $Sr(Ti_{0.95}Nb_{0.05})O_{3-d}$ to $Sr(Ti_{0.65}Nb_{0.35})O_{3-d}$). When RP-type planar faults are isolated they run parallel to the {001} low-index zone axes of the perovskite structure. A similar structural phenomenon was observed in STNO with excess of CaO. Again, ordered and/or random 3D networks of RP-type planar faults were observed in the STNO grains (Figure 3). In very thin regions of CaO-doped STNO specimen many orthogonal loops of RP faults were observed that were not detected in SrO doped STNO (Figure 4). The EDX analysis from a single fault and from the matrix showed higher concentration of Ca at the fault. This is in agreement with previously reported investigations[3] since smaller Ca ions are easier incorporated at the RP fault than in the perovskite matrix. The TEM and STEM investigations thus confirmed that the addition of SrO and/or CaO to the STNO perovskite solid solution is structurally compensated via the formation of RP-type planar faults within the STNO grains. Finally, thermoelectric measurements confirmed that the existence of RP-type faults in the perovskite STNO matrix reduced the thermal conductivity of this oxide thermoelectric material.

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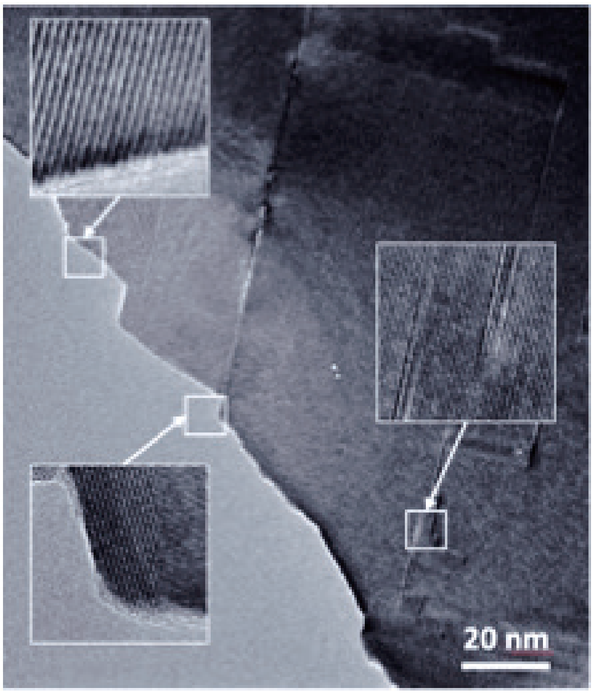

Figure 1. Bright-field TEM image of SrO-doped STNO. The following three regions are observed: the region with ordered RP faults, STNO perovskite solid solution and region with isolated RP faults.

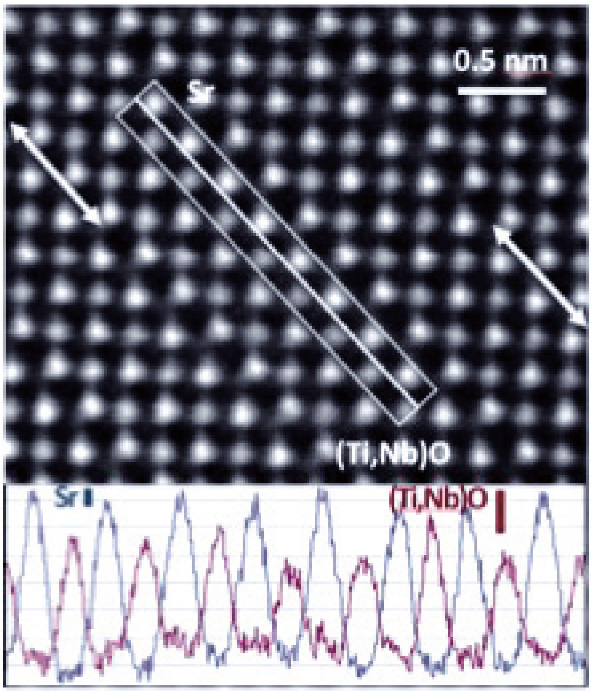

Figure 2. HR HAADF STEM micrograph of RP faults in SrO-doped STNO as seen in the [001] zone axis. Sr and mixed (Ti,Nb)O atomic columns are distinguished due to different intensities. Large scatter in measured intensities of (Ti,Nb)O atom columns is observed.

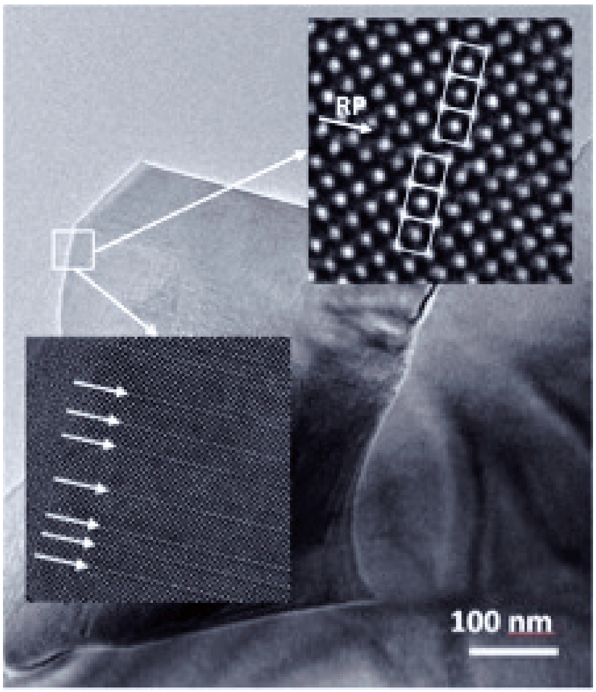

Figure 3. Bright-field TEM micrographs of CaO-doped STNO grains. The insets show the region with ordered RP faults. The RP faults are marked with arrows.

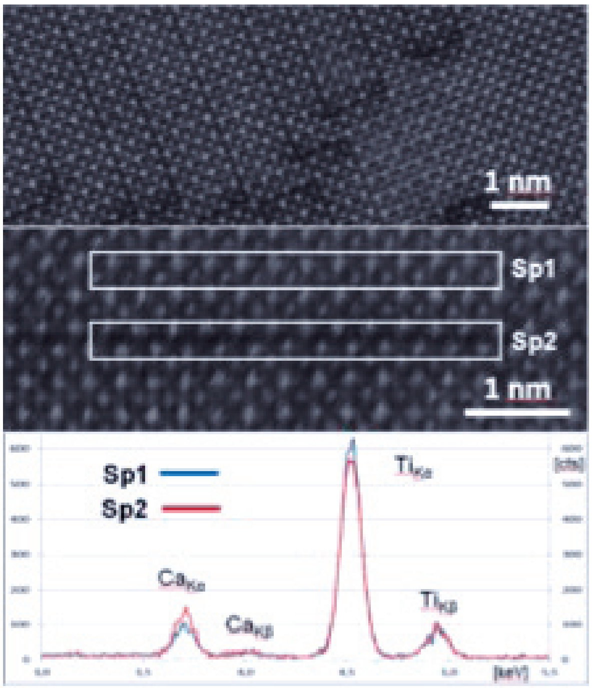

Figure 4. HAADF STEM image of RP loops in thin region of CaO-doped STNO. The EDX spectra acquired from marked frame scans shows that the Ca content at the fault is higher as compared to the matrix.