

## The change of oxygen vacancy ordering in a nonstoichiometric La-Sr-Co-perovskite during TEM investigation

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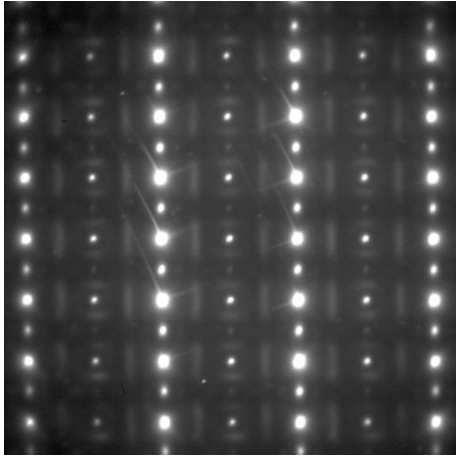
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Perovskite oxides are an important group of oxygen-deficient materials with several potential technological advantages. Especially, strontium-cobalt based perovskites exhibit a high ionic conductivity in addition to a high electronic conductivity [1], and are used for solid oxide fuel cells, oxygen transport membranes and gas sensors.

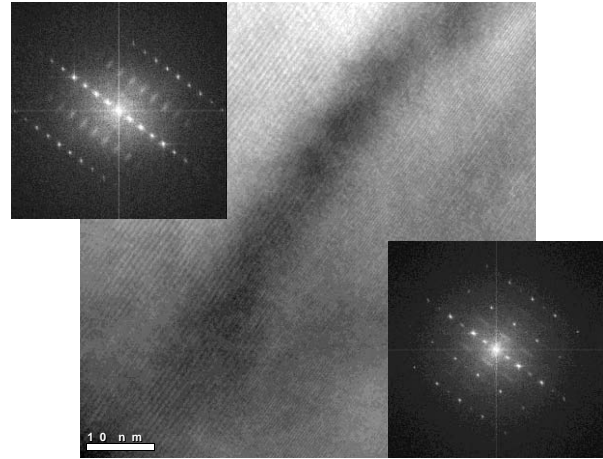
The nonstoichiometric perovskite  $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$  ( $\delta = 0.29$ ) with the space group  $I4/mmm$  reveals a superstructure in the X-ray powder diffraction (XRD) pattern [2]. The superstructure from the tetragonal unit cell can also be observed in the electron diffraction patterns of the main zone axis  $[1\ 0\ 0]$  and  $[0\ 1\ 0]$ . The superstructure along the c-axis is the result of oxygen vacancies in statistically every second oxygen-octahedron-layer [2]. This can be seen as an oxygen vacancy ordering. To this very short and simple kind of ordering there is also a short range ordering observable in electron diffraction patterns as diffuse scattering (Fig. 1). Since the sample exhibits domains [3] (crystallographic different orientated) and these domains are smaller than the smallest SA-aperture it is not possible to distinguish the diffuse reflections of the different orientated domains in the diffraction pattern. In the Fourier Transformation (FFT) of high-resolution TEM images the diffuse scattering is also observable and can therefore distinguished between the domains on the two sides of the boundary (Fig. 2). These diffuse reflections can be simulated [4] with the formation of the oxygen vacancies by positive and negative correlations in different directions (Fig. 3). The formation of ordered oxygen vacancies, which also results in charge ordering of the metal ions, in some zone axis also yields satellite reflections, which can be interpreted as a modulation (Fig. 4).

The fine structure of the O-K ionization edge is dependent of the orientation and crystal structure and may change during the investigation in the electron microscope (Fig. 5). This was systematically investigated by EELS. As the sample has a high ionic conductivity and the O-K edge fine structure is sensitive to the concentration of vacancies [5] it seems that the electron beam induces the movement of oxygen (respectively vacancies) and also changes the local concentration of oxygen vacancies. This change can also be accompanied by a modification of the superstructure, diffuse scattering, or modulation during the investigation in the TEM.

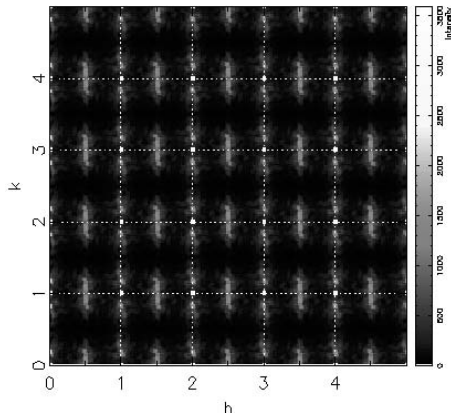
1. E. Bucher et al., *Solid State Ionics* **152/153** (2002) p417.
2. C. Gspan et al., *J. Solid State Chem.* **181** (2008) p2976.
3. I. Letofsky-Papst et al., *Microsc. Microanal.* **8** (Suppl. 2) (2002) p618
4. T. Proffen and R. Neder, *J. Appl. Crystallogr.* **30** (1997) p171.
5. D.A. Muller et al., *Nature* **430** (2004) p657.



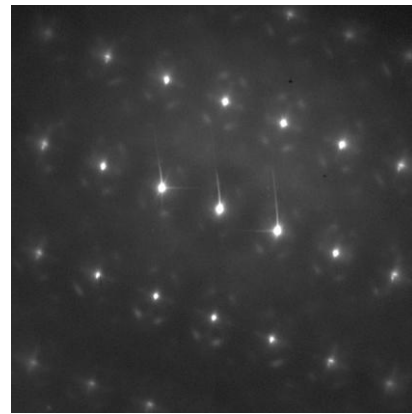
**Figure 1.** SAED pattern in [210].



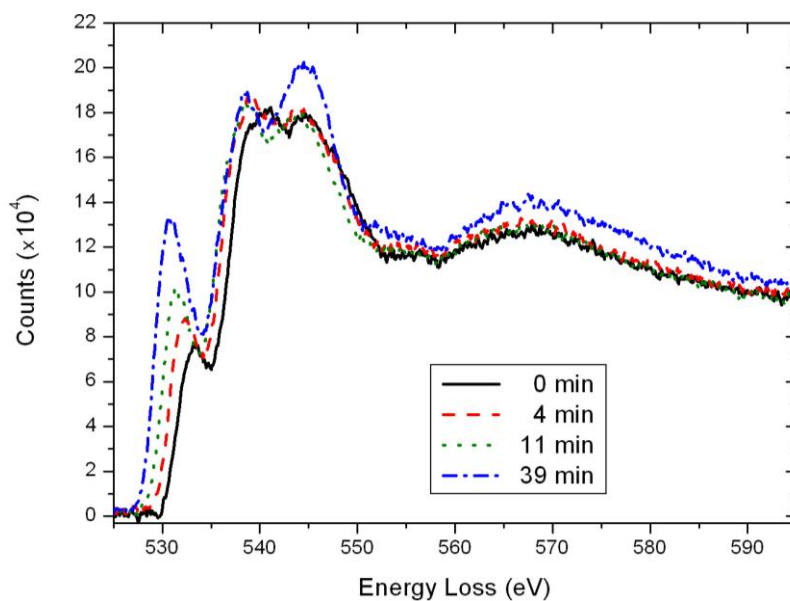
**Figure 2.** HRTEM at a boundary in [210]. The insets show the FFT with the diffuse reflections from the domains.



**Figure 3.** Simulation for diffuse scattering



**Figure 4.** SAED in [223] with satellite reflections



**Figure 5.** The change of the O-K edge fine structure during the investigation.