HRTEM study of heat induced La_2NiO_4 surface degradations

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Perovskite type oxide materials with high oxide-ion conductivity are intensively studied as candidate materials for high-temperature cathodes in solid oxide fuel cells, as well as for membranes in ceramic oxygen generators [1]. The latter application is currently gaining a lot of interest also for the development of oxygen separation membranes, which enable a more efficient carbon combustion but also the capture of carbon dioxide for emission-free power plants. For all these applications, the long term stability of the functional materials under realistic conditions is of extreme economic relevance and is therefore investigated thoroughly.

It has been reported, that the candidate material lanthanum nickelate, La_2NiO_4, especially in its higher-order Ruddlesden-Popper (RP) phases $La_{n+1}Ni_nO_{2n+1}$ (n=2, 3), provides better stability in the temperature range around 1000 °C compared to other materials, while retaining good oxygen ion transport and high electrical conductivity [2]. We investigated the long-term stability of this material by keeping a single crystal of La_2NiO_4 over 13 days in air at a temperature of 1000 °C. This treatment caused a degradation of the crystal surface by growth of crystallite islands as shown in Fig. 1(a). The target of our investigations is to clarify which processes are responsible for the degradation of the single crystal surface and lead to the formation of crystallites. For this purpose we applied high-resolution transmission electron microscopy in order to determine the structure of the crystallites with a special focus on the structure at the interface to the bulk material.

TEM samples have been prepared by focused ion-beam (FIB) cutting and successive ion milling. The FIB lamellas contain the interface between bulk and crystallites for cross sectional view in a transmission electron microscope; see Fig. 1(b). High-resolution transmission electron micrographs have been recorded with an FEI Titan 80-300 electron microscope operated at 300 kV accelerating voltage. Close to optimum imaging conditions have been applied with a small negative spherical aberration and a small over focus providing low delocalization and bright contrast at positions of atom columns [3]. We found that the crystallites are structured predominantly in the higher-order RP phases mentioned above. However, a disordered stacking of the perovskite structure was observed at the interface between bulk and crystallite. Figure 2(a) shows an example micrograph of frequently occurring stacking faults with a missing perovskite layer in the periodic $La_4Ni_3O_{10}$ phase observed away from the crystallite-bulk interface. Close to the interface, the layered structure along the bulk *c* axis is non-periodic over several nanometers as shown in Fig. 2(b).

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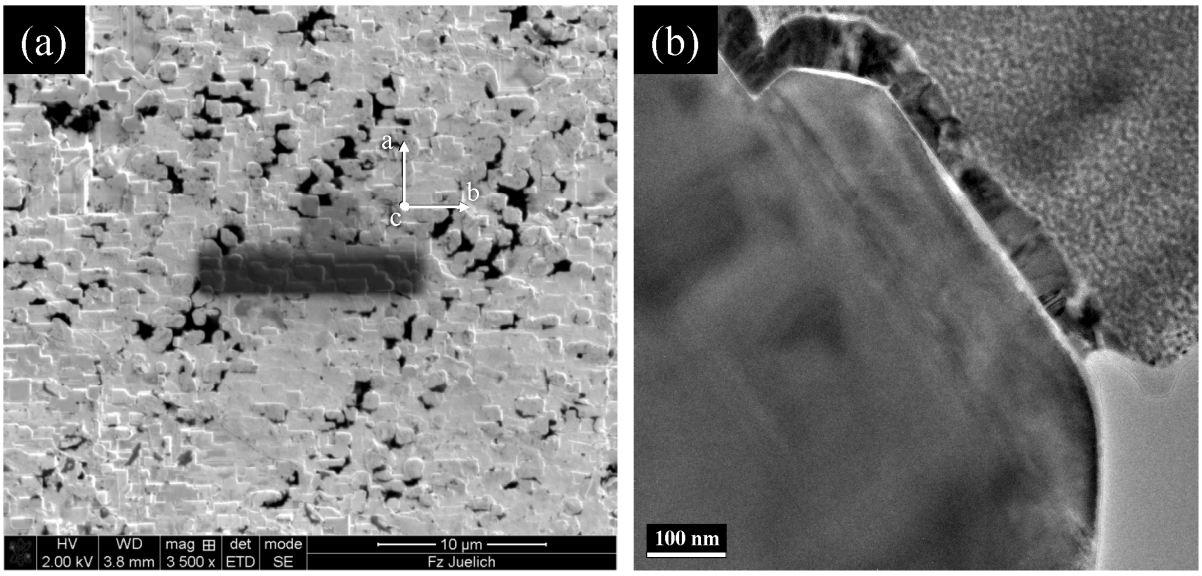

Figure 1. (a) Scanning electron micrograph of a degraded (001) surface of a La_2NiO_4 single crystal. The darker area in the image center marks the position of the lamella cut by the focused ion beam. (b) Transmission electron micrograph of the prepared FIB lamella showing one of the crystallites.

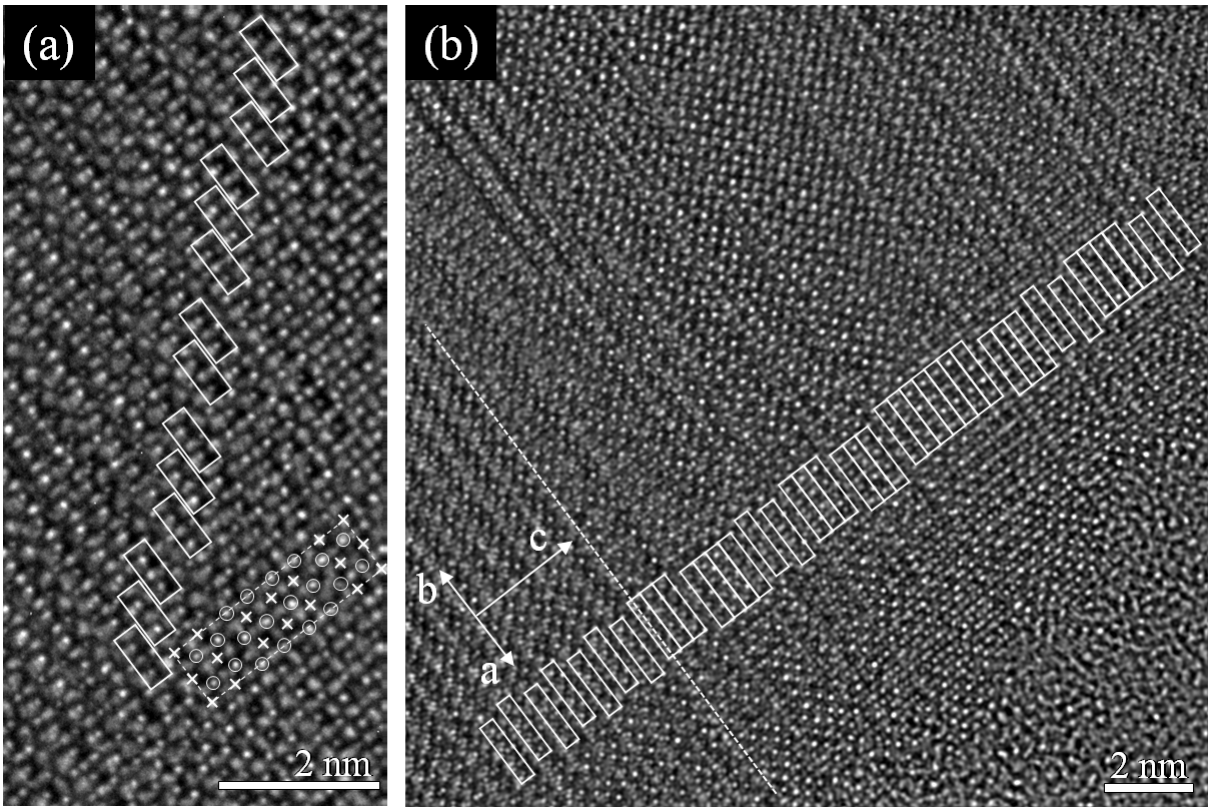

Figure 2. HRTEM images of a lanthanum nickelate crystallite in projection along the [110] zone axis. (a) Area away from the bulk-crystallite interface showing the projected structure of $La_4Ni_3O_{10}$ with a stacking fault in form of a missing perovskite layer. The projected model structure of one unit cell is drawn with small circles at positions of La atom columns and crosses at Ni-O columns. The intensity peaks between La columns and Ni-O columns correspond to positions of pure oxygen atom columns. (b) Area close to the bulk-crystallite interface (dashed line) showing a non-periodic structure. In both images the perovskite layers are marked by small rectangles.

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