In-situ TEM studies of a phase transition in $Ca_2Fe_2O_5$

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The oxygen deficient perovskite $Ca_2Fe_2O_5$ which is of the brownmillerite-type structure exhibits a structural phase transition at ca. 970 K from space group *Pnma* (a=0.54 nm, b=1.48 nm, c=0.56 nm) to a modulated structure with an aperiodic sequence of FeO_4 tetrahedral chains, described by the superspace group *Imma(00γ)s00* [1,2]. In the present study *in-situ* high-temperature TEM was used in order to prove the co-existence of both phases within a coexistence range of ca. 25 K.

Polycrystalline material was pulverized, sonicated in ethanol and dispersed on a holey carbon film on a Cu grid. *In-situ* TEM was performed with the Stuttgart JEM-ARM1250 high-voltage atomic resolution microscope operated at 1250 kV (point resolution 0.12 nm) using a GATAN heating stage and a drift-compensating device.

The hypothesis of phase co-existence was proved by dark-field TEM (DF) (Fig.1), selected area electron diffraction (Fig.2) and high-resolution imaging (Fig.3). At 1100 K the entire grain under observation showed the modulated structure by the presence of satellite reflections in (h01) layer (Fig. 2a). The modulation wave vector of $\boldsymbol{q}$ = 0.58c* determined from the diffraction pattern is in good agreement with results from X-ray diffraction experiments [1]. By carefully lowering the temperature the two-phase regime was approached were reflections from the primitive lattice (which are not allowed in the HT phase) and satellite reflections show up simultaneously (Fig. 2b). The DF micrographs in Fig 1 show the coexistence of the phases in real space. Domains of the high-temperature phase (HT) can be identified by fringes caused by the modulation (see enlarged insets). The domains of the low-temperature phase (P) grow upon lowering the temperature. Within the P phase residual defects are observed which were analyzed to be antiphase boundaries (APBs). Application of the Geometrical Phase Analysis (GPA) [3] method resulted in a shift of the lattice fringes of π (i.e., half a fringe distance) both parallel and perpendicular to the boundary (Fig. 4). Such APBs are formed during the growth of the P phase when two P domains get in contact which are shifted by a displacement vector of $\mathbf{R}$ = ½ [111] (this centering vector is lost during the HT – P transition). An APB can be modeled in a way such that the substructure of octahedral layers stays intact whereas the configuration of the tetrahedral layers changes across the boundary.

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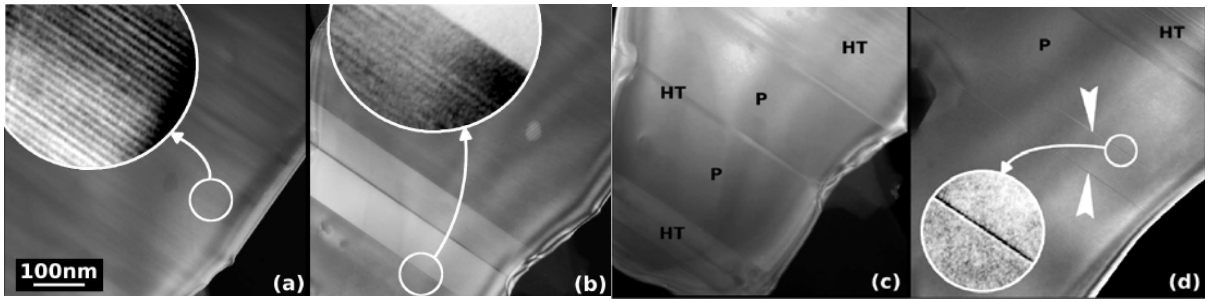


Figure 1. DF images (aperture size 4.2 nm^{-1}) of the domain structure at temperatures from 995 K (a) to 948 K (d). High-temperature phase and low-temperature phase are labeled HT and P, respectively. At 995K the whole crystal exhibits the modulated structure of the HT phase. With lowering the temperature domains of the *Pnma* phase appeared (b) and grew larger (c), within which antiphase boundaries remained, marked by arrowheads in (d).

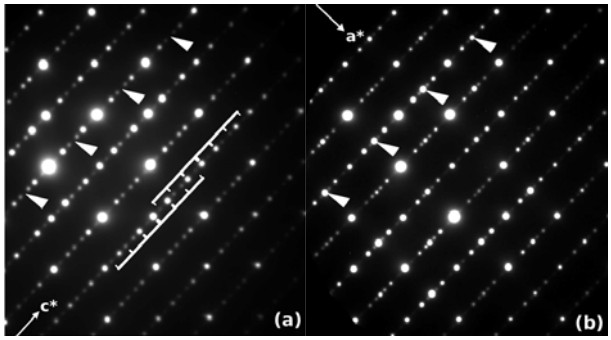
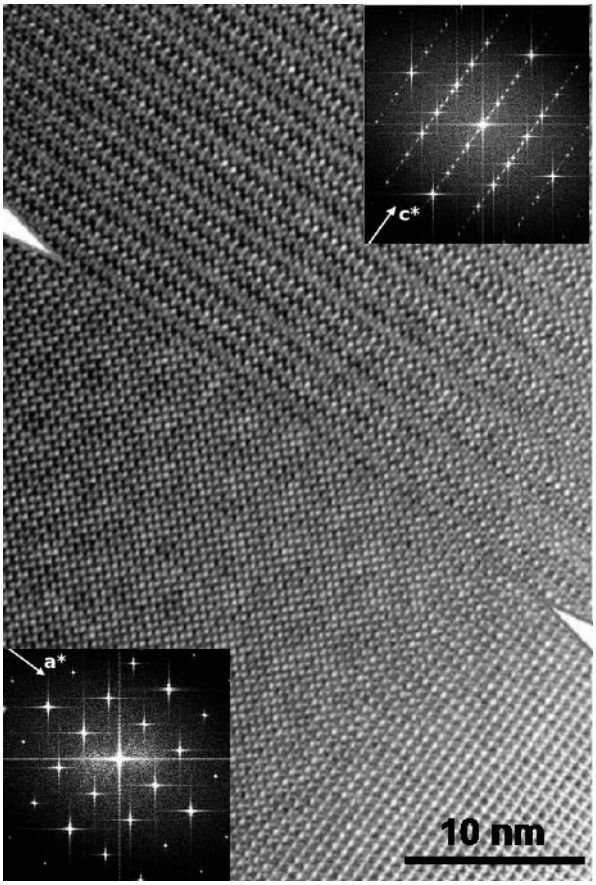


Figure 2 (top). Diffraction patters of the modulated HT phase at 1100K (a) and the two-phase domain structure at 975 K. The comb-shaped markers in (a) indicate a main reflection and satellites up to the 3rd order. Arrowheads mark the P-reflections in (b) and the positions of the missing P-reflections in (a).

Figure 3 (right). HREM micrograph of a phase boundary between *Pnma* (lower left) and *Imma(00γ)s00* (upper right) domains recorded at 970 K. Zone axis [010], FT patterns as inset.



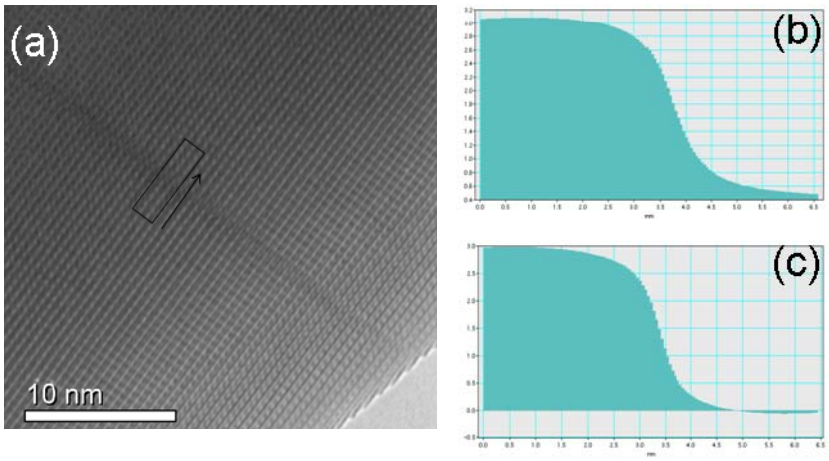


Figure 4. HRTEM of an antiphase boundary (a) and line scans perpendicular to boundary of the geometrical phase of the lattice fringes parallel (b) and perpendicular (c) to the boundary. The line scans are averaged over a distance of 1.6 nm parallel to the boundary.