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Crystallographic Analysis of Transition Al_2O_3 Phases Under the Constrains of Complex Intergrowth and Disorder

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Transition aluminas are heavily used in catalytic applications, both as catalysts and catalytic supports [1]. While much research interest in transition aluminas is naturally directed towards understanding of surfaces and catalytic properties, more basic questions regarding the crystallographic nature of transition aluminas remain a subject of ongoing debate [2-4]. Due to the high degree of structural disorder, and limitation associated with the synthesis of transition aluminas (γ-Al_2O_3, δ-Al_2O_3, θ-Al_2O_3) in isolated forms, the conventional diffraction approaches cannot be used for crystallography analysis.

In the current study we present a crystallographic analysis of complex structures of δ-Al_2O_3 and θ-Al_2O_3 based on quantitative real-space interpretation of HAADF STEM images in combination with electron diffraction. The HAADF STEM observations were performed with an aberration corrected FEI Titan 80-300.

In the case of δ-Al_2O_3, we identified the structure as a complex planar intergrowth of four variants. The complexity of intergrowth arises due to the presence of two distinct intergrowth modes, which differ by intergrowth direction and variants selection [4]. An example of the two intergrowth modes, denoted as $\delta_{1,2}$-Al_2O_3 and $\delta_{2,3,4}$-Al_2O_3, is shown in Figure.1. The first type consists of δ_1-Al_2O_3 and δ_2-Al_2O_3 and the second type consists of δ_2-Al_2O_3,δ_3-Al_2O_3 and δ_4-Al_2O_3. The challenges associated with crystallographic analysis come from the difficulty of identifying suitable orientations that are not affected by crystal overlap, and naturally from derivation of full crystallographic parameters from a limited number of zone axis measurements. It will be shown how quantitative analysis of image intensities, local symmetries and phase relationship between the zones enabled us to unambiguously derive the Al and O coordinates in the above described structures. Ab-initio DFT methods have been used for structural refinement. Examples of simulated HAADF images and corresponding crystal structures (only Al are displayed) are included in Figure.1.

The structure of θ-Al_2O_3 has been found to accommodate a different type of structural disorder. It contains a high density of interlinked lattice disorder sites, which break crystallographic periodicity along two principal directions, as shown in Figure 2. The presence of disorder in θ-Al_2O_3 is recognized as a series of high intensity spots in HAADF images. It will be shown that the overall structure can be rationalized as an intergrowth of "β-Ga_2O_3" structural type, which was previously considered exclusively for θ-Al_2O_3, with δ_3-Al_2O_3 motifs that share the periodicity of β-Ga_2O_3 phase. The structural interpretation together with HAADF simulations of the intergrowth are shown in Figure 2.

As a part of this work we will show how the derived structural models of δ-Al_2O_3 and θ-Al_2O_3 can be used for ensemble level analysis of transition aluminas using recursive stacking XRD approaches [5].

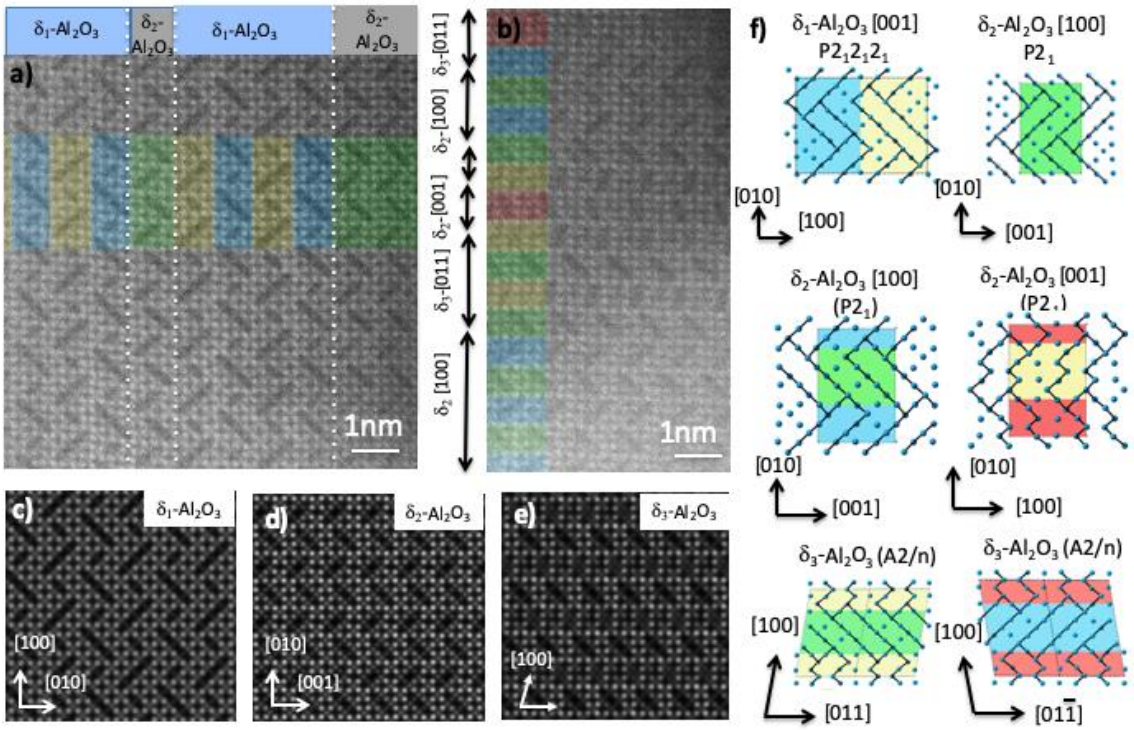

Figure 1. (a) Structural intergrowth of δ1- and δ2-Al2O3 as revealed along the cube [100]FCC_O. (b) Structural intergrowth of δ2- and δ3-Al2O3 as revealed along the cube [100]FCC_O. (c,d,e) Corresponding HAADF simulations of δ1-Al2O3 and δ2-Al2O3 and δ3-Al2O3. (f) Crystal projections of δ1-Al2O3, δ2-Al2O3 and δ3-Al2O3 (only Al displayed).

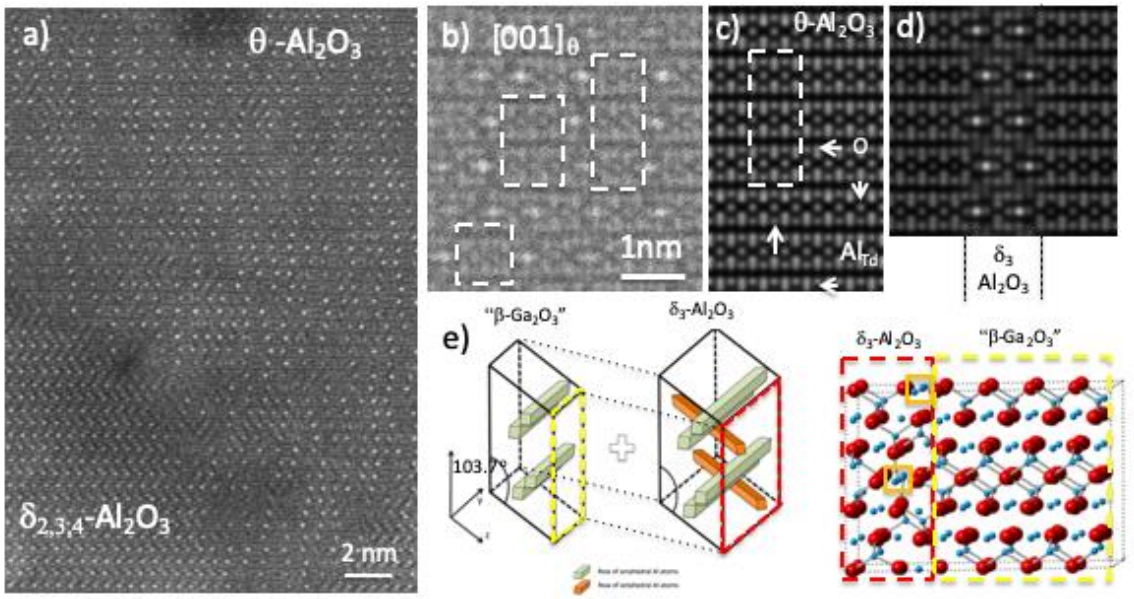

Figure 2. (a,b) HAADF observations of microstructural disorder in θ-Al2O3. (c) HAADF image simulation of θ-Al2O3 assuming β-Gal2O3 structural type. (d) HAADF image simulation of θ-Al2O3 with the intergrowth of δ3-Al2O3. (e) Crystallographic interpretation of θ-Al2O3 structure.

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