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Supporting Information

Quantification of High-Temperature Transition Al_2O_3 and Their Phase Transformations**

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SUPPLEMENTARY INFORMATION:

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Transition aluminas investigated in this work were obtained from dehydration of Boehmite (*Sasol*). The samples were heat treated in a tube furnace at 1050°C for a period of 2-48 hours. X-Ray Diffraction (XRD) patterns were collected utilizing a Panalytical MPD Bragg-Brentano diffractometer equipped with Cu Kα radiation, a variable divergence slit, and a post-diffraction monochromator. Rietveld refinements of microstructure was performed using recursive stacking approach, as implemented in TOPAS 5. We use super-cell structures built by recursive stacking. The intergrowth structure of δ-Al_2O_3 contains 200 layers and 8000 atoms. The θ-Al_2O_3 contains 500 layers and 5000 atoms.

The effect of structural intergrowth on diffraction intensities for individual phases was evaluated with DIFFAX. DIFFAX is a recursive stacking simulation code developed by Treacy et. al [16] for understanding structural intergrowth.

Intergrowth in $\delta_{1,2}$-Al_2O_3 is formulated as a recursive stacking of four layers. The rules for stacking of individual layers in $\delta_{1,2}$-Al_2O_3 and creating an intergrowth structure under the probability of occurrence for each variant are listed in Table S1. The proportion of δ_1-Al_2O_3 is controlled by probability value (δ_1%), and δ_2-Al_2O_3 by probability value δ_2% = (100-δ_1%).

Table.S1. Stacking sequence probabilities for the formation of the $\delta_{1,2}$-Al_2O_3 intergrowth structure. The values show the probability of the next (i.e. $(n+1)^{th}$ layer) given the identity of the n^{th} layer. The value of δ_1% represents volume fraction of δ_1-Al_2O_3 and δ_2% the volume fraction of δ_1-Al_2O_3.

	Layer 1 (n+1)	Layer 2 (n+1)	Layer 3 (n+1)	Layer 4 (n+1)
Layer 1 (n)	-	δ_1%	-	δ_2%
Layer 2 (n)	δ_1%	-	δ_2%	-
Layer 3 (n)	-	δ_1%	δ_2%	-
Layer 4 (n)	δ_1%	-	-	δ_2%

Intergrowth in $\delta_{2,3,4}$-Al_2O_3 is formulated as a recursive stacking of eight layers differing only by their rotational and translation arrangement. The rules for stacking of individual layers in $\delta_{2,3,4}$-Al_2O_3 intergrowth is listed in Table S2. The sequence of layers for the individual variants in the intergrowth is defined by probability δ_x%. Unlike in the previous case of $\delta_{1,2}$-Al_2O_3, the recursive stacking in $\delta_{2,3,4}$-Al_2O_3 requires that the layers are translationally aligned during stacking and these offsets are included in Table S2.

Table.S2. Stacking sequence rules for intergrowth structures of $\delta_{2,3,4}$-Al_2O_3., showing probabilities for the $(n+1)^{th}$ layer given the identity of the n^{th} layer. The value of δ_2%, δ_3%, δ_4% represents the fractions of δ_2-Al_2O_3, δ_3-Al_2O_3 and δ_4-Al_2O_3 respectively. The layers 5^*, 6^*, 7^*, 8^* are identical with layers 1, 2, 3, 4 but with the origin displaced by [0.5,0.5,0]. The numbers in square brackets indicate the translation along *x* and *y* required for each stacking operation.

	Layer 1 (n+1)	Layer 2 (n+1)	Layer 3 (n+1)	Layer 4 (n+1)	Layer 5^* (n+1)	Layer 6^* (n+1)	Layer 7^* (n+1)	Layer 8^* (n+1)
Layer 1 (n)	-	δ_2% *R=[0,0]*	-	δ_3% *[-0.25,0.25]*	-	δ_4% *[0,0]*	-	-
Layer 2 (n)	δ_2% *[0,0]*	-	δ_3% *[0,0]*	-	δ_4% *[0,0]*	-	-	-
Layer 3 (n)	-	δ_3% *[0.25,-0.25]*	-	δ_2% *[0,0]*	-	-	-	δ_4% *[0,0]*
Layer 4 (n)	δ_3% *[0,0]*	-	δ_2% *[0,0]*	-	-	-	δ_4% *[0,0]*	-
Layer 5^* (n)	-	100% *[0.5,0.5]*	-	-	-	-	-	-
Layer 6^* (n)	100%	-	-	-	-	-	-	-

	[0.5,0.5]							
Layer 7* (n)	-	-	-	100% *[0.5,0.5]*	-	-	-	-
Layer 8* (n)	-	-	100% *[0.5,0.5]*	-	-	-	-	-

Twinning in θ-Al_2O_3 can be formulated relatively simply as the recursive stacking of two layers. The rules for recursive stacking in θ-Al_2O_3 are listed in Table S3. The transition from one layer to identical layer corresponds to an un-twinned configuration, while transitions between differing layers corresponds to twinning, with a probability of (twin%). Translational offsets required to accomplish stacking are reported in Table.S3.

Table.S3 Rules for stacking formation of twinning in θ-Al_2O_3.

	Layer 1 (n+1)	Layer 2 (n+1)
Layer 1 (n)	(100-twin)% *R=[-0.25,0.5]*	twin% *R=[-0.25,0.5]*
Layer 2 (n)	twin% *R=[0.25,0.5]*	(100-twin)% *R=[0.25,0.5]*