

COMMENTS

Comment on “Examination of Spinel and Nonspinel Structural Models for γ -Al₂O₃ by DFT and Rietveld Refinement Simulations”

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Recently, Sun et al.¹ compared different bulk models for γ -alumina using DFT simulations and Rietveld refinement. Their main conclusion is that spinel-based models accurately reproduce the features of diffraction pattern and they rule out our recently proposed “nonspinel” model.^{2–4} In this comment, we give a critical analysis of their results.

First, we must recall why solving the γ -alumina bulk structure is a challenge, being the subject of many experimental works and recent theoretical investigations. Most of these crucial experimental data are described in a detailed review by P. Euzen and colleagues,⁵ which Sun et al.'s paper seems to have overlooked. γ -Al₂O₃ belongs to the class of materials of so-called transition aluminas produced by calcination of aluminum hydroxides (boehmite, gibbsite, bayerite). The structure of a transition alumina is mainly determined by the nature of the starting aluminum hydroxide and by the thermal treatment. For γ -alumina, the starting material is the monohydroxide, boehmite γ -AlOOH. The phase transformation from boehmite into γ -alumina occurs between about 450 °C and 700 °C, depending on the degree of crystallinity of boehmite. For higher temperatures, phase transformation to other transition alumina polymorphs occurs: δ -alumina (above 700–800 °C), θ -alumina (above 1000 °C). In this case, the stable α -alumina (corundum) is recovered above 1100–1200 °C. The nonspinel model proposed in ref 2 has been established by the theoretical study of boehmite calcination, following a reaction path for the solid–solid dehydration reaction dictated by a principle of minimal structural change.

The distinction between γ -, δ -, and θ -alumina is mainly based on significant differences of their diffraction patterns. Their common structural features are that the oxygen atom sublattice is a distorted face centered cubic one, and that aluminum atoms sit in the tetrahedral (Al_{IV}) and octahedral (Al_{VI}) interstices of the oxygen network. During calcination, aluminum atoms diffuse into the O atoms lattice: the Al_{IV} percent increases from γ -alumina (typically 20–30%) to θ -alumina (typically 40–50%). As a consequence, these transition aluminas should be

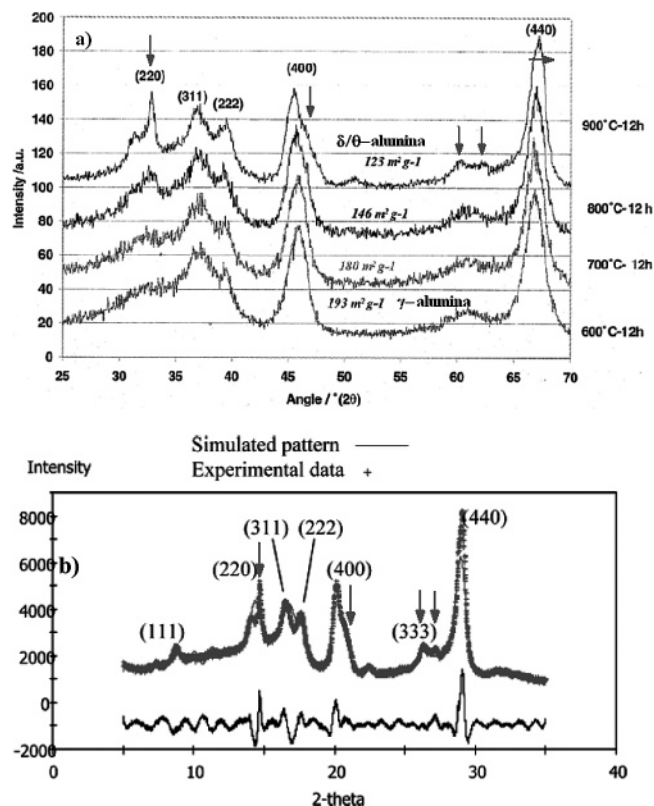


Figure 1. (a) XRD patterns (X-ray copper source) of alumina samples, obtained from boehmite and calcined at different temperatures (600, 700, 800, and 900 °C). The spinel structure (*hkl*) indices and the sample surface area (SBET in m²·g⁻¹) are reported (from ref 6). (b) SXPD pattern by Sun et al. (X-ray $\lambda = 0.69876$ Å; see ref 1). Arrows represent the features, listed in the text, of the transition from γ -alumina to δ -alumina (and start of θ -alumina development).

mainly considered as a continuum of metastable structures instead of well-defined crystalline compounds. These considerations highlight the difficulties encountered to establish rigorous models of γ -alumina bulk structure: such elucidation requires one to consider with great care the preparation conditions and the experimental background of the alumina samples submitted for any investigation.

In their work, Sun et al. used a commercial sample (Davicat AL2700) to obtain their reference X-ray diffraction (XRD) pattern of what they claim to be γ -Al₂O₃. A careful examination of the pattern reveals that the commercial sample is not made of γ -Al₂O₃ but rather of δ -alumina (with the start of θ -alumina development), called “ δ/θ -alumina” in what follows. Indeed, the following features (see also Figure 1a) reflect the transition from γ - to δ/θ -alumina, as shown by previously published studies:^{2,5,6}

- (i) the rise of the (220) reflection,
- (ii) the shoulder of the (400) reflection,
- (iii) two peaks at about 27° (2 θ) (for $\lambda = 0.69876$ Å) or 63° (2 θ) (for a copper source),
- (iv) slight shift of the (440) reflection toward a larger angle.

In the absence of further sample characterizations (²⁷Al

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NMR), we strongly suspect that the commercial sample is not a γ -alumina sample, and was calcined at a temperature above 700 °C.

Concerning the Rietveld refinement, the authors reject the nonspinel model because this model is “completely out of phase with the experimental observed synchrotron X-ray powder diffraction (SXPD) pattern at 2θ between 13° and 19°”. In these region, the pattern exhibits characteristic peaks of δ/θ -alumina, especially the (220) reflection. In γ -alumina samples, the (220) reflection is more diffuse because of the disorder of tetrahedral sites (see Figure 1a). Hence, it is not surprising that the nonspinel model of γ -alumina proposed in ref 2 does not reproduce the SXPD pattern of Sun et al. In contrast, it must be seen as a proof of the validity of the nonspinel model for γ -alumina. We do not claim that the nonspinel model proposed in ref 2 is the most accurate one for γ -alumina structure. However, it provides the best compromise between the size of the bulk structure tractable by ab initio calculation and accurate reproduction of experimental γ -alumina properties (XRD diagram, Al_{IV} content, bulk modulus,⁴ etc.).

In their conclusion, the authors claim that “the spinel-related model can represent major features of γ - Al_2O_3 , reasonably well”. Considering that γ -alumina has a spinel-based structure leads to arbitrarily limiting the configuration space to some specific configurations. The recent works by Wolverton and Hass,⁷ and Paglia et al.⁸ provide further theoretical and experimental evidence of the presence of nonideal spinel sites in the γ -alumina structure. As also found by Wolverton and Paglia, the cation positions (expressed in the $Fd\bar{3}m$ symmetry) are of spinel type

8a and of nonspinel type 48f for the tetrahedral sites, and of nonspinel type 16c and of spinel type 16d for the octahedral sites. The octahedral 16c nonspinel sites can be regarded as the remnant fingerprint of the boehmite precursor: the so-called “ $\text{S}_{0,0}$ matrix” (Al_2O_3 network before migration of octahedral aluminum in tetrahedral sites, as defined in ref 2) contains cations in 16c and 16d octahedral positions only. These fully consistent results are completely overlooked or are reported in a misleading way by Sun et al.

For all these reasons, we think that the determination of the γ -alumina structure by Sun et al.¹ with reference to a commercial sample that is not fully characterized is strongly questionable.

References and Notes

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