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Distribution of tetrahedral and octahedral Al sites in gamma alumina

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Abstract

Experimental and computational studies of γ-Al_2O_3 show that $70 \pm 2\%$ of Al ions occupy octahedral interstitial sites in the fcc oxygen structure, and the rest tetrahedral sites. The experimental data come from ^{27}Al MAS NMR and the theoretical results from ab initio quantum mechanical energy calculations for nine superlattice structures, analysed to extract various parameters which were then fed into a Monte Carlo simulation of the γ-Al_2O_3 structure. The simulation throws new light on the reasons for the structural disorder.

1. Introduction

Gamma alumina has uses in pharmaceuticals, as a catalyst support and as a filler in paints and explosives. Most practical uses rely on the fact that the material is invariably microcrystalline [1]. While the oxygen ions form a well-defined face centred cubic (fcc) structure, the Al ions are to some degree disordered, occupying both octahedral (Oh) and tetrahedral (T) interstitial sites as shown by the environment-sensitive infrared and Raman vibration spectroscopies [2]. Near the crystal surface the disorder in the bulk allows a wide diversity of relaxation of Al positions under surface electrostatic and elastic forces, giving a low surface energy [3] which in turn tends to give the material its highly dispersed form.

The disordered nature of γ-Al_2O_3 is therefore basic to its various properties, and we present the first results of computational and experimental studies of this disorder in terms of the fraction F_{Oh} of Al ions occupying the Oh sites. The material is often described as having a defective spinel structure [4]. The spinel structure has three cations per four oxygen ions (two on Oh and one on T sites) which has to be reduced by one-ninth for Al_2O_3. The fraction F_{Oh} can vary between 62% and 75% according to how many cation vacancies are on the Oh or the T sites. The fraction F_{Oh} of octahedral Al does not appear to have been established previously, and we have determined it by two independent methods. The first is experimental using ^{27}Al magic-angle-spinning (MAS) nuclear magnetic resonance (NMR); the second is a three-stage computational study.

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2. Solid-state NMR

γ-Al_2O_3 and α-Al_2O_3 were prepared by dehydration of pseudoboehmite (Catapal B) for 24 h at 973 and 1373 K, respectively [5]. X-ray diffraction (XRD) patterns of as-prepared γ-Al_2O_3 and α-Al_2O_3, which were confirmed using the JCPDS database, show no other crystalline impurity (Fig. 1). The very broad peak of γ-Al_2O_3 indicates partial disorder in the atomic arrangement. To the best of our knowledge, the quantitative ratios of the populations of the octahedral and tetrahedral Al sites have not been determined, probably due to spectroscopic difficulties.

^{27}Al MAS NMR was used to measure the occupancy of different Al sites. The very short (< 10°) pulses [6], high (10–12 kHz) MAS rates and high magnetic field (9.4 T) [7] ensured that the spectra are quantitatively reliable. The ^{27}Al MAS NMR spectrum (Fig. 2a) of γ-Al_2O_3 gives two resonances at 64.2 and 6.8 ppm assigned to tetrahedral and octahedral Al, respectively [8], with the occupancies of 30 and 70 ± 1%, respectively. The ^{27}Al NMR spectra of γ-Al_2O_3 measured at 120 K show the same peak shape and position and occupancy of Al tetrahedral and octahedral site as at 293 K. The aluminium sites in γ-Al_2O_3 are therefore in the same chemical environment at 293 and 120 K. The ^{27}Al MAS NMR spectrum of α-Al_2O_3 (Fig. 2b) gives a single resonance at 12.3 ppm, showing that Al is present exclusively in the octahedral sites.

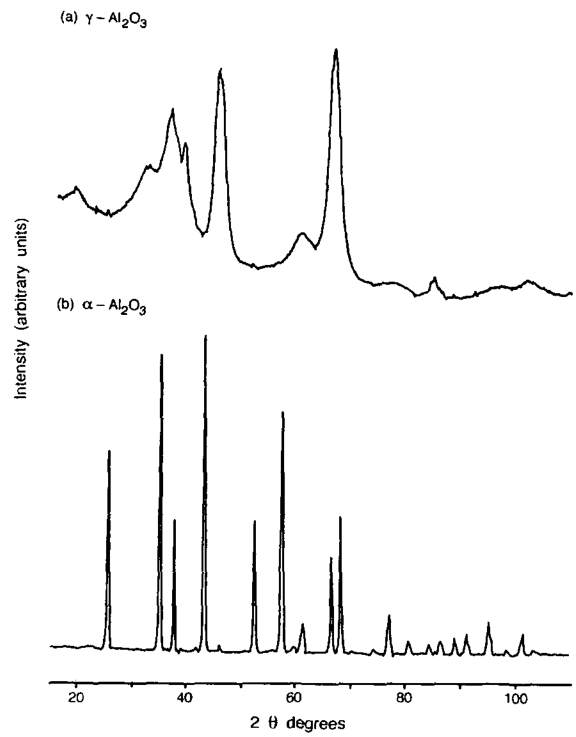

Fig. 1. XRD patterns of (a) γ-Al_2O_3 and (b) α-Al_2O_3 prepared by dehydration of pseudoboehmite at 700°C and 1100°C for 24 h, respectively.

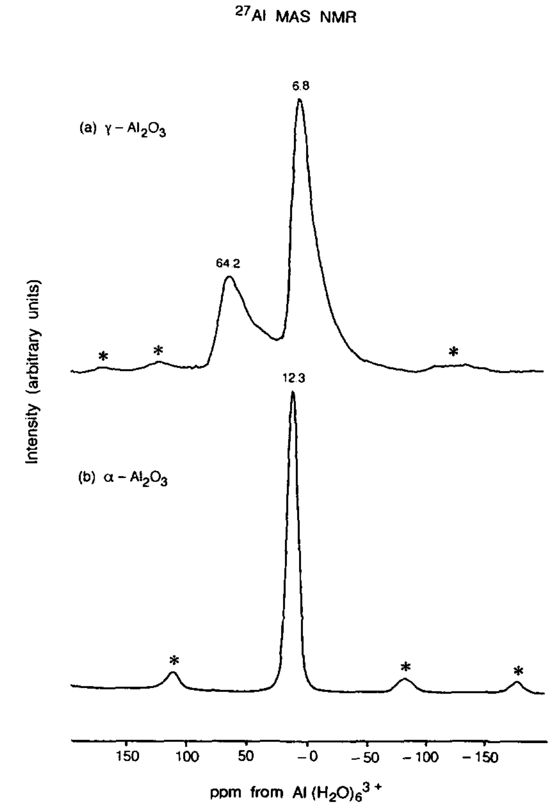

Fig. 2. ^{27}Al MAS NMR spectra of (a) γ-Al_2O_3 and (b) α-Al_2O_3. Asterisks denote spinning sidebands.

3. Computational study

In order to deduce the occupancy ratio of the Oh and T sites, it is necessary to simulate the equilibrium of the whole system. This of course involves approximations, but the methodology is rigorous and the ab initio electronic structure calculations provide some reliable energies.

We assume that the total energy of the system of Al ions in the fcc oxygen structure can be written as

$$E = E_0 + \mu(N_{Oh} - N_T) + \Sigma\Sigma J(\boldsymbol{r}_i, \boldsymbol{r}_j) \quad (1)$$

where N_{Oh} and N_T are the total numbers of Al ions on Oh and T sites, respectively, and μ is the inherent energy difference between the two types of site. The last term in (1) is summed over all pairs, and $J(\boldsymbol{r}_i, \boldsymbol{r}_j)$ is the interaction between the ith and jth Al ions situated at $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$. This is entirely analogous to the treatment of Si/Al ordering in the mineral cordierite [9]. The first stage is to set up a database of energies and structures from which the parameters in (1) can be determined by fitting. We chose nine 'artificial' crystal structures, all with an orthorhombic superlattice cell of dimensions 5.599 Å × 4.849 Å × 6.857 Å containing twelve oxygen ions in the fcc structure with the spacing found in γ-Al_2O_3 [4]. The eight Al ions are distributed differently between the Oh and T sites in the nine cases, the number in Oh sites extending over the full range from zero to eight in order to determine μ as well as is possible.

The energies of the nine structures were computed by ab initio electronic structure calculations, solving the Schrödinger equation for the whole system using the density functional method with the usual local density approximation for exchange and correlation [10]. This was considered as the only reliable representation of the interatomic bonding, particularly for the energy difference between Oh and T coordination for which, in a different context, a reputable empirical shell model for the ions had given disastrous results [11]. The method chosen for the ab initio electronic structure calculations has been reviewed [10] and is widely used for calculations on solids in physics and materials science, for example sliding at grain boundaries [12]. More recently the technique has been applied to questions of chemical interest including catalysis on zeolites [13], molecular adsorption and dissociation at metallic [14,15] and oxide [16] surfaces, and defects in oxides [17,18]. The ions were represented by norm-conserving optimised pseudopotentials [19] and the electron orbitals expanded in plane waves. The local density approximation was used for the exchange and correlation functional with the parametrisation by Pardew and Zunger [20] of the Monte Carlo calculations of Ceperley and Alder [21]. This gave a good lattice constant and bulk modulus, as it has done for other oxides [17,18], so that no generalised gradient corrections were applied. The electron system was converged to self-consistency and the Al ionic positions relaxed to equilibrium using the CASTEP code. The oxygen positions in this first study were not yet relaxed because of slow convergence and limited computer resources. It was found that the Al atoms mostly lie off-centre, tending to form three shorter Al–O bonds particularly in the Oh positions.

The second stage of the theoretical analysis involved fitting the parameters of the structural energy (1) to the data base of nine energies of the ab initio calculations. Of course, the database is not nearly large enough (and can never be large enough with ab initio calculations) to determine the large number of $J(\boldsymbol{r}_i, \boldsymbol{r}_j)$ parameters if we distinguish all those with geometrically distinct vectors $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ unrelated by symmetry. We were therefore forced to assume that the J_{ij} fit a more or less smooth radial function, and lumped together all $J(\boldsymbol{r}_{ij})$ with $\boldsymbol{r}_{ij}$ in the range $(r_m \pm 0.2)$ Å representing them by one number $J(r_m)$ using six bins with $r_m = 2.6, 3.0, \ldots, 4.6$. We plan to extend the database and its analysis, but in the meantime we have also ignored in $J(\boldsymbol{r}_i, \boldsymbol{r}_j)$ the difference between i, j in the Oh or T sites.

The energy per superlattice cell for each of our database structures is then

$$E = E_0 + \mu(N_{Oh} - N_T) + \sum_{m=1}^{6} J(r_m) N(r_m), \quad (2)$$

where $N(r_m)$ is the number of pairs of Al ions with separation in the range $(r_m \pm 0.2)$ Å. A fit of (2) to the nine structural energies gives the parameters listed in Table 1. We note that, as expected, μ is negative, i.e. the Oh site has inherently lower energy. The $J(r_m)$ represent a repulsive interaction of modest strength, corresponding to a Coulombic screened

Table 1
Values of the fitted parameters (in eV)

μ	J (2.6)	J (3.0)	J (3.4)	J (3.8)
−1.3	0.6	0.7	0.1	0.1

effective charge of less than one electron on the aluminium atoms.

The final stage is to feed the so-determined parameters into a simulation of the Al ions distributing themselves among all the possible sites to minimize the total energy. This was applied to 576 Al ions hopping amongst the interstitial Oh and T sites of an fcc structure of 864 oxygen ions, with periodic boundary conditions, starting from various initial configurations of the Al ions. Analogous simulations on α-Al_2O_3 with an hcp oxygen structure always resulted in the correctly ordered structure, which gives confidence in our methodology and parameters. The simulations for γ-Al_2O_3 always resulted in a disordered state with a fraction $F_{Oh} = 70 \pm 3\%$ of Al on the Oh sites, irrespective of the starting conditions which included random and ordered structures with F_{Oh} initially varying from 0 to 100%. The interactions in Table 1 are much larger than $k_B T$, so that temperature is not an important factor. The experimental value $F_{Oh} = 70 \pm 1\%$ given earlier agrees well with the theoretical value from the simulations which were completed before the ^{27}Al MAS NMR measurements were begun, giving added confidence to the result.

The simulations also shed some light on the reason why Al in γ-Al_2O_3 is disordered. In α-Al_2O_3 the Al ions are evenly spaced in their ordered pattern on the Oh sites among the hcp oxygen structure. A trial-and-error search with the fcc oxygen structure for γ-Al_2O_3 showed that no such evenly spaced ordered structure for the Al ions can be formed using the Oh sites only. Some of the Al–Al distances turn out to be too small, and if one starts with such a configuration the simulation shows that some aluminium ions jump to the adjacent T sites under the influence of close Al neighbour(s). This interaction is large enough to overcome the inherent energy difference μ between the occupation of the Oh and T sites. Once disorder sets in, no subsequent ordering is observed, presumably because there is some incommensurability in the ratio of two Al ions per total of nine sites of type Oh and T. We plan to study the structure in more detail and to determine how closely it resembles the spinel structure.

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