

# Mechanism of structural transformations during thermal decomposition studies of aluminium hydroxide polymorph

Thimmasandra Narayan Ramesh

Department of Studies and Research in Chemistry and Centre for Advanced Materials, Tumkur University, Tumkur 572 103

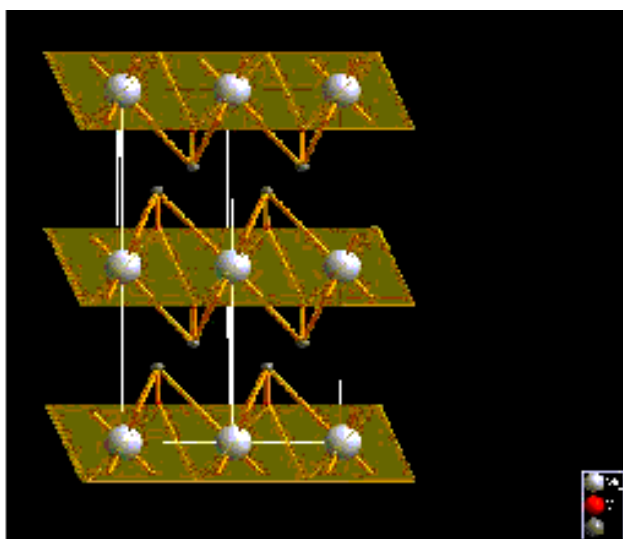
\*Author for correspondence: [adityaramesh77@yahoo.com](mailto:adityaramesh77@yahoo.com)

**Abstract :** Gibbsite, bayerite nordstrandite and doyelite are the different polytypic modifications of aluminum hydroxide. In this paper, we have investigated the thermal decomposition of gibbsite phase of aluminium hydroxide by isothermal heating at regular intervals of temperature. The structural changes incurred on heating the gibbsite phase was monitored using powder X-ray diffraction measurements. On heating the sample to 250°C, Al(OH)<sub>3</sub> transforms to AlOOH (boemite phase) and one mole of water is released. The boemite phase of AlOOH on further heating to high temperatures (600°C) leads to formation of defective spinel phase (Al<sub>2</sub>O<sub>3</sub>)<sub>0.133</sub>. The structure of defective phase of (Al<sub>2</sub>O<sub>3</sub>)<sub>0.133</sub> is retained even on heating to 870°C. The defective (Al<sub>2</sub>O<sub>3</sub>)<sub>0.133</sub> phase on suspending in water for 24 h, does not lead to rehydration nor reconstruction to gibbsite/boemite phase.

**Keywords:** Aluminium hydroxide, Gibbsite, Boemite, defect spinel, thermal decomposition, crystal structure

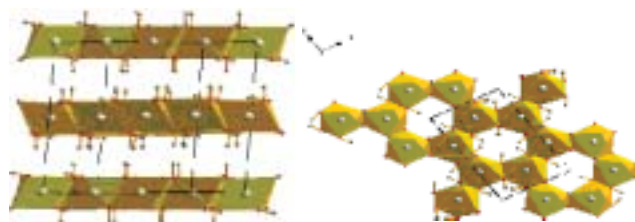
## 1. INTRODUCTION

Aluminium hydroxide crystallizes in different polymorphic modifications i.e., gibbsite, bayerite, norstrandite, doyelite [1-4]. These polytypic modifications exhibit layered structure and the crystal structure of these polytypes derived from mineral brucite prototype [4]. The structure of brucite comprises of metal hydroxide sheets stacked on top of each other at regular intervals. The structure sequence of metal hydroxide sheets can be represented by AcB AcB AcB — where A and C represents the position of hydroxyl ions while b denotes the position of divalent metal ion i.e magnesium (see Figure 1) [5].



**Figure 1** Crystal structure of bruite (magnesium hydroxide)

Aluminium hydroxide derives its crystal structure from prototype of brucite mineral. The structure of gibbsite comprises of metal hydroxide sheets stacked on top of each other at regular fashion. The anion constitute a hexagonal close packing in which cations occupy 2/3<sup>rd</sup> of the interstitial octahedral sites and 1/3<sup>rd</sup> are vacant. These vacant sictes are arranged in a periodic manner and the filled ocatahedral sites share three edtes with their adjacently filled octahedral. These sites. In an ideal gibbsite structure, the anion packing stacking sequence is AcB BcA AcB BcA ———. In reality, the sheets are slightly shifted along the a-direction thus crystallizing in monoclinic system. If the shift is along both ‘a’ and ‘b’ direction, then it will be a triclinic system [6,7]. Figure 2 shows the idealized crystal structure of gibbsite.



**Figure 2** Crystal structure of gibbsite

### Bayerite

The idealized crystal structure of bayerite is represented by the anionic stacking sequence AB AB AB AB ——— [8]. Figure 3 shows the crystal structure of Bayerite in which the oxygen ions of one layer are located above the hollows in the next sandwich. The anion layer sequence is ABABABA (h.c.p). The crystal structure has been

reported in two different space groups i.e P-3 and P21/c which comprises of two set of equivalent protons in the voids.

**Nordstrandite**

The crystal structure of nordstrandite comprises of a mixture of bayerite and gibbsite type of stacking sequence i.e AB BA AB BA and AB AB AB AB leading to AB AB BA BA AB — or AB BC CA AB BC CA — type of arrangement [8]. Figure 4 shows the crystal structure of nordstrandite.

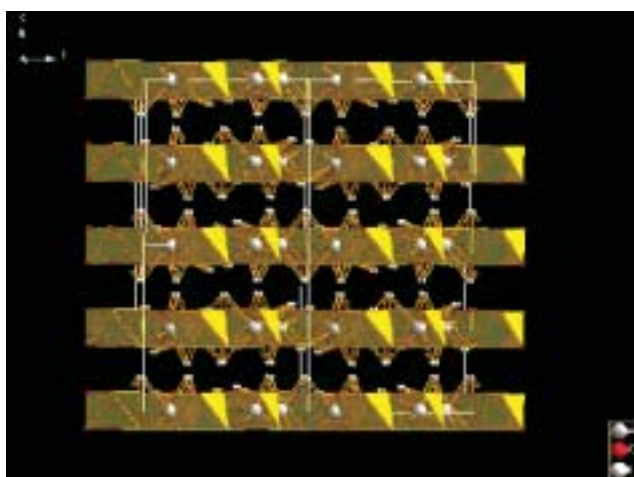


Figure 3 Crystal structure of bayerite.

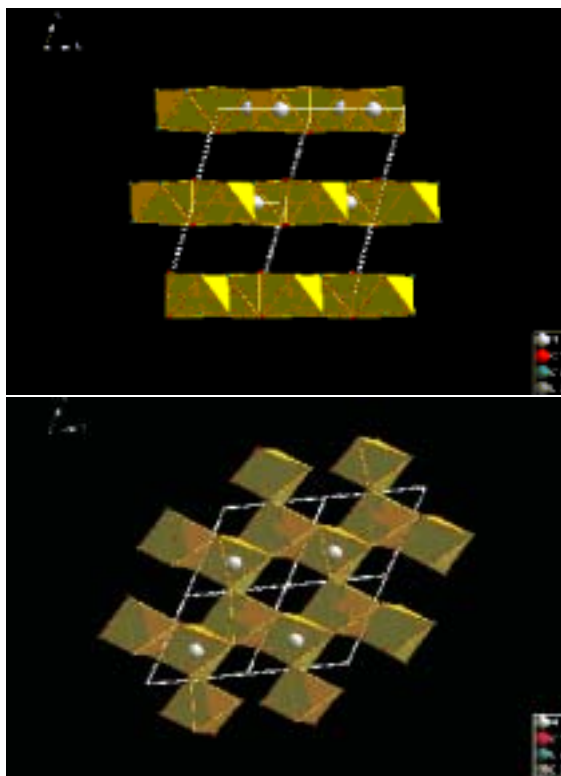


Figure 3 Crystal structure of nordstrandite.

The structure of doyleite crystallizes in monoclinic system [9]. In this article the structural transformation of aluminium hydroxide-gibbsite phase when subjected to thermal treatment and the products obtained were examined to determine the phase formation during the intermediate stages of heating to get an insight into the structural changes.

**2. EXPERIMENTAL SECTION**

Gibbsite phase of aluminium hydroxide was procured from commercial source and used as such.

The sample was characterized by powder X-ray diffraction (PXRD) using a Bruker D-8 Advance X-ray powder diffractometer (Cu Ka source,  $\lambda=1.5418 \text{ \AA}$ ). Data collection was obtained at a scan rate of  $4^\circ 2\theta \text{ min}^{-1}$ ;  $2\theta$  steps-  $0.05^\circ$ . Gibbsite phase of aluminium hydroxide was subjected to isotherm heating at different intervals of temperature (RT and 250, 300, 600, 800, and  $870^\circ \text{C}$ ) for 1 h each and allowed to cool to room temperature prior to the measurement of X-ray powder diffraction data.

**3. RESULTS AND DISCUSSION**

Figure 5 shows the powder X-ray diffraction pattern of gibbsite phase of aluminium hydroxide (top trace) compared with the simulated patterns of gibbsite (bottom trace) and bayerite (middle trace). Dehydration of gibbsite results in the release of water molecules with the formation of aluminium oxyhydroxide during which half of the anions must leave the crystal structure

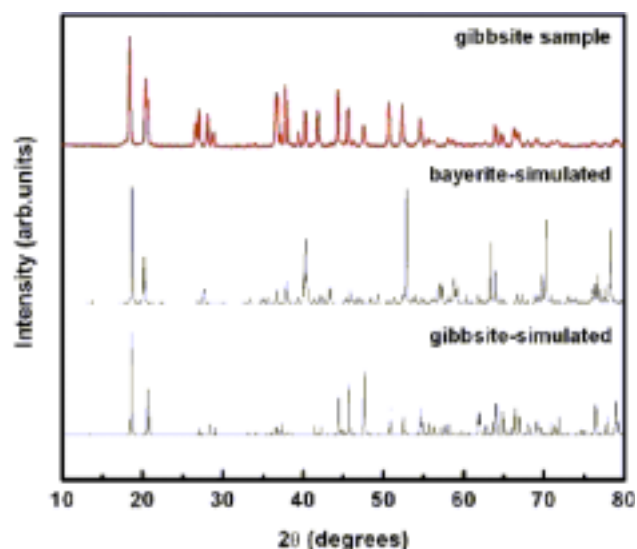
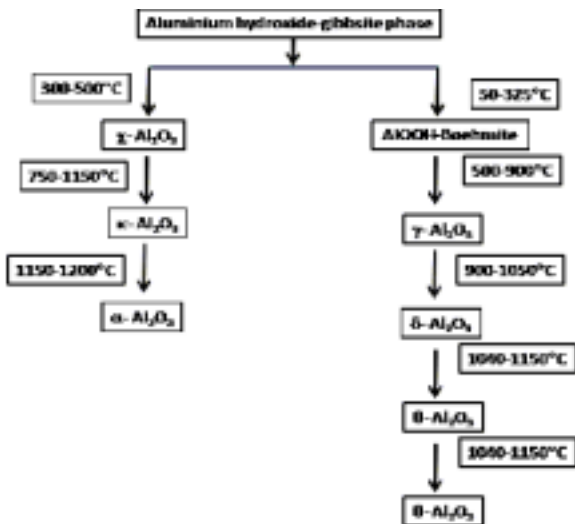


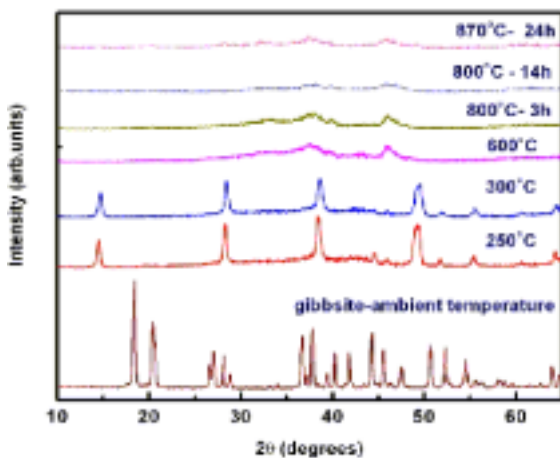
Figure 5. powder X-ray diffraction pattern of aluminium hydroxide-gibbsite phase (top trace) compared with the simulated patterns of gibbsite-bottom trace and bayerite-middle trace).

Thermal decomposition of aluminum hydroxide could proceed via the formation of aluminium oxyhydroxide or direct conversion to aluminium oxide without any intermediate phase [10]. Lippens classified the metastable aluminas ( $Al_2O_3$ ) when calcinations of gibbsite was carried out at atmospheric pressure [11] (see Figure 6).



**Figure 6** Flow chart of different phases formed during the decomposition of gibbsite phase of aluminium hydroxide.

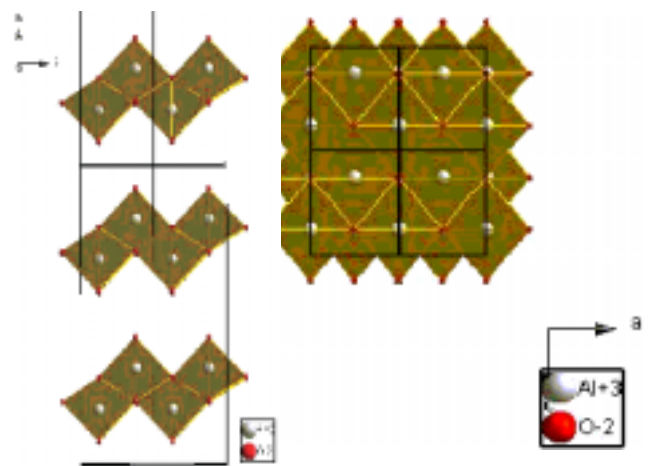
Finely divided products are formed which can transform directly to alumina between 250°C while crystalline phase of the gibbsite sample on calcinations leads to the formation of aluminium oxyhydroxide. In Figure 6 is shown the different phases of aluminium oxide formed during the heat treatment is demonstrated. Figure 7 shows the powder X-ray diffraction patterns of aluminium hydroxide on heating to different temperatures.



**Figure 7.** PXRD patterns of aluminium hydroxide-gibbsite phase on heating to different temperatures.

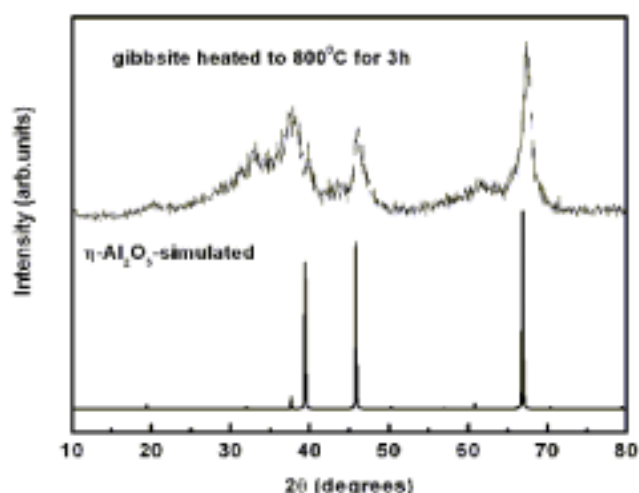
Thermal decomposition of aluminium hydroxide generates metastable oxides which are poorly crystalline in nature. The structure of these products depends strongly on the initial structure of the hydroxide. On heating gibbsite, we observe boehmite phase of  $AlOOH$  at 250°C and during the process half of the anions are expelled from aluminium hydroxide and the packing sequence of the anions changes significantly. If the sample is crystalline, it may lead to the formation of the boehmite phase of aluminium oxyhydroxide [12, 13].

If the crystallite size of the  $AlOOH$  is in micrometer range, then pseudo-boehmite is observed while the  $AlOOH$  is in the nanometer range, then we observe boehmite. Boehmite structure comprises of double chains of edge sharing octahedra which has the anionic stacking sequence BB CC AA BB CC— [14]. The boehmite phase is metastable and its formation is always kinetically favoured at lower temperature.



**Figure 8.** Crystal structure of aluminium oxyhydroxide (boehmite phase) along a and b-directions.

The boehmite phase of  $AlOOH$  on heating to higher temperature (600 °C) lead to the formation of defective spinel phase of  $(Al_2O_3)_{0.133}$  rather than perfect  $Al_2O_3$  Figure 8 shows the powder X-ray diffraction pattern of the gibbsite heated to 800 °C.



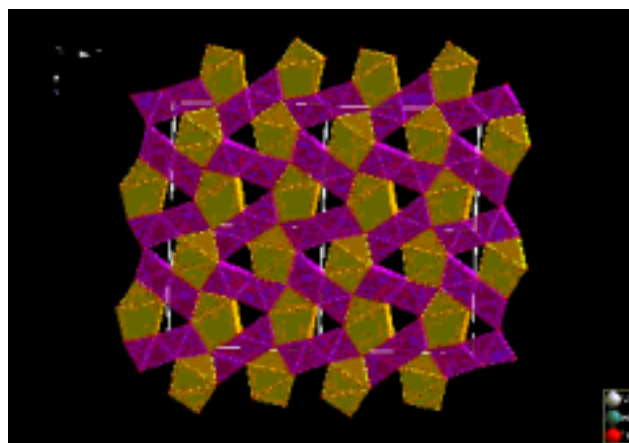
**Figure 9. Powder X-ray diffraction pattern of aluminium oxide obtained on heating boehmite to 800 °C (upper trace) compared with the simulated powder X-ray diffraction pattern of h-Al<sub>2</sub>O<sub>3</sub> (lower trace).**

The thermal decomposition of boehmite reveals that a cation deficient inverse spinel modification is formed with low crystallinity.

Dehydration of boehmite requires short range rearrangement of anions in the crystal structure thus leading to the formation of defect-alumina [15]. The phase transition from boehmite to alumina occurs via topotactic transformation and the energy required is low [16]. During the formation of defective h- (Al<sub>2</sub>O<sub>3</sub>)<sub>0.133</sub>, half of the anions are eliminated from the aluminium oxyhydroxide, due to which the packing sequence of anions changed drastically. Figure 9 shows the powder X-ray diffraction patterns of defective phase of (Al<sub>2</sub>O<sub>3</sub>)<sub>0.133</sub>.

#### Normal spinel

The structure of the spinel comprises of anions arranged in cubic close packed arrangement i.e ABC ABC ABC— in which divalent metal ions such as magnesium occupies tetrahedral and aluminium (III) ion occupies half of the octahedral sites in the lattice [8]. Figure 10 shows the crystal structure of spinel phase of MgAl<sub>2</sub>O<sub>4</sub>.

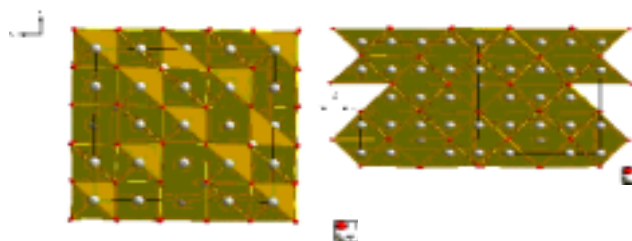


**Figure 10 shows the crystal structure of normal spinel (model compound-MgAl<sub>2</sub>O<sub>4</sub>).**

#### Inverse spinel

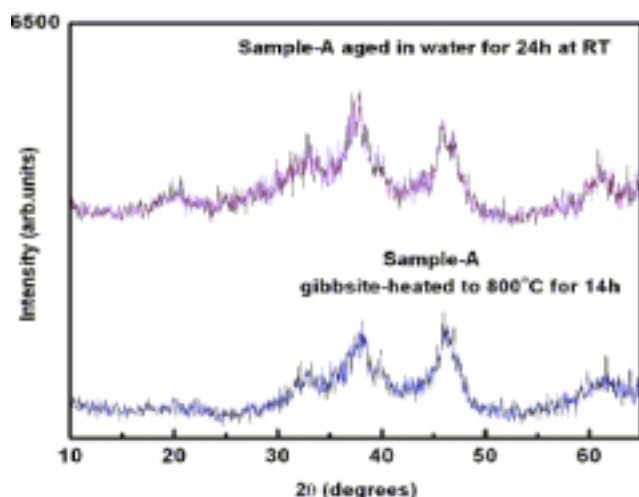
In case of inverse spinel, both the divalent and trivalent ions are uniformly distributed in the octahedral and tetrahedral sites of which divalent ions are preferably octahedrally coordinated [8].

The defective phase of (Al<sub>2</sub>O<sub>3</sub>)<sub>0.133</sub> is retained even on heating to 870°C. The structure of defective spinel phase (Al<sub>2</sub>O<sub>3</sub>)<sub>0.133</sub> is shown in Figure 11.



**Figure 11. Crystal structure of defective phase of alumina along different crystallographic directions.**

The defective (Al<sub>2</sub>O<sub>3</sub>)<sub>0.133</sub> phase on suspending in water for 24 h, does not lead to rehydration nor formation of boehmite phase of AlOOH/gibbsite phase of aluminium trihydroxide (see Figure 12). This indicates that the defective alumina is thermodynamically stable and does not lead to any changes in the structure or the composition of the sample.



**Figure 12 : powder X-ray diffraction patterns of Gibbsite phase of aluminium hydroxide calcined to 800°C (14h) (lower trace)-sample A; sample-A aged in water for 24h (upper trace)**

#### 4. CONCLUSIONS

The data provides insight into the understanding of reconstruction process in hydrotalcites. The decomposed products of hydrotalcite on suspending in water reconstructs back to hydrotalcite phase. If the phase formed during the decomposition of aluminium hydroxide leads to formation of defective phase of  $(Al_2O_3)_{0.133}$  then it may not undergo reconstruction in water. Thus the result provides significant information that memory effect depends on the nature of the phase obtained during decomposition.

#### 5. ACKNOWLEDGEMENTS

TNR gratefully thanks Prof. P. Vishnu Kamath, Department of Chemistry, Bangalore University for XRD measurements and laboratory facilities and his unconditional support throughout his career.

#### 6. REFERENCES

1. R. Demichelis, Y. Noel, B. Civalleri, C. Roetti, M. Ferrero, R. Dovesi, The Vibrational Spectrum of  $\delta$ -AlOOH Diaspore:

An Ab Initio Study with the CRYSTAL Code, *J. Phys. Chem. B* 111, 2007, 9337.

2. Y. Noel, R. Demichelis, F. Pascale, P. Ugliengo, R. Orlando, R. Dovesi "Ab initio quantum mechanical study of gamma-AlOOH boehmite: structure and vibrational spectrum" *Phys. Chem. Miner.*, 36, 2009, 47-59.

3. R. Demichelis, Y. Noel, C. M. Zicovich-Wilson, C. Roetti, L. Valenzano, R. Dovesi, *Journal of Physics: Conference Series*, 117, 2008, 012013.

4. R. Demichelis, B. Civalleri, Y. Noel, Al. Meyer, R. Dovesi, Structure and stability of aluminium trihydroxides bayerite and gibbsite: A quantum mechanical ab initio study with the Crystal06 code *Chem. Phys. Lett.* 2008, 465, 220.

5. H. R. Oswald, R. Asper, In Preparation and crystal growth of materials with layered structures R. M. A. Lieth, Ed.; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1977; Vol. 1, p 71.

6. G. R. Clark, K.A.Rodgers, G. S. Henderson, The crystal chemistry of doyleite,  $Al(OH)_3$ , *Z Kristallogr* 213, 1998, 96-100.

7. H. Saalfeld and O. Jarchow, "Die Kristallstruktur Von Nordstrandit,  $Al(OH)_3$ ," *Neues Jahrb. Mineral. Abh.* 109, 1968, 185-191.

8. A. F. Wells, *Structural Inorganic Chemistry*, 4th Edition, Oxford: Clarendon Press, 1975.

9. C. Y. Chao, B. J. Sabina, A. C. Roberts, Doyleite, a new polymorph of  $Al(OH)_3$ , and its relationship to bayerite, gibbsite and nordstrandite. *Can. Miner.* 23 (1985) 21-28.

10. H. SAALFEED, the dehydration of gibbsite and the structure of a tetragonal, *Mineralogical Society*, 3, 19, 249.

11. The formation and thermal decomposition of aluminium hydroxide doped with Fe(III) and Cr(III), J. VAN DIJK, PhD Thesis, 1976.

12. P. Alphonse and M. Courty, Structure and thermal behavior of nanocrystalline boehmite, *Thermochimica Acta*, 20, 2005, 75-89.

13. K. WEFERS and C. MISRA Oxides and hydroxides of aluminium. *Aloca Technical Paper* 19 (1987) 92 (revised)

14. G. G. christoph, C. E. corbato, D. A. hofmann, R. tettenhorst, the crystal structure of boehmite, *Clays and Clay Minerals.* 27, 81-86.

15. *Handbook of sol-gel science and technology. 3. Applications of sol-gel.* edited by Sumio Sakka, Springer, 2005.

16. R.-S. Zhou and R. L. Snyder, Structures and transformation mechanisms of the  $\eta$ ,  $\gamma$  and  $\theta$  transition aluminas, *Acta Cryst.* B47, 1991, 617-630.