

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244405074>

# Evidence of FCC Crystallization of SiO<sub>2</sub> Nanospheres

ARTICLE *in* LANGMUIR · NOVEMBER 1997

Impact Factor: 4.46 · DOI: 10.1021/la970589o

CITATIONS

238

READS

30

6 AUTHORS, INCLUDING:



**Hernán Míguez**

Spanish National Research Council

164 PUBLICATIONS 5,332 CITATIONS

SEE PROFILE



**Francisco Meseguer**

Spanish National Research Council

174 PUBLICATIONS 5,195 CITATIONS

SEE PROFILE



**Jose S Moya**

Spanish National Research Council

256 PUBLICATIONS 4,667 CITATIONS

SEE PROFILE



**Luis Vázquez**

Spanish National Research Council

236 PUBLICATIONS 4,671 CITATIONS

SEE PROFILE

# Evidence of FCC Crystallization of SiO<sub>2</sub> Nanospheres

H. Míguez,<sup>†,‡</sup> F. Meseguer,<sup>\*,†,‡</sup> C. López,<sup>†,‡</sup> A. Mifsud,<sup>§</sup> J. S. Moya,<sup>†</sup> and L. Vázquez<sup>†,‡</sup>

*Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco 28049, Madrid, Spain, Unidad Asociada CSIC-UPV, Departamento de Física Aplicada, Camino de Vera s/n, 46022 Valencia, Spain, and Instituto de Tecnología Química (UPV-CSIC), Avda, de los Naranjos s/n, 46022 Valencia, Spain*

*Received June 5, 1997. In Final Form: September 3, 1997\**

It is well-known that stacking of hard spheres results in close-packed structures. However, until recently, it was not clear which of the various possible phases (cubic, hexagonal, mixed, or random) was the stable one. We have performed a microscopy characterization of solid crystals made of monodisperse SiO<sub>2</sub> nanometric spheres. It was found that, for a wide range of particle diameters, the cubic phase is the only one present. This largely serves to confirm recent theoretical calculations by L. V. Woodcock which conclude that the cubic phase is the most stable one. This opens new prospects in the application of colloidal crystals to photonic band gap engineering.

The assembly of colloidal particles has attracted a great deal of attention from both the theoretical and experimental scientific communities. Many theoretical studies have been performed in order to determine which of the possible phases, face centered cubic (fcc), hexagonal close-packed (hcp), combinations of series belonging to them, or random stacking, is that of thermodynamic equilibrium for a close-packed structure of hard spheres. Only recently, Woodcock,<sup>1</sup> using computer simulations, has shown that the stacking of hard spheres in an fcc arrangement is the most stable one. Although Pusey et al. have shown that a tendency toward fcc ordering exists in slowly grown crystals of sterically stabilized poly(methyl methacrylate) nanospheres,<sup>2</sup> as far as we know, no experimental evidences have been shown that colloidal hard spheres crystallize in a pure fcc phase. We herewith present strong experimental evidence that natural sedimentation of aqueous dilute suspensions of SiO<sub>2</sub> nanospheres results in a crystalline fcc structure. A scanning electron microscopy (SEM) study of the sample morphology focused on crystalline facets obtained after sample cleavage is performed in order to demonstrate the existence of long range fcc ordering.

Ordered arrangements of nanometric particles can be a viable route to obtain systems with three-dimensional periodic modulation of the dielectric constant with a lattice parameter of less than 1  $\mu\text{m}$ , which, at the present time, is the main challenge in the field of photonic band gap technology.<sup>3,4</sup> In this sense, a sophisticated method<sup>5</sup> has been developed in order to force the colloidal crystallization in the fcc phase, which is more interesting, as a full photonic band gap is predicted for an appropriate index contrast realization.<sup>6</sup>

The SiO<sub>2</sub> spheres were synthesized following the Stöber–Fink–Bohn<sup>7</sup> method. Nanospheres with a diameter  $\phi$  ranging from 200 to 500 nm and a dispersion smaller

than 5% were obtained through strict control of the reaction conditions.<sup>8</sup> Afterward, dilute suspensions (10<sup>10</sup> spheres/cm<sup>3</sup>) of these spheres were allowed to sediment onto a pristine surface of a poly(methyl methacrylate) substrate (roughness  $< \phi/10$ ). Full sedimentation was attained after a long period of time (between 2 and 4 weeks).

The sample morphology was characterized with a JEOL-6300 scanning electron microscope. A detailed study of the growth surface by atomic force microscopy can be found elsewhere.<sup>9</sup> In Figure 1a such a surface of a sample made of 415 nm spheres is shown. A close-packed triangular arrangement, common to the different possible stackings of layers, can be seen. In order to discriminate between the different possible phases, it is essential to investigate the internal ordering through the characterization of lateral facets as obtained by sample cleavage. Several kinds of arrangements were observed, all of which are compatible only with the fcc structure. In Figure 1b, a square arrangement can be clearly observed, which can only correspond to a {100} type face of an fcc structure. No facet of an hcp structure can show such an arrangement. Figure 1c shows an image of an internal {111} type facet. This is morphologically equivalent to the growth surface, but it is oriented in a direction which forms an angle of 70.5° with the former. Again, no facets belonging to an hcp system may present such a structure. Figure 1d is an example of a {110} type surface. The arrangement here is a rectangular lattice where the particles are one  $\phi$  apart in one direction and  $\phi\sqrt{2}$  apart in the other. Similar sorts of arrangements exist in the hcp structure, but there the ratio between the rectangle sides is  $\phi\sqrt{8/3}$ . This facet is less frequently found due to its low density, which makes its appearance unlikely after cleavage.

In order to further investigate the different crystalline planes occurring in the samples, micrographs of the different types of terraces observed in the cleaved edge were obtained. A typical result is shown in Figure 2, where several facets can be observed. In the center of the picture, a corner formed by two triangular symmetry

\* To whom correspondence should be addressed at Unidad Asociada CSIC-UPV. E-mail: fmeseg@fis.upv.es.

<sup>†</sup> Instituto de Ciencia de Materiales de Madrid (CSIC).

<sup>‡</sup> Unidad Asociada CSIC-UPV.

<sup>§</sup> Instituto de Tecnología Química (UPV-CSIC).

© Abstract published in *Advance ACS Abstracts*, October 1, 1997.

(1) Woodcock, L. V. *Nature* **1997**, *385*, 141.

(2) Pusey, P. N.; van Megen, W.; Barlett, P.; Ackerson, B. J.; Rarity, J. G.; Underwood, S. M. *Phys. Rev. Lett.* **1989**, *63*, 2753.

(3) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059.

(4) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, *386*, 143.

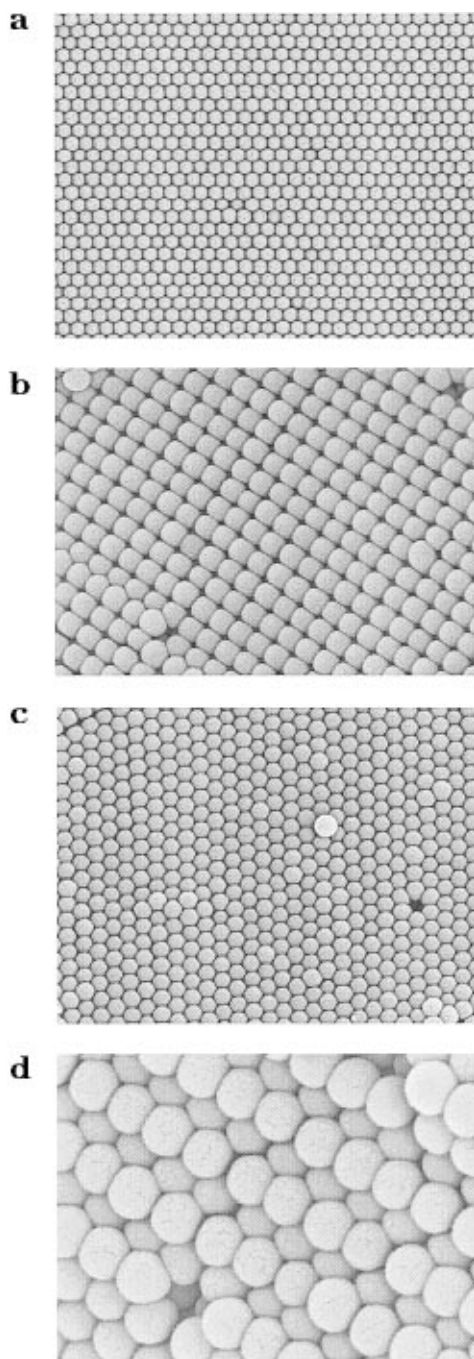
(5) van Blaaderen, A.; Ruel, R.; Wiltzius, P. *Nature* **1997**, *385*, 321.

(6) Sözüer, H. S.; Haus, J. W. *Phys. Rev. B* **1992**, *45*, 13962.

(7) Stöber, N.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(8) Mayoral, R.; Requena, J.; Moya, J. S.; López, C.; Cintas, A.; Míguez, H.; Meseguer, F.; Vázquez, L.; Holgado, M.; Blanco, A. *Adv. Mater.* **1997**, *9*, 257.

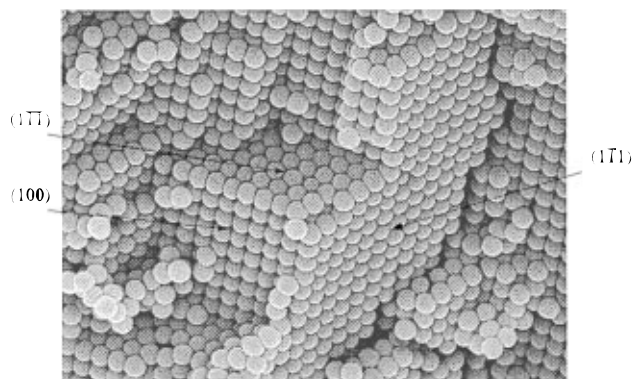
(9) Salvarezza, R. C.; Vázquez, L.; Míguez, H.; Mayoral, R.; López, C.; Meseguer, F. *Phys. Rev. Lett.* **1996**, *77*, 4572.



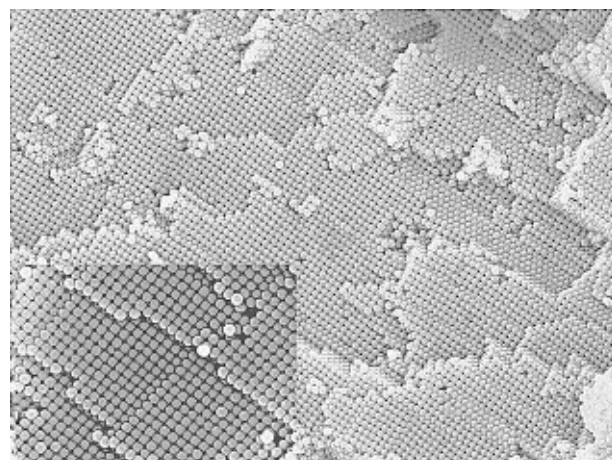
**Figure 1.** SEM micrographs of top (a) and different kinds of lateral surfaces observed in a cleaved edge (b–d). All images correspond to a sample made of 415 nm diameter spheres. Although the triangular arrangement observed in the top surface (a) could correspond to any of the possible stacking sequences of sphere layers, the square, triangular, and rectangular arrangements observed in the cleaved edges (shown in b, c, and d, respectively) are only compatible with an fcc packing, since any crystalline face of a hexagonal or a random system would never show these sorts of ordering.

planes and one square symmetry plane, that is, two  $\{111\}$  facets and a  $\{100\}$  type facet of an fcc system, may be seen.

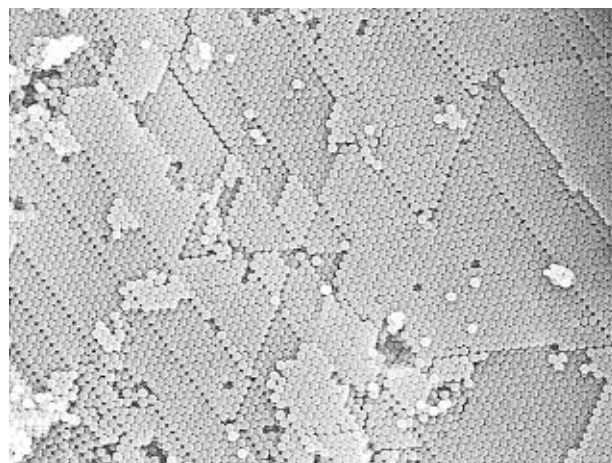
Wide ordered domains appear in both the top surface and the cleaved edges. Thus in Figure 3 a low magnification image shows wide  $\{100\}$  areas where coherence is kept all through the picture and beyond, which means hundreds of microns. In the inset we can see (at a higher magnification) how different (100) layers are stacked in an interleaved way, which again supports the assumption of fcc ordering. Figure 4 shows wide  $\{111\}$  areas in which



**Figure 2.** SEM micrograph of a cleaved edge of a sample made of a 415 nm diameter sphere. Different crystalline planes occurring in the sample can be seen. Facets corresponding to the  $\{100\}$  and  $\{111\}$  set of planes of an fcc structure can be observed. The relative orientation of the mentioned planes can be clearly seen as well.



**Figure 3.** SEM micrograph of a large  $\{100\}$  type facet observed in a cleaved edge. As can be seen, the ordering is coherent through the whole field. The interweaving of the  $\{100\}$  type layers can be observed in the inset.



**Figure 4.** SEM micrograph of a large internal  $\{111\}$  type domain. This result, along with that shown in Figure 3, indicates that long range ordered domains are formed in the lateral surfaces. Terraces one layer high, which belong either to  $\{100\}$  or  $\{111\}$  facets, can be seen.

different layers can be seen. It can also be seen how the slopes connecting the terraces are either  $\{100\}$  type (steps running from top left to bottom right in the picture) or  $\{111\}$  type facets (steps running horizontally in the picture). Of course, in a random stacking no such regular arrangements, as those presented here, could be found.

The crystal presents dislocations and vacancies similar to those that can be seen in an ordinary solid state crystal.

Samples with different lattice parameters, which are varied through the sphere diameter, have been thoroughly scanned, and only the fcc arrangements mentioned above were observed. This indicates that the crystallization in the cubic system does not depend on the sphere diameter at least over the range employed in this study.

Regarding the mechanism that could favor the formation of long range fcc packing, some important facts are worth mentioning. It is well-known that silica particles in aqueous suspensions behave as hard spheres.<sup>10</sup> Indeed, the sedimentation profile of monodisperse silica particles accurately follows the Stokes law.<sup>8</sup> In addition, as has been recently shown, the growth of a crystalline phase through natural sedimentation from a suspension of monosized spheres is described by the Edwards–Wilkinson (E–W) growth equation. In the E–W model the surface relaxation takes place through adsorption/desorption processes.<sup>11</sup> In our system, because of the relatively high thermal energy, the silica particles can sample many different adsorption sites before being pinned at a minimum energy one. Therefore, spheres located at unfavorable sites are allowed to reorganize in a more stable arrangement. On the other hand, once two layers are stacked (AB packing), the spheres of the next layer can be stacked either in ‘A’ type sites, giving rise to an ABA packing, or in a ‘C’ type site, resulting in ABC packing. In terms of gravitatory energy, ‘A’ and ‘C’ sites are indistinguishable. So the same probability exists for either stacking sequence, eventually leading to the hcp phase if

the growth sequence is ABABAB..., to the fcc arrangement if it is ABCABC..., to different mixtures of them, or to a random arrangement if otherwise. So, in the absence of any other interaction, a random stacking of close-packed layers should be expected. However, computer simulations recently performed by Woodcock<sup>1</sup> showed that the stacking of hard spheres in an fcc structure is more stable than that in an hcp structure by an amount of Gibbs free energy of  $0.005RT$  per mol, which corresponds to  $\Delta G = 0.13$  meV per particle. More recent on-going calculations by the same author<sup>12</sup> show that this value is about two times too large. Therefore, ‘C’ sites could be favored with respect to ‘A’ ones. This fact, along with the successive adsorption/desorption processes that the particle undergoes, which allow it to sit in the minimum energy site, could explain why the fcc structure is favored.

In conclusion, we have shown clear experimental evidence that SiO<sub>2</sub> nanospheres arrange in a crystalline fcc structure through natural sedimentation. This has been observed for spheres with diameters ranging from 0.2 to 0.5  $\mu\text{m}$ . Moreover, the production of a pure fcc structure can be the first step in a route to overcome the present technical obstacle to obtain three-dimensional periodic dielectric materials with lattice parameters of less than 1  $\mu\text{m}$  and, therefore, to apply solid arrangements of nanospheres to photonic technology.

**Acknowledgment.** We would like to thank P. Tarazona, V. Fornés, E. Chacón, and J. Requena for useful discussions and M. Planes for the SEM characterization. This work has been partially financed by the CICyT (Grant MAT94-0727) and the Ramón Areces Foundation.

LA970589O

(10) Iler, R. K. *The Chemistry of Silica*; John Wiley & Sons: New York, 1979.

(11) Barabasi, A. L.; Stanley, H. S. *Fractal Concepts in Surface Growth*; Cambridge University Press: Cambridge, England, 1995.

(12) Woodcock, L. V. Private communication.