

LETTER TO THE EDITOR

Rigid-Disordered Models for Inorganic Structures:
The Case of Zirconia Nanopowders

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A static disordered model is proposed to justify the high-symmetry X-ray diffraction patterns of ZrO_2 nanopowder. In particular, the cubic phase is interpreted as a disordered monoclinic phase, i.e., the phase that is stable at room temperature. © 1994 Academic Press, Inc.

It is well known that X-ray diffraction patterns of organic molecular crystals may show a higher than expected symmetry, due to the so-called rigid-disorder state [1]. It was recently also shown that a variety of minerals display lower symmetries than would be expected from their X-ray diffraction patterns [2]. Here, for the first time, the high symmetry found in the room-temperature X-ray diffraction patterns of nanocrystalline ZrO_2 powders is interpreted in terms of a structure described by a rigid-disordered model, mixed with a small amount of an ordered monoclinic phase. The X-ray diffraction pattern, simulated according to the proposed model, is in good agreement with the measured powder pattern. This model is also supported by the recent observation that the short-range structure of amorphous zirconia resembles the monoclinic ZrO_2 structure [3]. On the basis of these findings, we propose that, in general, low-temperature metastable phases can be derived from the stable phase by introducing static disorder effects. The important implication is that the coordination of an atom can be very similar to that obtained in the stable phase. It is also possible to explain the high-symmetry X-ray diffraction patterns often obtained for high-temperature phases, not only in organic molecular crystals, but also in inorganic structures.

Fine ZrO_2 powders, used as catalyst supports, have been prepared employing low-temperature chemical reactions, such as the thermal decomposition of hydrous zirconia [4, 5]. The factors controlling the appearance of metastable tetragonal and cubic phases in ZrO_2 at room temperature, resulting from the calcination of amorphous precursors, are still controversial. Several interpreta-

tions, based on crystallite sizes, strains or lattice defects, presence of impurities, and structural similarities between the amorphous precursors and the metastable phases were reported by several authors [6–14].

Nanocrystalline powders of ZrO_2 were obtained as described elsewhere [15]. All the diffraction experiments have been performed on a PW1800 Philips diffractometer with a 0.02° (2θ) scanning step in the range $20^\circ < 2\theta < 140^\circ$. The simulations were performed using the CERIOUS program [16].

In Fig. 1a, the projection of the monoclinic structure onto the (a , b) plane is shown. The first step in the procedure, leading to a rigid-disordered model, is a transformation of the monoclinic phase to a pseudocubic structure described in a cell with $a = 0.513$ nm (Fig. 1b). A rigid-disordered model is then obtained by generating couples of Zr atoms and by shifting them to position their centers of gravity at the sites occupied by Zr atoms in the ZrO_2 cubic phase. For the sake of simplicity, among the several possible ways of generating couples of Zr atoms, we chose that given by the operation

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

performed by a binary axis passing through the origin. We believe that this kind of disorder can explain the observed tetragonal symmetry often found in X-ray diffraction patterns of ZrO_2 nanopowders, since one of the three axes is not involved in the transformation. Similar results can be obtained by introducing more complex operations for generating disordered structures. These disordered states cannot be excluded, although there is no experimental evidence to sustain them.

The diffraction patterns simulated for the cubic and for the disordered models are shown in Fig. 2, together with

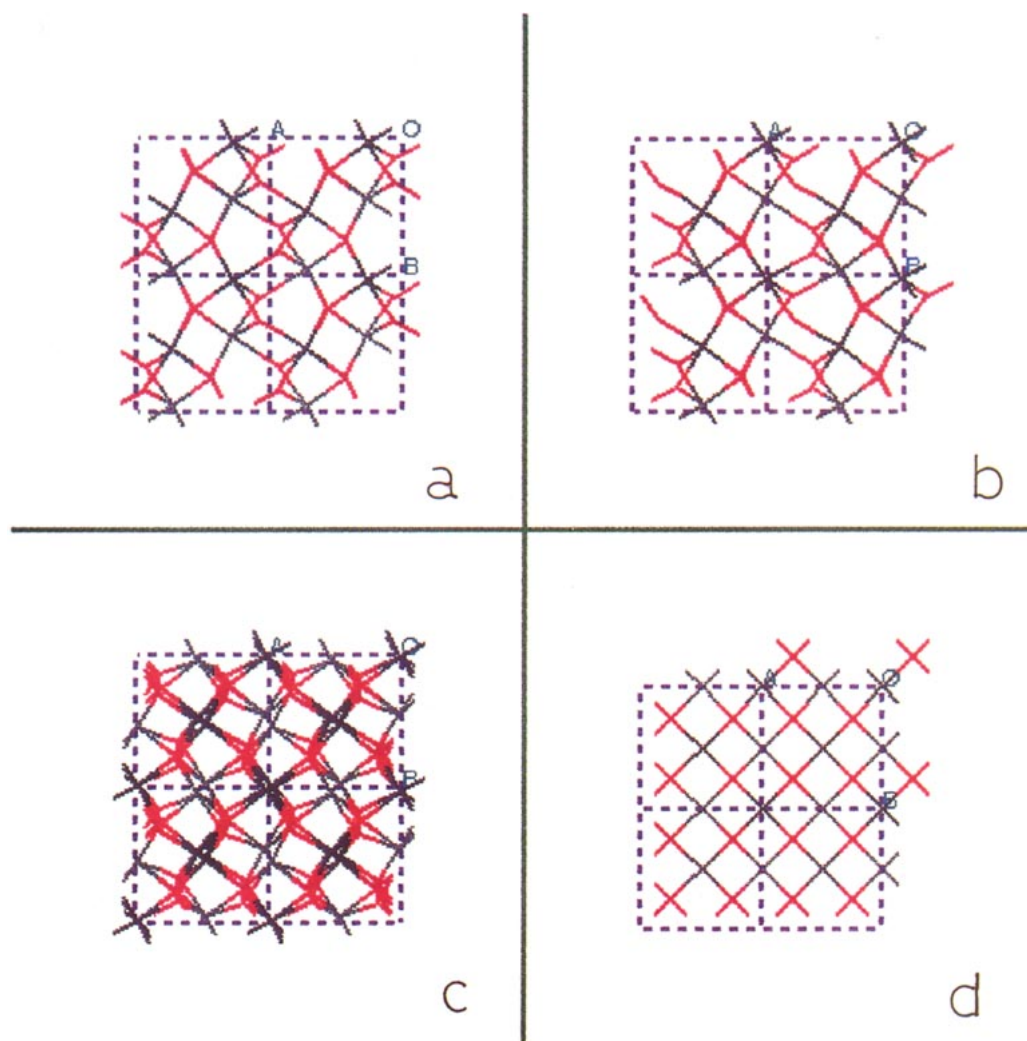


FIG. 1. (a) Projection of the ZrO_2 monoclinic structure onto the (a, b) plane. (b) The same as (a), but distorted to a pseudocubic structure. (c) The same as in (b), but distorted by the generation of "twin" Zr atoms by the operation. (d) Projection of the ZrO_2 cubic structure.

the experimental pattern. All the simulated patterns were obtained under the hypothesis of crystallite sizes of 6 nm. The low-angle shoulder of the peak at $2\theta = 29^\circ$ is due to the presence of the ordered monoclinic phase, evaluated to be about 20% by Rietveld refinement [17].

It is interesting to note that at high 2θ angles, the structure factors computed for the model of the cubic phase are larger than those determined from the experimental data, while the agreement between the diffraction pattern of the monoclinic disordered model and the measured powder pattern is good. Good agreement between the experimental pattern and that simulated for the cubic model can be obtained only by introducing into the simulation a very large temperature factor, hence damping the high-angle reflections. This constitutes further evidence of the presence of rigid disorder, since the experimental pattern was measured at room temperature.

In this disordered model, the Zr coordination is the same as that found in the reasonable low-temperature monoclinic phase (with a coordination number of 7), as expected. Indeed, the short-range structure of amorphous zirconia was recently found by radial distribution analysis and resembles the monoclinic ZrO_2 structure [3]. Moreover, the Raman spectra of ZrO_2 nanopowders never exhibited cubic symmetry [18–20]. A model of stabilized zirconia was recently proposed in which the Zr atoms have a coordination number of 7 [21]. In general, it seems possible that the coordination number of zirconium in the room-temperature zirconia phases is always 7.

This type of reasoning can be generalized. Many non-rigid-disordered models are based on some type of motion and are usually refined by relying heavily on the use of imprecise high- 2θ parts of the powder patterns. Rigid-

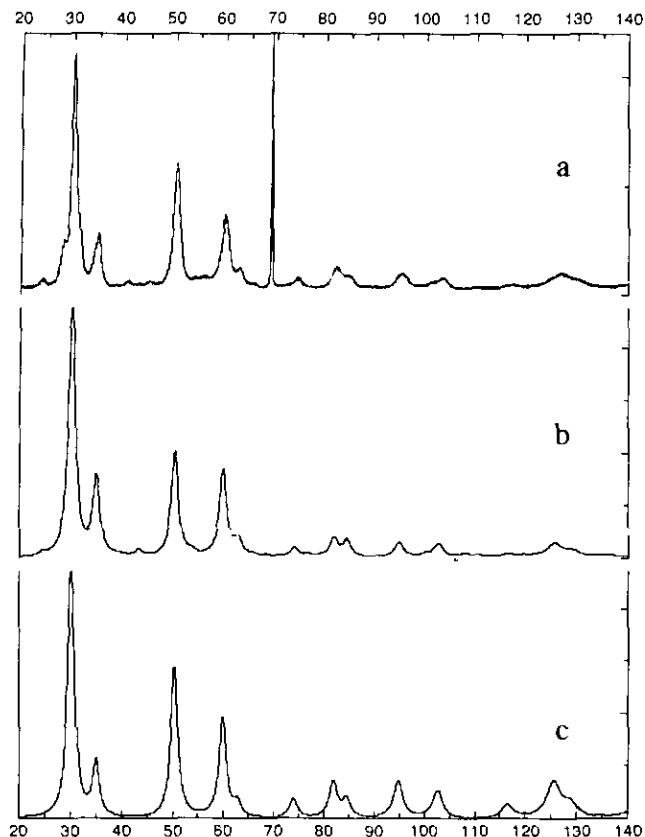


FIG. 2. (a) Experimental pattern. The sharp peak at about 69° is due to the single-crystal sample holder. (b) Pattern simulated for the model of Fig. 1c. (c) Pattern simulated for the model of Fig. 1d.

disordered models can more sensibly substitute for the former ones and be a starting point for the interpretation of many phase transformations. This implies that in most cases, the high-temperature phase can be a disordered variety of the low-temperature phase, as indicated by the

group-subgroup relationship often found between the high- and low-temperature crystal structures.

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REFERENCES

1. A. I. Kitaigorodsky, "Molecular Crystals and Molecules." Academic Press, New York, 1973.
2. M. Akizuki and H. Nishido, *Am. Mineral.* **73**, 1434 (1988).
3. Y. W. Zeng, G. Fagherazzi, F. Pinna, S. Polizzi, P. Riello, and M. Signoreto, *J. Non-Cryst. Solids* **155**, 259 (1993).
4. P. D. L. Mercera, J. G. Van Ommen, E. B. M. Doesburg, A. J. Burggraaf, and J. R. H. Ross, *Appl. Catal.* **57**, 127 (1990).
5. E. Bernstein, M. G. Blanchin, R. Ravelle-Chapuis, and J. Rodriguez-Carvajal, *J. Mater. Sci.* **27**, 6519 (1992).
6. M. I. Osendi, J. S. Moya, C. J. Serna, and J. Soria, *J. Am. Ceram. Soc.* **68**, 135 (1985).
7. F.-C. Wu and S.-C. Yu, *J. Mater. Sci.* **25**, 970 (1990).
8. R. C. Garvie, *J. Phys. Chem.* **82**, 218 (1978).
9. Y. Murase and E. Kato, *J. Am. Ceram. Soc.* **66**, 196 (1980).
10. B. H. Davis, *J. Amer. Ceram. Soc.* **67**, C168 (1984).
11. R. Srinivasan, L. Rice, and B. H. Davis, *J. Am. Ceram. Soc.* **73**, 3528 (1990).
12. M. Yashima, T. Noma, N. Ishizawa, and M. Yoshimura, *J. Am. Ceram. Soc.* **74**, 3011 (1991).
13. P. F. Becher and M. V. Swain, *J. Am. Ceram. Soc.* **75**, 493 (1992).
14. A. Methivier and M. Pijolat, *J. Catal.* **139**, 329 (1993).
15. J. Clearfield, *Inorg. Nuclear Chem.* **11**, 169 (1959).
16. CERIOUS molecular modeling software for materials research from Molecular Simulations Inc. of Burlington, MA, and Cambridge, U.K.
17. I. C. Hill and C. J. Howard, *J. Appl. Crystallogr.* **20**, 467 (1987).
18. C. H. Perry, D. W. Liu, and R. P. Ingel, *J. Am. Ceram. Soc.* **68**, C184 (1985).
19. M. Ishigame and T. Sakurai, *J. Am. Ceram. Soc.* **60**, 367 (1977).
20. V. G. Keramidis and W. B. White, *J. Am. Ceram. Soc.* **57**, 22 (1974).
21. L. E. Depero and M. Zocchi, *J. Solid State Chem.* **103**, 528 (1993).