

Hafnia Powders (HfO₂): Elaboration and Characterization by Transmission Electron Microscopy

A. Lakhli,*, Ch. Leroux,† P. Satre,* B. Durand,‡ M. Roubin,* and G. Nihoul†,1

*Matériaux à Finalités Spécifiques, EA1356 and †Matériaux Multiphasés et Interfaces, EA1357, Université de Toulon, BP 132, 83957 La Garde Cedex, France; and ‡ENSCMu, 3 Rue A. Werner, 68093 Mulhouse, France

Received February 28, 1994; in revised form May 23, 1995; accepted May 24, 1995

HfO₂ is very similar to ZrO₂; the powder preparation routes developed for ZrO₂ ceramics are equally applicable to HfO₂ ceramics. Cubic HfO₂ stabilized by yttrium oxide was prepared at low temperature (<1000°C) by oxalic precursors pyrolysis or via molten salts reaction. The powders obtained were characterized by X-ray diffraction, granular distribution, and transmission electron microscopy. TEM has been proved to be the best technique to characterize the powder size homogeneity, chemical composition, and crystallographic structure. © 1995 Academic Press, Inc.

1. INTRODUCTION

Several methods can be used to prepare powders suitable for sintering. The powders have to be fine, to be characterized by a narrow granular distribution, and to be homogeneous in chemical and crystallographic composition. Low temperature treatments generally make it possible to reach these objectives. In some cases, these methods also yield powders with large surface areas. They are used in heterogeneous catalysis as supports for hydrogenation catalysts (1). We have been interested in hafnium oxide HfO₂, a ceramic with a high melting point which has not been frequently studied, unlike its homolog zirconium oxide ZrO₂ (2). This ceramic is considered to be potentially useful for structural applications. The stable low temperature HfO₂ phase has a monoclinic structure. It exhibits several transformations with increasing temperature: monoclinic-tetragonal (1720°C), tetragonal-cubic (2600°C), and cubic-liquid (2800°C). The tetragonal phase is not very different from the cubic structure; the ratio c/a is nearly 1. Cubic hafnium oxide can be stabilized at room temperature by yttrium oxide Y₂O₃, the proportions of Y₂O₃ being given by the phase diagram (3). The cubic HfO₂ ($a = 0.511$ nm) phase has a fluorite-type structure, in which each Hf⁴⁺ ion is coordinated by eight equidis-

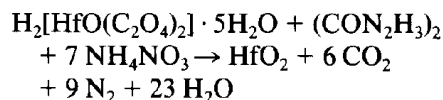
tant O²⁻ ions and each O²⁻ ion is tetrahedrally coordinated by four Hf⁴⁺ ions. The tetragonal to monoclinic transformation temperature is several hundred degrees higher than that for ZrO₂. This transformation is associated with a volume expansion. We have used three methods to prepare hafnia powders and will compare the effect of each method on particle size, powder morphology, and crystallographic structure, using transmission electronic microscopy.

2. EXPERIMENTAL PROCEDURE

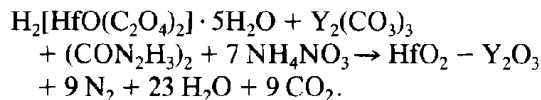
(a) Preparation Methods

1. *Heating decomposition of oxalic precursors.* We have used hafnium oxalic acid H₂[HfO(C₂O₄)₂] · 5H₂O in which yttrium is introduced by reaction with yttrium carbonate. The progressive elimination of the solvent produces a gel which is then subjected to heat treatment (4). This precursor has been treated at 450°C (sample A), 600°C (sample B), 700°C (sample C), and 900°C (sample D).

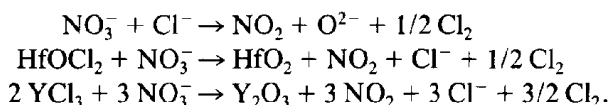
2. *Pyrolysis of oxalate precursors in the presence of a redox mixture.* We have used the flash decomposition method (5) in the presence of ammonium nitrate NH₄NO₃ and oxalic acid dihydrazide (CON₂H₃)₂ (sample E). Fine-particles of titanates were already prepared this way (5). The redox mixture, having a low ignition temperature, not only pyrolyses the oxalate precursor but also produces large quantities of gases, which results in formation of a fine, foamy oxide product. The precursor is the previous oxalic complex, which by heating produces either the solid-solution Hf_{1-2x}Y_{2x}O_{2-x}□_x or pure HfO₂. The reaction starts at 350°C and proceeds according to the equations



¹ To whom correspondence should be addressed.



3. *Molten salt reactions.* The preparation of several oxides by molten salt reactions is well known (6). It has been successfully applied to the preparation of pure zirconia (7) or of yttria-stabilized tetragonal zirconia (8). We used it to prepare yttria-stabilized cubic hafnia. The molten salts involve a mixture of NaNO_3 – KNO_3 (54 mole% KNO_3) which melts at 222°C . The precursors are HfOCl_2 or HfCl_4 and YCl_3 . The temperature of the mixture was chosen to be 500°C (sample F). HfO_2 precipitates in the molten environment which generates O^{2-} ions by an oxydoreduction reaction:



The simultaneous addition of HfOCl_2 and YCl_3 leads straight to the formation of the indicated solid-solution.

(b) Characterization

Samples thus prepared were then studied by X-ray diffractometry to obtain information on the structure of phases and on the size of the diffracting domains at the limit of detection by X rays.

Grain size determinations were also used to obtain information on the size of the aggregates and agglomerates. These yield average results and unfortunately depend on the method used. The analysis was made by sedimentation velocity measurements in aqueous solutions buffered to pH 7 and containing sodium polymethacrylate.

Samples were studied by transmission electron microscopy using a Jeol 2000 FX instrument, operated at an

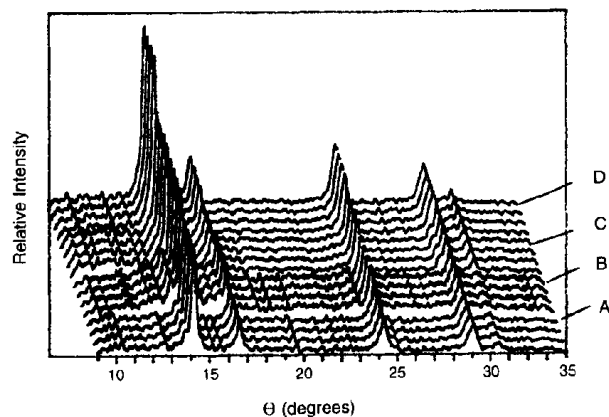


FIG. 1. X-ray diffraction patterns of HfO_2 – Y_2O_3 (20 mole%) samples heated for 24 hr at: 450°C (A), 600°C (B), 700°C (C), and 900°C (D).

accelerating voltage of 200 kV (corresponding wavelength 2.51 pm). This apparatus can be operated in the analysis mode and in imaging and diffraction modes. Three types of information can be obtained:

(i) The shape, size, and homogeneity of distributions: the powder is imaged, without any grinding (or at most gentle grinding). Many areas, of course, will be too thick for details to be seen, but their shape will be recognized and possible faceting can be observed.

(ii) Crystallographic information: the electronic diffraction pattern corresponds to an area of 200 nm in diameter. It allows us to distinguish between cubic HfO_2 , monoclinic HfO_2 , and, possibly, cubic Y_2O_3 by recognizing the pattern and measuring the parameters. However, most of the time, ring patterns are obtained (corresponding to a large number of diffracting domains in different orientations); what we can then measure are only the reticular distances in the samples. The different hafnia phases have many similar reticular distances, as Table 1 shows. In particular, the cubic (111) distance (2.95 Å) and the monoclinic $(-1, -1, 1)$, $(-1, 1, 1)$, $(1, 1, 1)$, and the $(1, -1, 1)$ distances (3.14 and 2.82 Å) give rise to rings so close together that they are just seen as one enlarged ring. However, some of the monoclinic reticular distances are not present in the cubic phase; this is helpful to distinguish between the two phases. Unfortunately, the tetragonal phase cannot be distinguished from the cubic one.

(iii) Analysis: this is done by X-ray spectroscopy of a sample area 40 to 60 nm in diameter. Oxygen and carbon cannot be detected but all elements with $Z > 11$ can be detected, which include hafnium and yttrium, so that the local atomic ratio of these two elements in the powder can be obtained. This helps to detect inhomogeneities and the possible existence of Y_2O_3 or any other yttrium compound.

TABLE 1

<i>h k l</i>	Cubic	Monoclinic
	d_{hkl} (nm)	d_{hkl} (nm)
0 0 1		.521
0 1 0		.517
1 0 0		.504
0 1 1		.367
1 1 0		.361
1 0 1		.336
-1 1 1	.295	.314
1 1 1	.295	.282
0 0 2	.256	.261
0 2 0	.256	.259
2 0 0	.256	.252

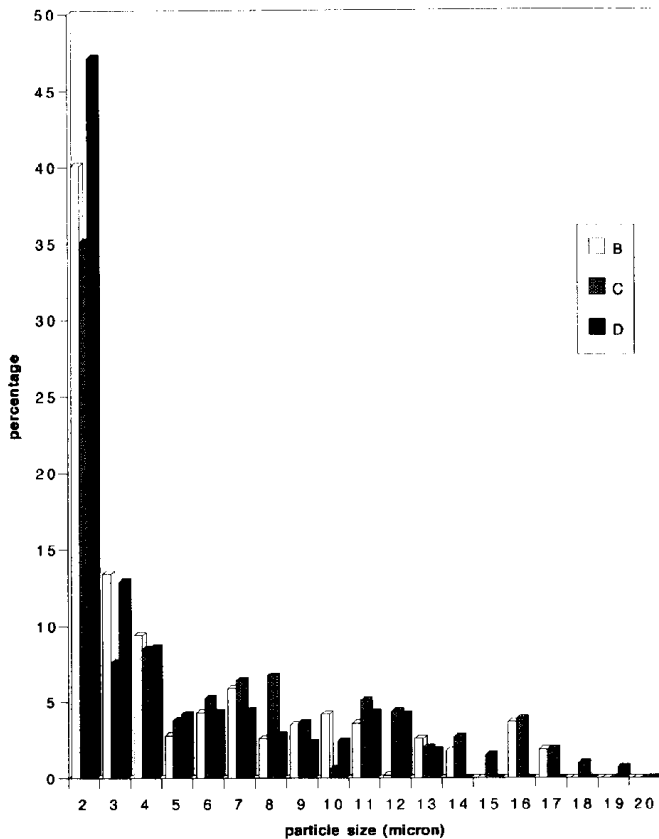


FIG. 2. Particle (agglomerate) size distribution of B, C, and D samples.

3. RESULTS OF THE POWDERS CHARACTERIZATION

All processes are started from a mixture of about 20% of Y₂O₃ and 80% of HfO₂, i.e., an atomic ratio of [Y]/[Hf] of 50% and an atomic percentage of 33% for yttrium and 67% for hafnium.

(a) Samples Obtained by Heat Treatment of Precursors

We first studied the powders obtained by decomposition of oxalic precursors at different temperatures.

Figure 1 shows the results obtained by X-ray diffraction on samples A–D. Only the peaks corresponding to the cubic hafnia appear; these are all rather narrow, which means that the diffracting domains are large and that the main contribution comes from cubic hafnia. However, no information is available on the existence of other phases present in small amounts or in small domains.

As the results on these different samples were not very different, gain size measurements were only done on samples B, C, and D. The results are shown in Fig. 2. The measured size corresponds to the size of the aggregates, since the dispersion method breaks only weakly bound

particles. The results of the size distribution were not very definitive; one can only state that the aggregates seem to have rather varied sizes.

Figure 3 shows some electron diffraction patterns and some TEM images obtained from a sample treated at 450°C. All diffraction patterns show rings, which proves that the sample is polycrystalline. This is confirmed by the images, where aggregates, with a size near 1 μm, are seen, which are obviously composed of small particles. Figure 3a shows an example where the hafnia (111) planes are imaged (reticular distance 0.3 nm); one can detect numerous different directions for these planes exhibiting the diffracting domains. The diffraction patterns are of two types. Some (Fig. 3b) correspond to a simple cubic structure: all reticular distances can be written as $a/(h^2 + k^2 + l^2)^{1/2}$ where h , k , and l are integers. The parameter a is then measured as 0.45 nm. Analysis on these aggregates, however, shows the presence of yttrium, but no hafnium nor any other heavy element is detected. These aggregates can only be composed of yttrium and of elements lighter than sodium ($Z = 11$). Since Y₂O₃ has a f.c.c. structure with a parameter $a = 1.06$ nm the observed diffraction pattern cannot correspond to this structure.

The other diffraction (Fig. 3c) pattern often encountered can correspond to a f.c.c. structure with a parameter close to 0.52 nm, which corresponds to cubic HfO₂. However, the rings are enlarged, especially the (111) ring, and some weak rings are also observed at radii not compatible with cubic hafnia. The diffraction pattern was then indexed as a mixture of a large amount of cubic hafnia and a small amount of monoclinic hafnia. Note that the existence of some monoclinic phase will lead not only to some additional rings but also to many rings very close to the cubic ones. Analysis performed on aggregates showing the above mixture of structures leads to a hafnium percentage of 85%. Finally, some aggregates (Fig. 3d) also exhibit a mixture of the two patterns, but the monoclinic phase is now more important: the hafnium concentration varies for these aggregates.

The general conclusion is then that the powder is highly inhomogeneous, contains much cubic HfO₂, but with a low percentage of yttrium and some pure unknown yttrium compound.

Figure 4 shows electron diffraction patterns and TEM images corresponding to the samples treated at 600°C. Figure 4a shows a general view of a sample which has not been ground. The size and shape of the agglomerates are clearly seen. We again see rings on the diffractograms but there are some examples of patterns corresponding to a single crystal which are easier to index, since angles can also be measured. These rings (Fig. 4b) correspond mainly to a cubic HfO₂ structure. The corresponding dark field image (Fig. 4c) shows some aggregates with small

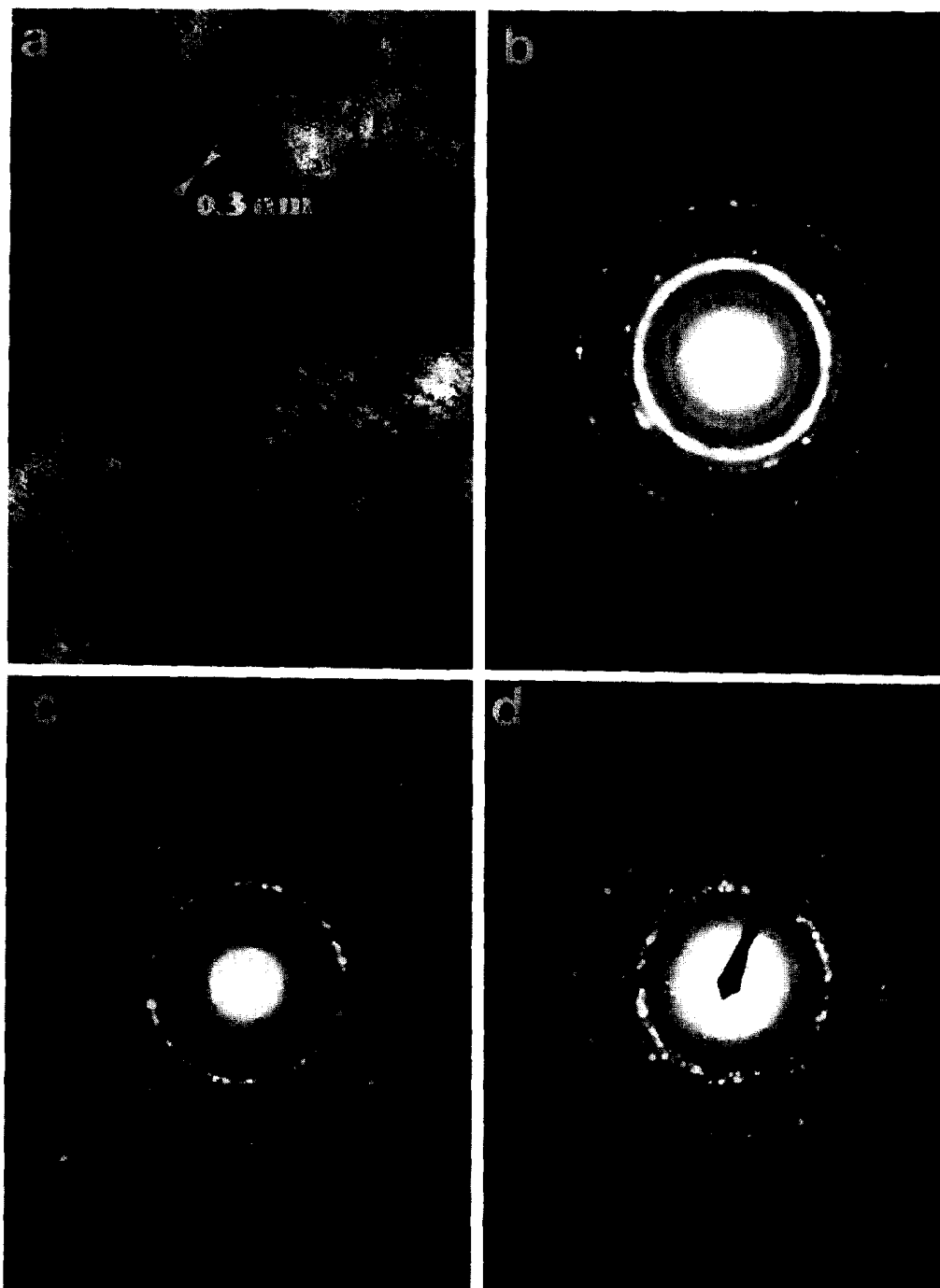


FIG. 3. TEM results on powder A: (a) HREM image of part of an aggregate. (b) Diffraction pattern which can only be indexed as cubic with a parameter of 4.5 \AA ; analysis on this region shows no hafnium. (c) Diffraction pattern corresponding to a polycrystalline aggregate with mainly cubic HfO_2 structure and some monoclinic structure. (d) Diffraction pattern showing a mixture of (b) and (c) patterns.

particles (4 to 10 nm) on which the analysis gave rise to variable hafnium concentration (e.g., 85% for the larger ones or 50% for the smaller ones). However, some examples of larger particles (130 nm) can be found; an example (Fig. 4d) of a diffraction pattern from a single cubic hafnia

crystal, oriented with its [112] axis parallel to the electron beam, is shown. The analysis leads to a hafnium concentration around 80%. It should be stressed that most of the diffraction patterns correspond to cubic HfO_2 .

As samples treated at 700°C were not very different

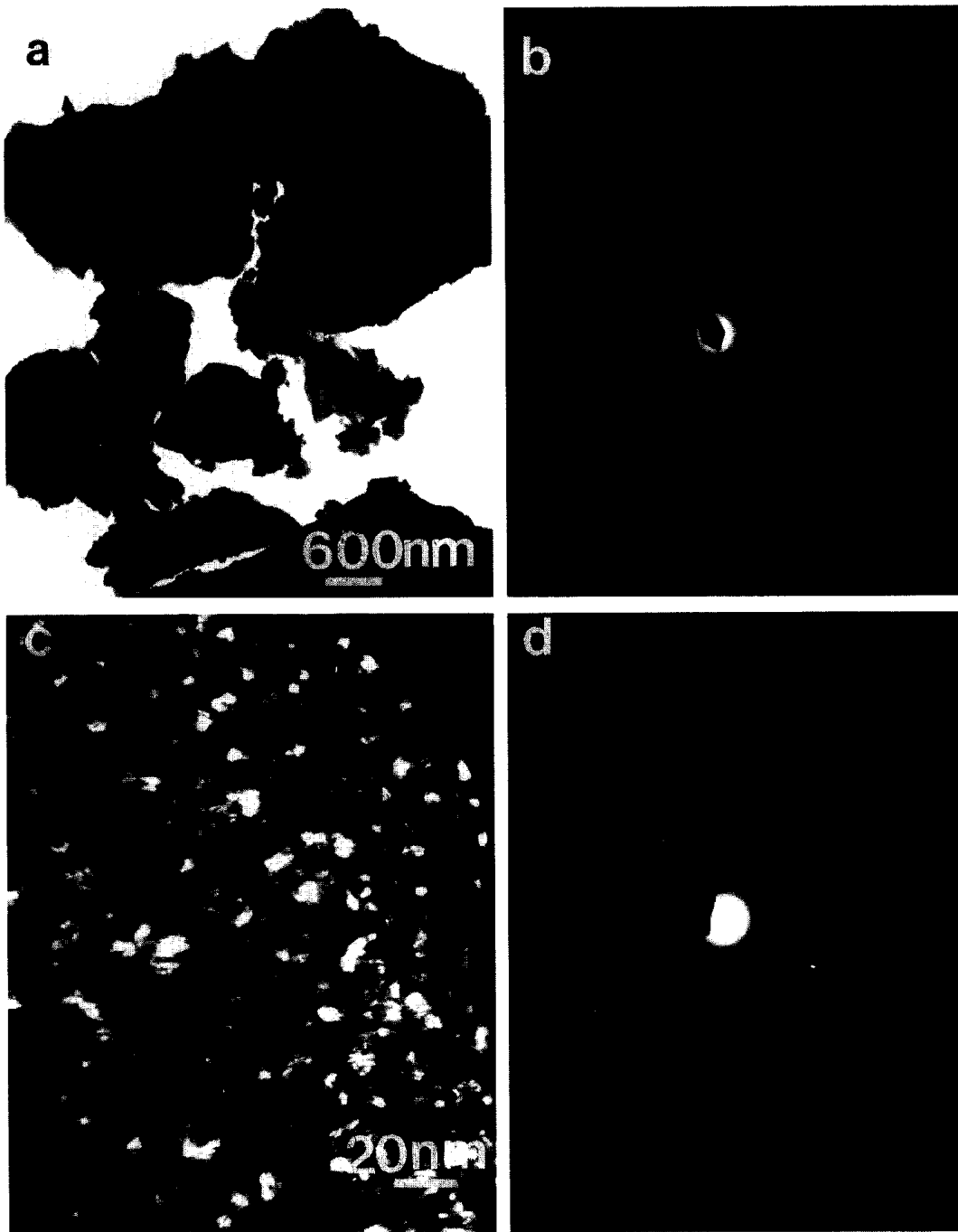


FIG. 4. TEM results on sample B: (a) General view of a nonground sample. (b) Diffraction pattern with rings corresponding to small particles of cubic HfO_2 . (c) Dark field image showing the small size of the diffracting domains; the white zones correspond to areas oriented such that the (111) planes diffract. (d) [112] diffraction pattern corresponding to a single crystal of cubic HfO_2 .

from the previous ones (see grain size and X-ray results) we have not studied them by TEM.

Results of TEM studies on samples *annealed at 900°C* are shown on Fig. 5. The particles (Fig. 5a) have a size between 10 and 30 nm; they are still aggregated. Again there are two phases (f.c.c. cubic hafnia with $a = 0.52$

nm, and the simple cubic phase with $a = 0.45$ nm, and no hafnium). Some aggregates show a monoclinic structure but there are now only a few of them (see Fig. 5b). A comparison between the diffraction patterns and the measured percentage of hafnium shows that the disappearance of the monoclinic structure is linked to a smaller

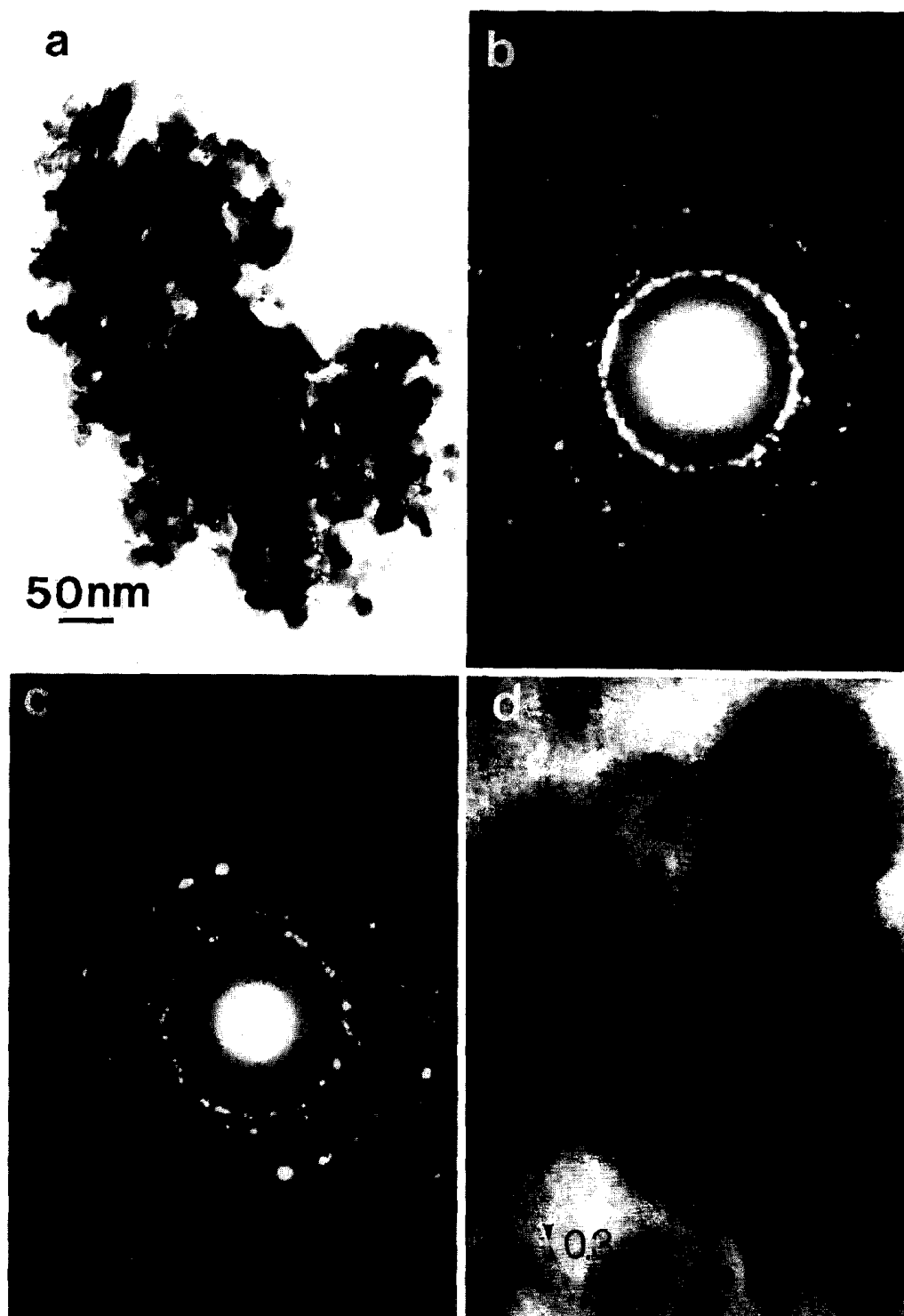


FIG. 5. TEM results on sample D: (a) General view of the sample. (b) Diffraction pattern with monoclinic structure. (c) Diffraction pattern with only cubic structure. (d) High resolution image showing the (111) planes.

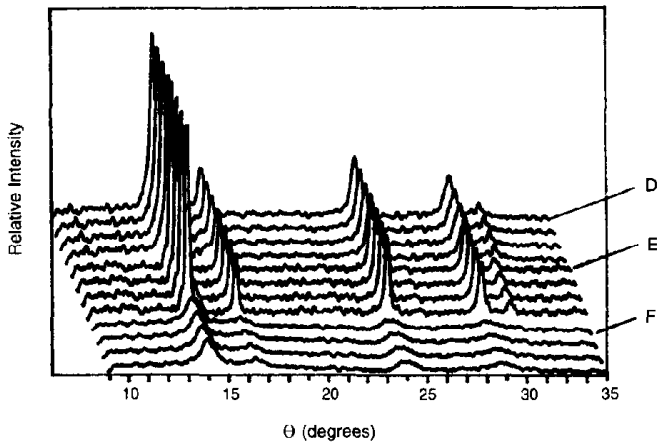


FIG. 6. X-ray diffraction patterns of D, E, and F samples.

percentage of hafnium: when no monoclinic structure is observed (Fig. 5c) the percentage of hafnium is roughly 65% (which was the percentage in the original mixture). Finally, some high resolution electron microscopy (HREM) images (Fig. 5d) have been obtained for the cubic (111) planes. They show the size of the coherent diffracting domains with good precision, as the (111) reticular distance is known to be 0.3 nm.

(b) Samples Obtained by Flash Reaction (E)

Figure 6 shows the results obtained by X-ray diffractometry on samples E and F. Results from sample D have been again shown on the same figure for easy comparison of the results. Only the peaks corresponding to cubic hafnia appear, and, for sample E, they are still narrow. For sample F they are much broader, showing that we now have obtained some small particles with diffracting domains less than 10 nm.

Figure 7 shows the results obtained by grain size measurements which indicate that the samples F and D correspond to the finest powders.

The electron microscopy results are shown in Fig. 8. No grinding was necessary for these observations. The simple unknown cubic structure no longer appears. Seven analyses performed on different aggregates all show a low percentage of yttrium (7%): they correspond to particles 20 to 50 nm in size and to a mainly cubic HfO₂ structure. These particles have platelet shapes (Fig. 8a). Smaller particles (5 to 10 nm) produce an enlarged ring pattern (Fig. 8b) which could correspond to a mixture of f.c.c. and monoclinic structures; the yttrium percentage is still 7%. Finally, we see some very small particles (<5 nm) for which the diffraction pattern is again composed of enlarged rings (Fig. 8c) and can correspond to a mixture of f.c.c. and monoclinic structures. The yttrium percentage, however, was 25%. Hence, the inhomogeneities are

smaller than for the preceding samples; nevertheless, some different structures coexist. Some HREM images (Fig. 8d) are also shown which give the shape of the particles.

(c) Samples Obtained From Molten Salts (F)

The last method produces much more homogeneous powder as is seen by inspection of Fig. 9. The observations were done on samples with no grinding performed. The analysis showed a uniform yttrium percentage of 35% (within experimental error). The diffraction patterns (Fig. 9a) consist of thin rings, nearly continuous, corresponding to a cubic HfO₂ structure, with no monoclinic ring visible, and only some weak spots. The particles are aggregated in a rather strange fashion in the shape of a bi-dimensional veil (Fig. 9b), sometimes elongated (Fig. 9c), with an average aggregate size around 1 μ m. The particles have a size of 10 nm, with a spherical slightly faceted shape. The HREM images (Fig. 9d) show some (111) cubic planes which permit the rather precise measurement of the particle size; some faceting of this particle is seen.

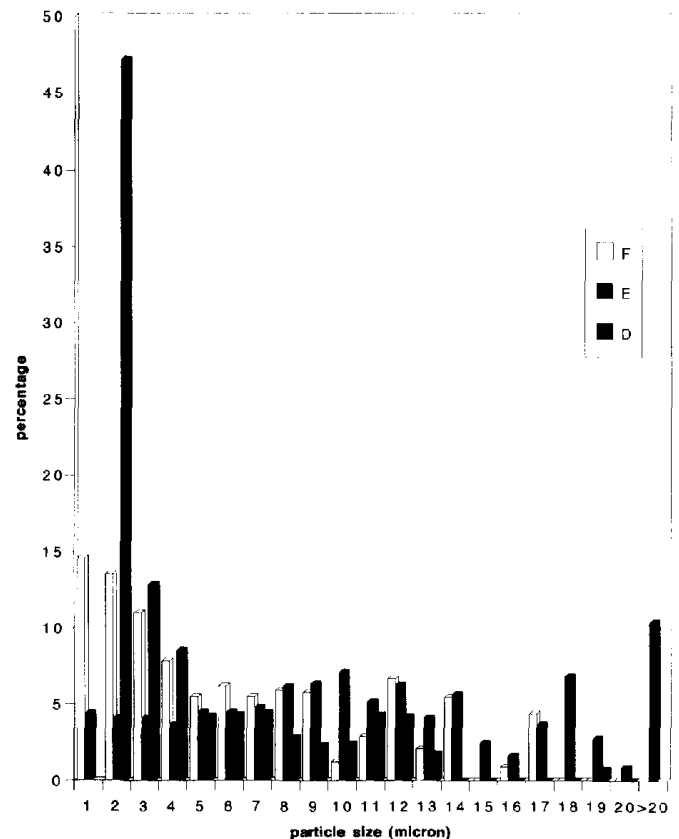
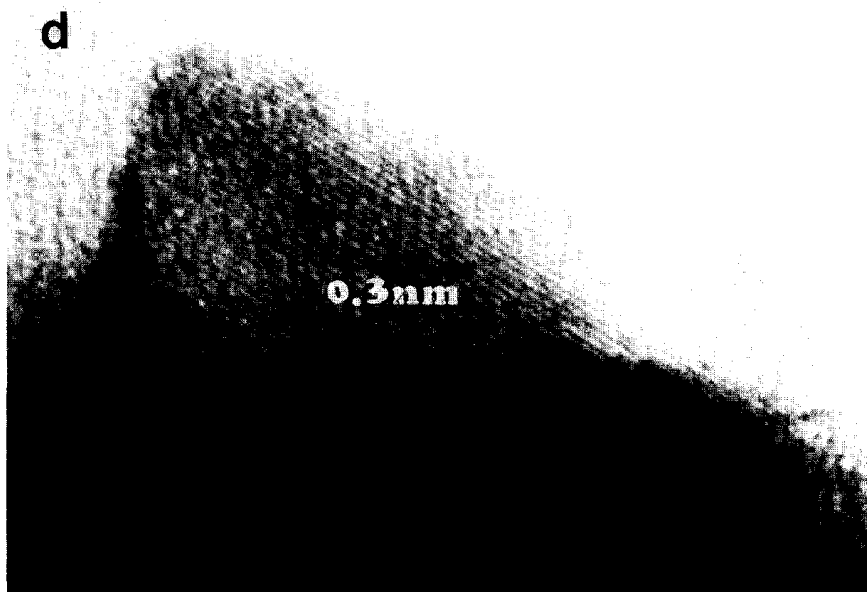
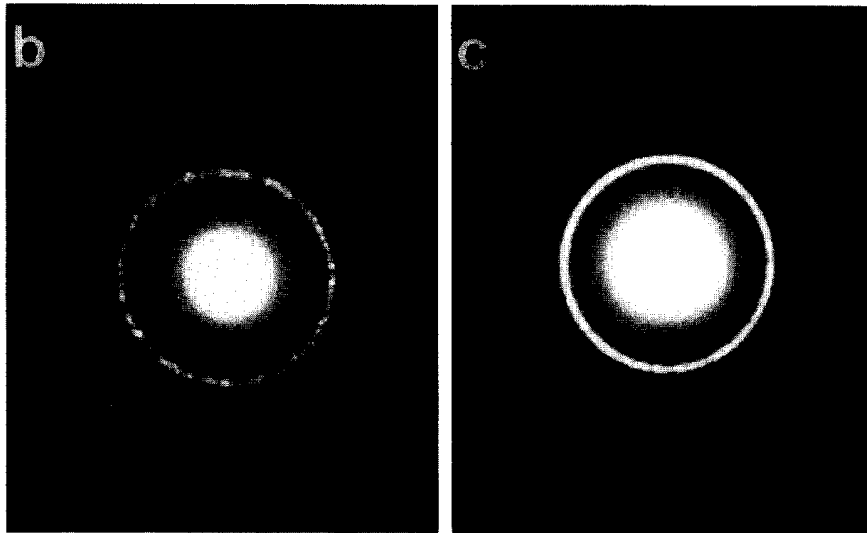
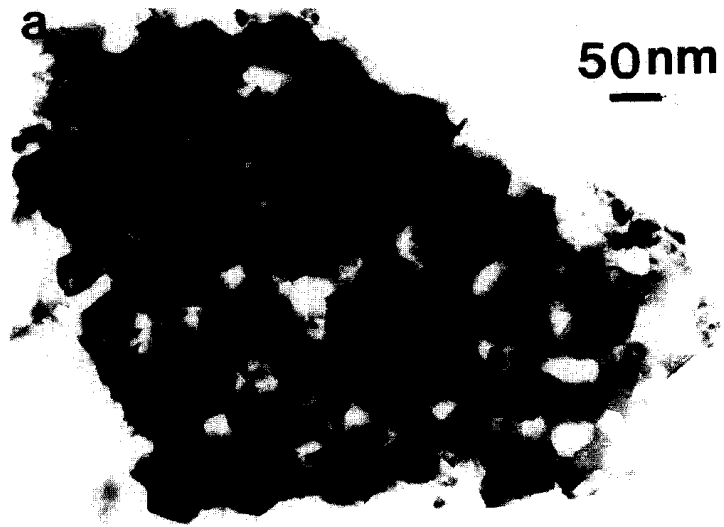


FIG. 7. Particle (agglomerate) size distribution of D, E, and F samples.



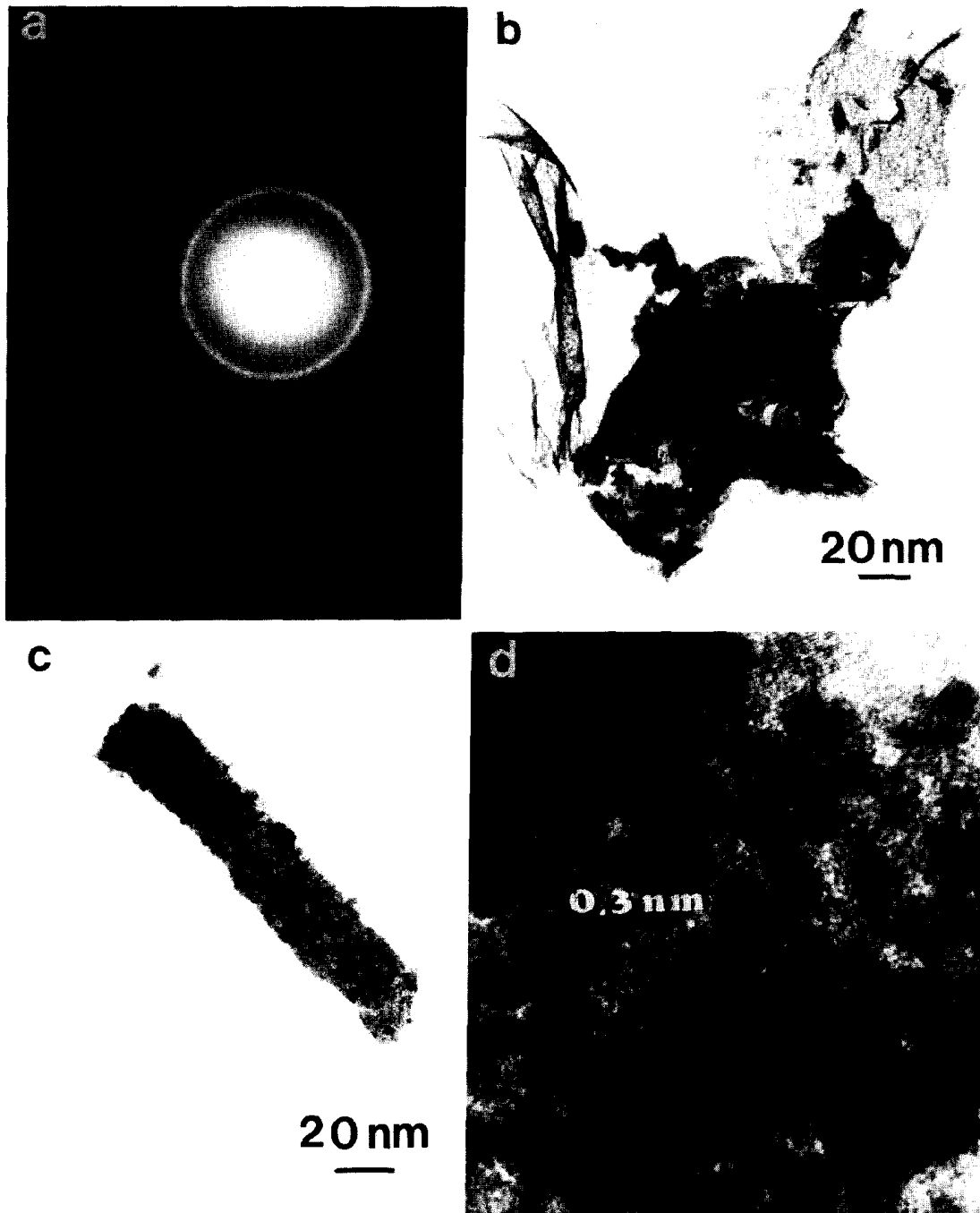


FIG. 9. TEM results on sample F: (a) Diffraction pattern with narrow continuous rings corresponding to small cubic HfO_2 crystallites. (b) Image showing the "veil" morphology of this sample. (c) Image showing some elongated aggregates. (d) HREM image exhibiting the facets on some small crystallites.

FIG. 8. TEM results on sample E: (a) Image of the sample showing some platelet morphology. (b) Diffraction pattern with dotted enlarged rings. (c) Diffraction pattern with continuous enlarged rings. (d) HREM image.

4. DISCUSSION

We first want to stress the importance of local electron microscopy. Classical methods of characterization for powders only yield macroscopic results and do not show the inhomogeneity of the powders if some of the phases present in the mixture are present in small quantities. Moreover, local analysis also provides information on composition inhomogeneities. Note again that X-ray diffraction measurements (Figs. 1 and 6) only show a single cubic phase, indicating that Y_2O_3 has completely entered into the HfO_2 lattice to form a stabilized cubic solid solution, in agreement with the phase diagram reported in the literature. However, TEM studies show the existence not only of a small proportion of monoclinic hafnia but also of an unknown yttrium compound. Local analysis also shows that the yttrium concentration is usually not homogeneous. In particular, the regions containing cubic hafnia often have a proportion of 75 to 80% hafnium, much larger than the expected average amount. This might explain the formation of a compound with no hafnium.

The unknown phase with no heavy element other than yttrium, has been detected both alone or mixed with hafnia. When on its own, the electron diffraction patterns show the characteristic rings with radii varying proportionally to $(h^2 + k^2 + l^2)^{1/2}$ where h , k , and l are integers. This corresponds to a simple cubic structure, with a parameter of 0.45 nm, but we have not found any yttrium compound with this structure in the literature. When this phase is mixed with the cubic hafnia, the reticular distances measured from the diffraction pattern correspond exactly to some observations reported in the literature as corresponding to $Y_2Hf_7O_{17}$ (9): in our case, we can divide them as rings produced by the f.c.c. hafnia and rings produced by the simple cubic phase, with the 0.45 nm parameter observed elsewhere. The local analysis which was performed does not correspond to a 2/7 ratio of yt-

trium to hafnium. The measured ratio (70% of hafnium and 30% of yttrium) rather corresponds to a composition $Y_2Hf_5O_{13}$. However, at this stage, it is difficult to be conclusive and we need some new observations to identify the exact compound present in the mixture HfO_2 - Y_2O_3 .

5. CONCLUSION

Powder morphology depends strongly on the synthesis used. Only transmission electron microscopy permits precise determination of the homogeneity of size, chemical, and crystallographic composition of the obtained powders. Only the powders obtained by the molten salts reaction produce a really homogeneous powder with good characteristics. Both X ray and TEM show that the particles have a small size, are cubic, and have the same proportion of hafnium (65%) as the average one used in the reaction. Sintering trials are being done on these different powders; the densities should be different depending on the preparation method.

REFERENCES

1. D. Hamon, M. Vrinat, M. Breyse, B. Durand, L. Mosoni, M. Roubin, and T. des Courieres, *Eur. J. Solid State Inorg. Chem.* **30**, 713, (1993).
2. J. Wang, H. P. Li, and R. Stevens, *J. Mater. Sci.* **27**, 5397, (1992).
3. V. S. Stubican, *Adv. Ceram.* **24**, 71, (1988).
4. A. Lakhli, P. Satre, A. Sebaoun, and M. Roubin, *Ann. Chim. (Paris)* **18**, 565, (1993).
5. M. Amala Sekar, G. Dhanaraj, H. L. Bhat, and K. C. Patil, *J. Mater. Sci.* **3**, 237, (1992).
6. B. Durand and M. Roubin, *Mater. Sci. Forum* **73-75**, 663 (1991).
7. M. Jebrouni, B. Durand, and M. Roubin, *Ann. Chim. (Paris)* **16**, 569 (1991).
8. M. Jebrouni, B. Durand, and M. Roubin, *Ann. Chim. (Paris)* **17**, 143 (1992).
9. M. Duclos, J. Vicat, and C. Deportes, *J. Solid State Chem.* **2**, 236 (1970).