

# High-Energy Milling of $\text{WO}_3$ Oxides: Amorphization and Reaction with $\text{Cs}_2\text{CO}_3$

Stéphane Laruelle and Michel Figlarz<sup>1</sup>

Laboratoire de Réactivité et de Chimie des Solides, URA CNRS 1211, Université de Picardie Jules Verne, 33, Rue Saint-Leu, 80039 Amiens Cedex, France

Received October 6, 1993; in revised form January 31, 1994; accepted February 2, 1994

IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

Three  $\text{WO}_3$  oxides with  $\text{ReO}_3$ -, pyrochlore-, and hexagonal-type structures have been studied in nonreactive and reactive grinding conditions by high-energy ball milling. In nonreactive grinding conditions, pyrochlore- and hexagonal-type  $\text{WO}_3$  oxides amorphize by collapse of the oxide structure. Monoclinic  $\text{WO}_3$  cannot be amorphized in these experimental conditions: the effect of high-energy ball milling is to decrease the crystallite size to a limit value. In reactive grinding conditions  $\text{WO}_3 + \text{Cs}_2\text{CO}_3$  mixtures lead to the formation of a lacunar cubic pyrochlore-type cesium tungstate. The reaction kinetics are strongly influenced by the  $\text{WO}_3$  oxide structure and its behavior in nonreactive grinding. The mechanochemical reactivity is higher for monoclinic  $\text{WO}_3$  and seems to depend on the presence of intercrystallite boundaries rather than on the amorphous oxide phase. © 1994 Academic Press, Inc.

## I. INTRODUCTION

The physical and chemical changes induced in various chemical systems by mechanical treatment produced by high-energy ball milling have led to extensive research during the past two decades. Following Benjamin's work in 1970 (1) on the preparation of nickel-based superalloys, the process of repeated cold welding and fracturing of metal powder particles during high-energy ball milling was named mechanical alloying (MA). A large number of investigations have been carried out in metallic systems on alloyed metastable, crystalline, or amorphous phases as well as on the mechanism of MA (2).

The physical and chemical changes induced by intensive grinding of nonmetallic systems were studied well before MA. The corresponding reactions were named tribochemical or mechanochemical reactions; review of this art can be found in some monographs (3-5). Examples include phase transition, amorphization, chemical decomposition, and various solid state reactions induced by intensive grinding. Following the rapid extension of MA,

there has been a new interest in mechanochemical reactions as a new powerful ambient temperature route for the formation of new materials.

The aim of this paper is to present the results we obtained in the study of different  $\text{WO}_3$  tungsten trioxides under intensive grinding conditions. Three different  $\text{WO}_3$  oxides with hexagonal, pyrochlore-, and  $\text{ReO}_3$ -type structures have been studied. The influence of  $\text{WO}_3$  structure on amorphization in nonreactive grinding conditions is first presented. The results obtained in reactive grinding conditions of  $\text{WO}_3 + \text{Cs}_2\text{CO}_3$  mixtures in the same experimental conditions as for nonreactive grinding are then discussed.

## II. EXPERIMENTAL

### II.1. Oxides Preparation and Characterization

The study was carried out with three different  $\text{WO}_3$  oxides. The reference  $\text{WO}_3$  oxide is the thermodynamically stable form with a  $\text{ReO}_3$ -type structure which can be described by a three-dimensional array of distorted ( $\text{WO}_6$ ) octahedra sharing all their corners (Fig. 1c). This oxide was prepared by dehydration of  $\text{WO}_3 \cdot \text{H}_2\text{O}$ .

The other two oxides which cannot be obtained from any of the stable forms are hexagonal and pyrochlore  $\text{WO}_3$ ; they have been prepared using the "chimie douce" routes (6). Hexagonal  $\text{WO}_3$  was prepared by dehydration of the precursor hydrate  $\text{WO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$  at about 300°C (6, 7). The structure of h. $\text{WO}_3$  is schematized in Fig. 1a and can be described by ( $\text{WO}_6$ ) octahedra sharing their corners and forming six-membered rings in the (001) plane; stacking of such layers along the *c* axis leads to the formation of hexagonal tunnels running along the axis (1D tunnels).

$\text{WO}_3$  with a pyrochlore-type structure and 3D tunnels was obtained from a pyrochlore-type ammonium tungstate after  $\text{NH}_4^+/\text{H}^+$  exchange and dehydration of the hydronium compounds (6, 8). The structure of p. $\text{WO}_3$  can

<sup>1</sup> To whom all correspondence should be addressed.

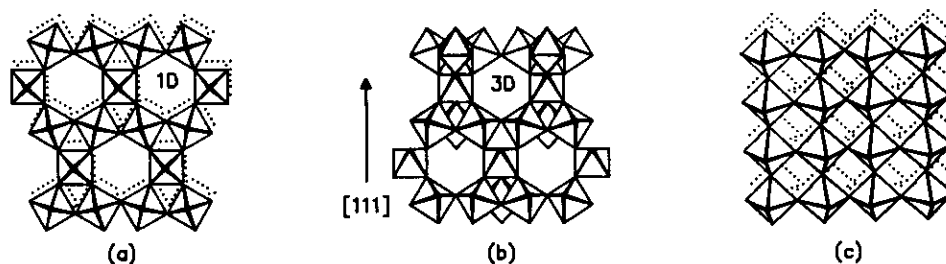


FIG. 1. The structures of WO<sub>3</sub> oxides: (a) structure of hexagonal WO<sub>3</sub>; (b) structure of pyrochlore WO<sub>3</sub> (stacking of the (111) planes along [111]); (c) the ReO<sub>3</sub>-type structure of monoclinic WO<sub>3</sub>.

be described in terms of distorted hexagonal trioxide layers. In the (111) plane the (WO<sub>6</sub>) octahedra are arranged as those in the h.WO<sub>3</sub> (001) plane; these layers are linked along the [111] direction by intermediary (WO<sub>6</sub>) octahedra, resulting in the three-dimensional interconnected tunnels (Fig. 1b). In fact, p.WO<sub>3</sub> presents a lacunar structure with 18 and 13% of W and O vacancies, respectively, compared with stoichiometric WO<sub>3</sub> (9).

### II.2. High-Energy Ball Milling Procedure

The high-energy ball milling experiments were performed with a SPEX mixer mill Model 8000. Milling was conducted in air. One steel ball was used in a cylindrical stainless steel vial 2.5 cm long × 1.27 cm in diameter. The charge ratio (mass of grinding ball/mass of powder charge) was 4.

Subsequent to milling, X-ray diffraction—with a PW1050 Philips diffractometer with CuK $\alpha$  radiation—was used to characterize the milled products. Two kinds of experiments were performed to study amorphization of WO<sub>3</sub> oxides and reaction of these oxides with Cs<sub>2</sub>CO<sub>3</sub> in such high-energy milling conditions.

## III. RESULTS AND DISCUSSION

### III.1. Amorphization of WO<sub>3</sub> Oxides

X-ray diffraction patterns of grinded ReO<sub>3</sub>-type WO<sub>3</sub> indicate it cannot be amorphized even after 80 hr of high-energy milling. X-ray diffraction line broadening and diminution in peak intensity are observed (Fig. 2). That indicates a reduction in crystallite size which reaches a limit value and does not change for times up to 80 hr. Due

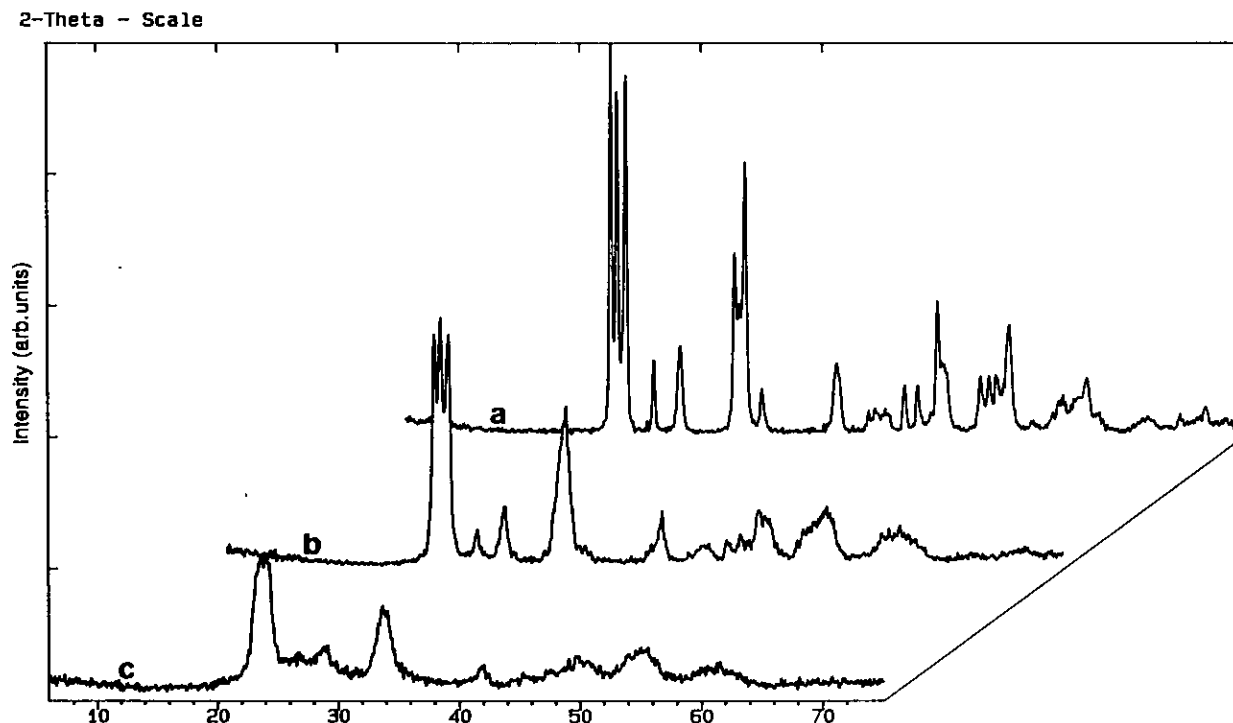


FIG. 2. X-ray diffraction patterns (CuK $\alpha$  radiation) of monoclinic WO<sub>3</sub> (a) and after grinding for 20 hr (b). The pattern after grinding for 80 hr (c) is characteristic of very fine crystallite sizes.

to diffraction peaks overlapping it is not possible to determine the mean crystallite size. In this case the effect of high-energy milling is to induce dislocations which move and gather, leading to intercrystallite boundaries and diminishing the crystallite size. However, the grinding energy was not powerful enough to decrease the crystallite size until the formation of an amorphous phase even when the charge ratio (mass of grinding ball/mass of powder charge) was increased.

In contrast with monoclinic  $\text{WO}_3$ , the metastable hexagonal- and pyrochlore-type  $\text{WO}_3$  oxides can be amorphized by grinding. The pyrochlore is the easiest to amorphize and grinding times required to obtain complete amorphization are 7 hr in our experimental conditions. X-ray analysis reveals reduction in peak intensities without noticeable broadening in the diffraction lines (Fig. 3). That indicates a completely different behavior compared to monoclinic  $\text{WO}_3$ : the effect of mechanical treatment does not produce a reduction in crystallite size but amorphization by structural collapse. For hexagonal  $\text{WO}_3$  the same general features have been observed but with some differences. Amorphization kinetics are much slower; indeed for 20 hr grinding there was only a partial amorphization (Fig. 4). Furthermore, at the end of the transformation, when amorphization is near completion, another transformation occurs: this is the recrystallization of the amorphous phase into the stable monoclinic  $\text{WO}_3$ .

The difference in behavior of these three  $\text{WO}_3$  oxides in such high-energy milling conditions can be tentatively related to their thermodynamic stability. Pyrochlore and hexagonal oxides are metastable phases with higher free energies compared to the monoclinic stable oxide and can evolve more easily into amorphous phases than the stable oxide. For the pyrochlore oxide the rapid amorphization compared to the hexagonal oxide can be related to its lacunar structure (9) which favors the structural collapse and amplifies the effect of mechanical treatment.

### III.2. Reaction of $\text{WO}_3$ Oxides with $\text{Cs}_2\text{CO}_3$ : Synthesis of Cubic Pyrochlore-Type Cesium Tungstate

We have conducted a comparative study to investigate the mechanochemical reactions involving the three  $\text{WO}_3$  oxides with cesium carbonate. This system was chosen because alkali tungstates can be synthesized by reacting  $\text{WO}_3$  with alkali carbonates in the solid state at various temperatures (10). In particular we have obtained a cubic pyrochlore-type cesium tungstate by reaction of hexagonal  $\text{WO}_3$  and  $\text{Cs}_2\text{CO}_3$  from a mixture corresponding to  $\text{Cs}/\text{W} = 2/3$  heated at  $300^\circ\text{C}$  during 12 days. In the same experimental conditions monoclinic  $\text{WO}_3$  presents a weak reactivity.

It was interesting to look at how the different behaviors of stable and metastable  $\text{WO}_3$  oxides under nonreactive grinding conditions could influence their behavior under

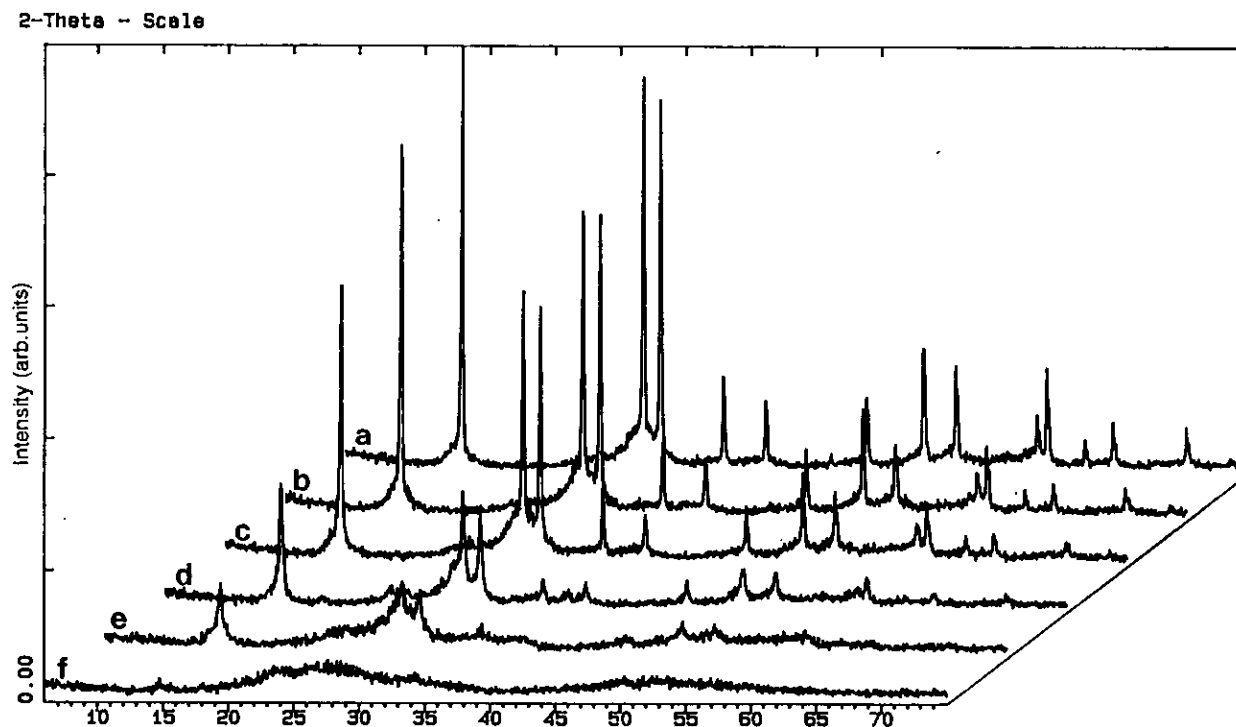


FIG. 3. X-ray diffraction patterns ( $\text{CuK}\alpha$  radiation) of pyrochlore  $\text{WO}_3$  (a) and after grinding for 30 min (b), 1 hr (c), 2 hr (d), and 3 hr (e). The pattern after grinding for 7 hr (f) is characteristic of a completely amorphous phase.

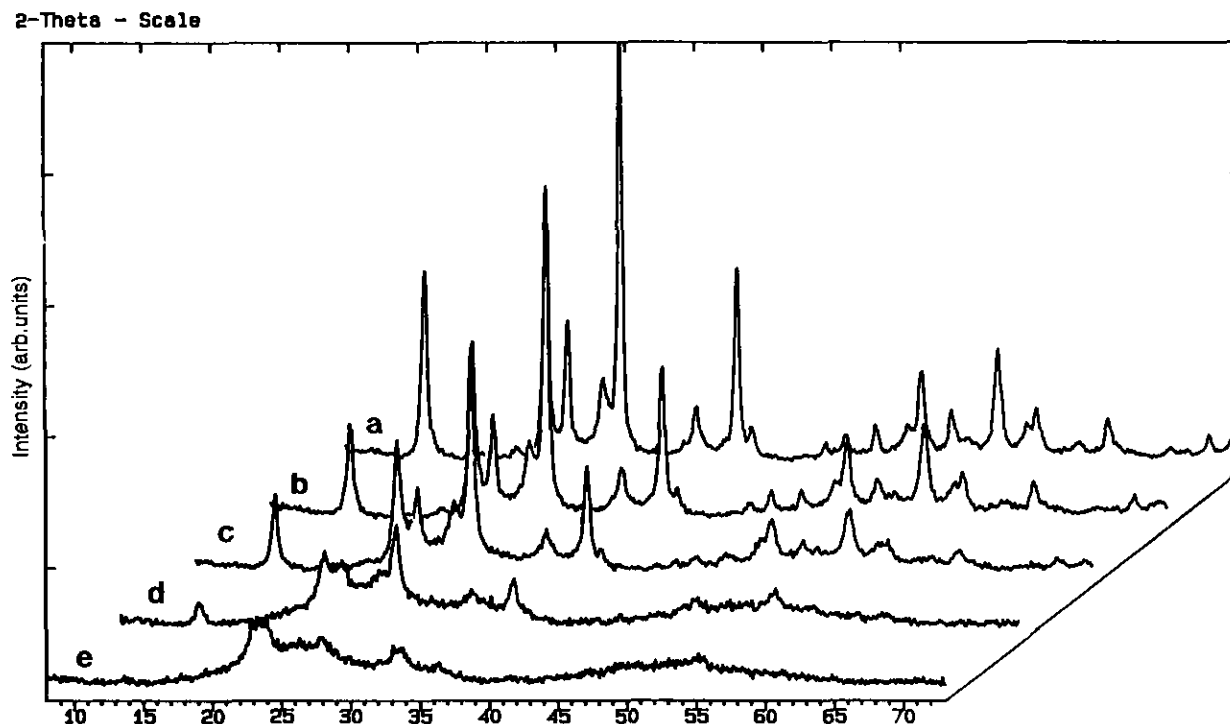


FIG. 4. X-ray diffraction patterns (CuK $\alpha$  radiation) of hexagonal WO<sub>3</sub> (a) and after grinding for 1 hr (b), 6 hr (c), and 10 hr (d). The pattern after grinding for 20 hr (e) is characteristic of a mixture of an amorphous phase and monoclinic WO<sub>3</sub> with very fine crystallite size.

reactive grinding conditions. For that purpose high-energy ball milling has been conducted with mixtures of WO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> in the ratio Cs/W = 2/3 and a charge ratio of 4.

In these experimental conditions, the three WO<sub>3</sub> oxides behave similarly, leading to the formation of cubic pyrochlore-type cesium tungstate, but the kinetics of the reactions are strongly influenced by the nature of the oxide.

X-ray diffraction patterns of milled hexagonal WO<sub>3</sub> + Cs<sub>2</sub>CO<sub>3</sub> are provided in Fig. 5 as an example. After the first few hours of grinding an orthorhombic phase appears (Fig. 5b); then, with more grinding time, the

pyrochlore phase appears after 15 hr. The transformation is complete in 50 hr, leading to a cubic pyrochlore-type cesium tungstate with very broad X-ray diffraction lines (Fig. 5c). As the milling time increases the crystallinity of the cubic pyrochlore phases also increases and the X-ray diffraction lines narrow (Fig. 5d).

For comparison, we have listed in Table 1 the different steps of the reaction for the three WO<sub>3</sub> oxides as a function of time. It appears that monoclinic WO<sub>3</sub> reacts much faster than the two metastable WO<sub>3</sub> oxides for which the kinetics are considerably slowed down.

Comparing these oxides' behavior during nonreactive and reactive grinding, it is worth noting that it is not the

TABLE 1  
Summary of Phases Formed in Milling WO<sub>3</sub> + Cs<sub>2</sub>CO<sub>3</sub> as a Function of Time (hr)

WO <sub>3</sub> + Cs <sub>2</sub> CO <sub>3</sub>	WO <sub>3</sub> + orthorhombic tungstate	WO <sub>3</sub> + orthorhombic tungstate + pyrochlore tungstate	Pyrochlore tungstate (broad X-ray diffraction lines)	Pyrochlore tungstate (well crystallized)
h.WO <sub>3</sub>	1	15	50	90
p.WO <sub>3</sub>	1	30	60	70
m.WO <sub>3</sub>	1	2	10	40

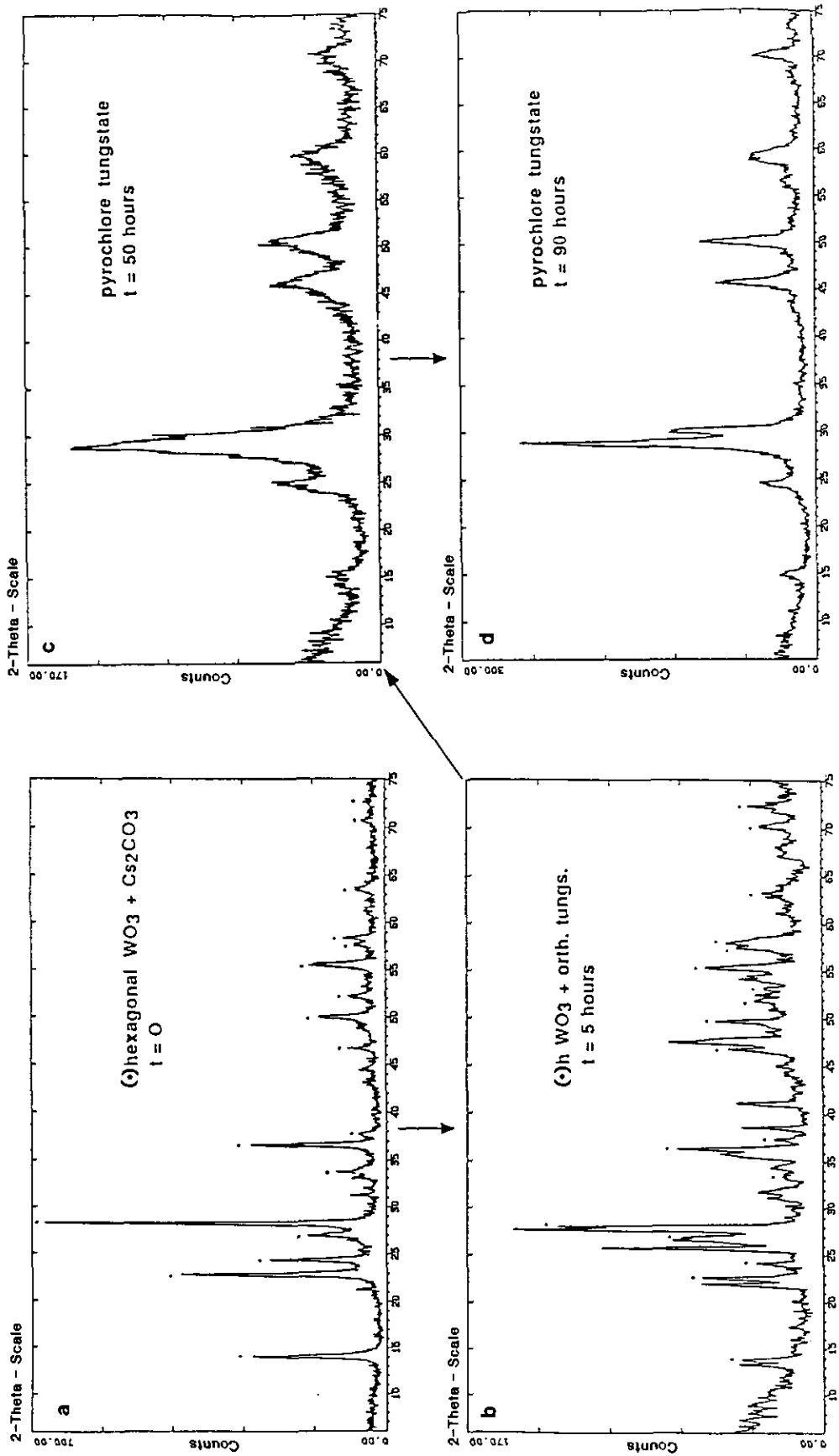


FIG. 5. X-ray diffraction patterns (CuK $\alpha$  radiation) of milled  $WO_3 + Cs_2CO_3$  as a function time: the starting mixture (a) and after milling for 5 (b), 50 (c), and 90 (d) hours.

TABLE 2  
Characteristics of Lacunar Cubic Pyrochlore-Type Cesium  
Tungstate and Synthesis Conditions

Cubic pyrochlore-type cesium tungstate obtained by	<i>a</i> (Å)	Reaction time (hr)	Reaction temperature (°C)
Solid state reaction h.WO <sub>3</sub> + Cs <sub>2</sub> CO <sub>3</sub>	10.326(7)	288	300
Reactive grinding of h.WO <sub>3</sub> + Cs <sub>2</sub> CO <sub>3</sub>	10.310(8)	90	RT
Reactive grinding of p.WO <sub>3</sub> + Cs <sub>2</sub> CO <sub>3</sub>	10.316(8)	70	RT
Reactive grinding of m.WO <sub>3</sub> + Cs <sub>2</sub> CO <sub>3</sub>	10.287(6)	40	RT

metastable oxides that amorphize during the milling process which present the highest reactivity, but the stable oxide for which the milling effect produces small crystallites. So, in these grinding reactive conditions, the WO<sub>3</sub> reactivity seems to be related to the presence of a large number of intercrystallite boundaries rather than to an amorphous phase.

The cubic pyrochlore-type cesium tungstates obtained by milling are very similar to the one prepared at 300°C by solid state reaction from hexagonal WO<sub>3</sub>. The refinement of the cell parameters gives values reported in Table 2. The experimental densities measured are also very comparable. We can conclude that the samples prepared by high-energy ball milling also present the lacunar structure with W and O vacancies, which characterizes the phase prepared at 300°C (10, 11).

The grinding times required to obtain these tungstate phases, between 10 and 90 hr depending on the WO<sub>3</sub> structure and the crystallinity of the tungstate, can appear long, but they are rather short in comparison with the solid state reaction h.WO<sub>3</sub> + Cs<sub>2</sub>CO<sub>3</sub> at 300°C which needs about 300 hr to be complete.

As is usually observed, high-energy ball milling also introduces some impurities from the steel ball and vial to

the sample; chemical analyses show that such contamination is 0.25% Fe, 0.04% Cr, and 0.05% Ni.

#### IV. CONCLUSIONS

We have investigated the structural effect on WO<sub>3</sub> oxide behavior in nonreactive grinding conditions. High-energy grinding induces amorphization of the metastable pyrochlore- and hexagonal-type WO<sub>3</sub> oxides with collapse of the precursor oxide structure. The stable monoclinic WO<sub>3</sub> cannot be amorphized; the effect of high-energy ball milling is to diminish the crystallite size to a limit value.

Reactive grinding of WO<sub>3</sub> + Cs<sub>2</sub>CO<sub>3</sub> mixtures leads to the formation, after milling times which depend on the WO<sub>3</sub> structure, of lacunar cubic pyrochlore-type cesium tungstate. Monoclinic WO<sub>3</sub> presents the fastest reaction kinetics compared with the two other oxides, showing that the mechanochemical reactivity is strongly dependent on the intercrystallite boundaries rather than on the amorphous oxide phase.

This work exemplifies the power of mechanochemical reaction as a new route for the preparation of new materials.

#### REFERENCES

1. J. S. Benjamin, *Metall. Trans.* **1**, 2943 (1970).
2. E. Arzt and L. Schultz (Eds.), "New Materials by Mechanical Alloying Techniques." Deutsche Gesellschaft für Metallkunde, Oberursel, 1989.
3. P. A. Thiessen, K. Meyer, and G. Heinicke, "Grundlagen der Tribochemie." Akademie-Verlag, Berlin, 1966.
4. G. Heinicke, "Tribochemistry." Akademie-Verlag, Berlin, 1984.
5. E. G. Avvakumov, "Mechanical Methods of Activating Chemical Processes." Nauka, Novosibirsk, 1986.
6. M. Figlarz, *Prog. Solid State Chem.* **19**, 1 (1989).
7. B. Gérard, G. Nowogrocki, J. Guenot, and M. Figlarz, *J. Solid State Chem.* **29**, 429 (1979).
8. A. Coucou and M. Figlarz, *Solid State Ionics* **28-30**, 1762 (1988).
9. A. Coucou, A. Driouiche, M. Figlarz, M. Touboul, and G. Chevrier, *J. Solid State Chem.* **99**, 283 (1992).
10. A. Driouiche, F. Abraham, M. Touboul, and M. Figlarz, *Mater. Res. Bull.* **26**, 901 (1991).
11. G. Chevrier, M. Touboul, A. Driouiche, and M. Figlarz, *J. Mater. Chem.* **2**, 639 (1992).