

## The Solvolytic Disproportionation of Mixed-Valence Compounds

### I. Pr<sub>7</sub>O<sub>12</sub>

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Received June 15, 1987; in revised form January 4, 1988

Pr<sub>7</sub>O<sub>12</sub> is an intermediate praseodymium oxide of mixed oxidation state. It is single phase with metal atoms occupying different types of crystallographic sites. In contact with dilute acid, among other solvents, the single-phase compound loses Pr<sup>3+</sup> ions to the solution and the residue is oxidized to PrO<sub>2</sub>. The morphology of the reaction, studied by electron microscopy, indicates that the dissolution follows extended crystal defects, probably dislocations, and involves the removal of all the oxide in the reaction path. This requires the transport of oxygen and electrons in the reaction zone where praseodymium is reduced with the concomitant oxidation of material adjacent to it. This reaction occurs without the destruction of the original framework because Pr<sub>7</sub>O<sub>12</sub> and the other intermediate oxides are fluorite-related and transform to fluorite-type PrO<sub>2</sub> without reconstruction. © 1988 Academic Press, Inc.

### Introduction

Inhomogeneous solids frequently react with percolating solutions to dissolve a reactive fraction. This process, called leaching, is historically associated with the selective removal of particular solid phases from a compositionally heterogeneous mixture, for example, the removal of native gold from its ores by cyanide complexation into solution. In this paper we are not concerned with heterogeneity at the level of separate phases as in gold ores but of heterogeneity of valence states at the atomic level. We choose examples of single-phase materials in which the same metallic element, present in two oxidation states and usually occupying two different crystallographic sites, is separated by the removal from the solid of one type of metallic ion. The other valence state remains in a solid residue.

The example to be reported here is the reaction of Pr<sub>7</sub>O<sub>12</sub> with water or dilute acids to give ultimately a solution of Pr<sup>3+</sup> (aq) and crystalline PrO<sub>2</sub>. This reaction was reported and discussed by Clifford (1). It is well known also in other systems such as in TbO<sub>x</sub> (1), Pb<sub>3</sub>O<sub>4</sub> (2), and Mn<sub>3</sub>O<sub>4</sub> (3).

Clifford discussed the "solvolytic disproportionation" of PrO<sub>x</sub> (1.5 < x < 2.0) with a variety of solvolytic agents (1). Brauer and Pfeiffer (4) undertook to study further the range of conditions and agents that could bring about this interesting separation. More recently Caro and his co-workers (5) have utilized this reaction to prepare PrO<sub>2</sub> without resorting to high temperatures and pressures.

The structure of Pr<sub>7</sub>O<sub>12</sub> has been found (6) to be isostructural with UY<sub>6</sub>O<sub>12</sub> as illustrated in Fig. 1. In Pr<sub>7</sub>O<sub>12</sub> the four Pr<sup>3+</sup> and three Pr<sup>4+</sup> occupy the six-coordinated and six seven-coordinated cation positions

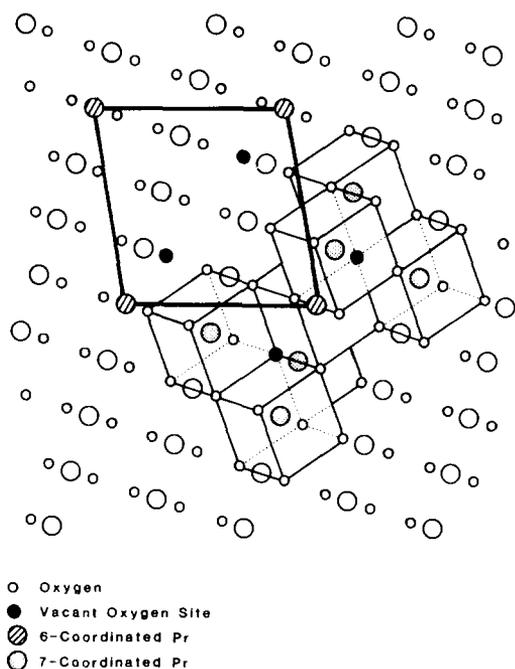
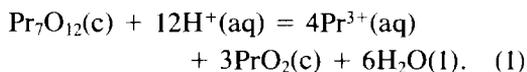


FIG. 1. A projection of the unit cell of Pr<sub>7</sub>O<sub>12</sub> along (211) (heavy solid lines). All the praseodymium atoms are cubically coordinated with oxygen in the fluorite structure as suggested by the cubes drawn about the metal atoms. There are two vacant oxygen sites (●) along the body diagonal of the parent fluorite unit cell in Pr<sub>7</sub>O<sub>12</sub> as shown. The atoms at the corners of the unit cell drawn are six-coordinated while all others are seven-coordinated.

about two empty oxygen sites along the threefold axis in the unit cell. The distribution of the cations among their sites has not definitely been settled, however, the symmetry of the rhombohedral structure (*R* $\bar{3}$ ) could easily be achieved by placing a Pr(1) ion in the six-coordinated site and having the six seven-coordinated sites occupied by averaged Pr(2) ions with an averaged charge resulting from the known electron hopping conductivity (7). This structure is related to fluorite PrO<sub>2</sub> by the ordered removal of one-seventh of the oxygen atoms.

The reaction studied in this work is



What is the mechanism of this selective dissolution? It must involve a surface process with the loss of Pr<sup>3+</sup> followed by a propagation of the reaction into the bulk. Overall, the loss of Pr<sup>3+</sup> to the solution results in the conversion of the oxygen-deficient fluorite structure to a filled fluorite structure by means of oxygen and possibly electron transfer. One must study the morphology of the reaction to determine the mechanisms that leave crystals of PrO<sub>2</sub> where none existed before. Since the original Pr<sup>4+</sup> ions are atomically dispersed, it would be helpful to investigate the reaction utilizing atomic-resolution electron microscopy.

### Experimental Part

The praseodymium oxide was obtained from Research Chemicals Inc. as the ignition product of an oxalate 99.999% pure. This material was subsequently heated in a muffle furnace at 1000°C for 12 hr. The furnace was then turned off and allowed to cool slowly in air to 200°C before removal to a desiccator for storage. The oxide, after treatment in the muffle furnace, was annealed for 2 days at a temperature of 850°C under 10 Torr of oxygen to assure a composition of Pr<sub>7</sub>O<sub>12</sub>.

The conditions used by Brauer and Pfeiffer (4) were approximated to produce PrO<sub>2</sub> from Pr<sub>7</sub>O<sub>12</sub>. One sample of Pr<sub>7</sub>O<sub>12</sub> was leached by boiling it in water for 3 hr followed by the dissolution of the Pr(OH)<sub>3</sub> formed by a 10% acetic acid solution. Another was prepared by stirring Pr<sub>7</sub>O<sub>12</sub> powder in a 5% acetic acid solution for 8 days. After treatment, each sample was washed carefully, first in distilled water, followed by a wash in absolute alcohol, then stored in a desiccator for examination in the microscope.

Each oxide specimen to be studied by HREM was dispersed in dry acetone and a drop of this suspension was applied to a holey carbon film on a microscope grid.

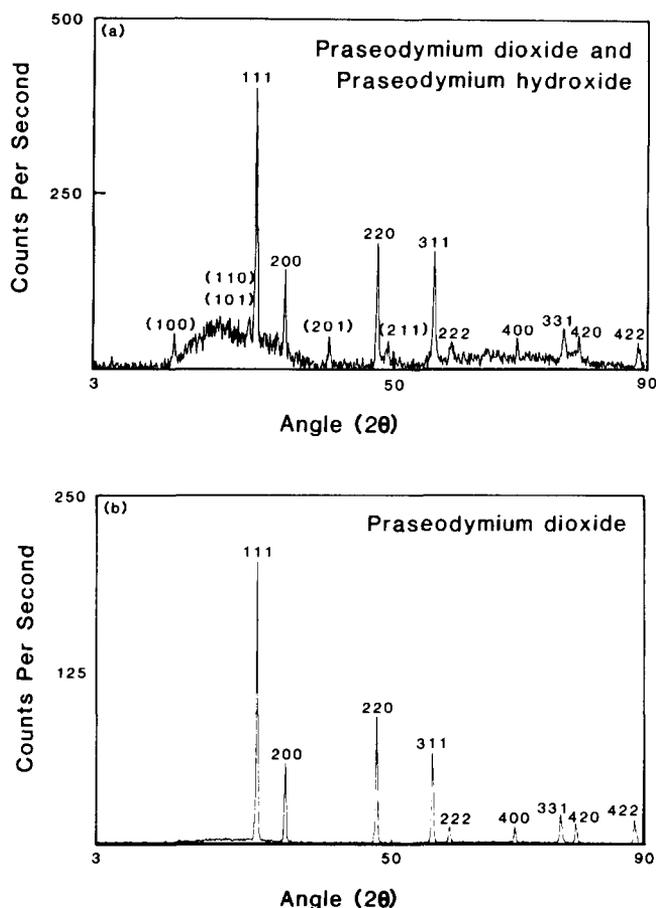


FIG. 2. X-ray powder diffraction pattern of leached  $\text{Pr}_2\text{O}_{12}$ . (a)  $\text{Pr}_2\text{O}_{12}$  leached with water to give a mixture of  $\text{Pr}(\text{OH})_3$  and  $\text{PrO}_2$ . Miller indices for the hydroxide are in parentheses. (b)  $\text{Pr}_2\text{O}_{12}$  leached with water and treated with acid to remove the  $\text{Pr}(\text{OH})_3$ .

The specimens thus prepared were examined in a JEM 200CX top-entry, high-resolution microscope with a double-tilt specimen holder and a  $\text{LaB}_6$  filament. The microscope was equipped with a TV image pick-up and viewing system.

## Results

X-ray diffraction patterns of the final leached product from the treatment with boiling water is shown in Fig. 2a. This pattern has reflections from both  $\text{PrO}_2$  and  $\text{Pr}(\text{OH})_3$ . Treatment with 10% acetic acid to

leach out the  $\text{Pr}(\text{OH})_3$  leaving only  $\text{PrO}_2$  is shown in Fig. 2b.

The crystals remaining after leaching consisted of a framework of re-entrant narrow wells from which the  $\text{Pr}(\text{OH})_3$  or  $\text{Pr}_2\text{O}_3$  had been removed leaving a skeleton of  $\text{PrO}_2$ . Although there appeared to be a preferred orientation of these re-entrant voids they did occur in many directions. Examination of Figs. 3a and 3b will show that this description fits more closely the water-leached crystal (Fig. 3a) than the acid-leached crystal Fig. 3b), yet they are not greatly dissimilar. The angles between the

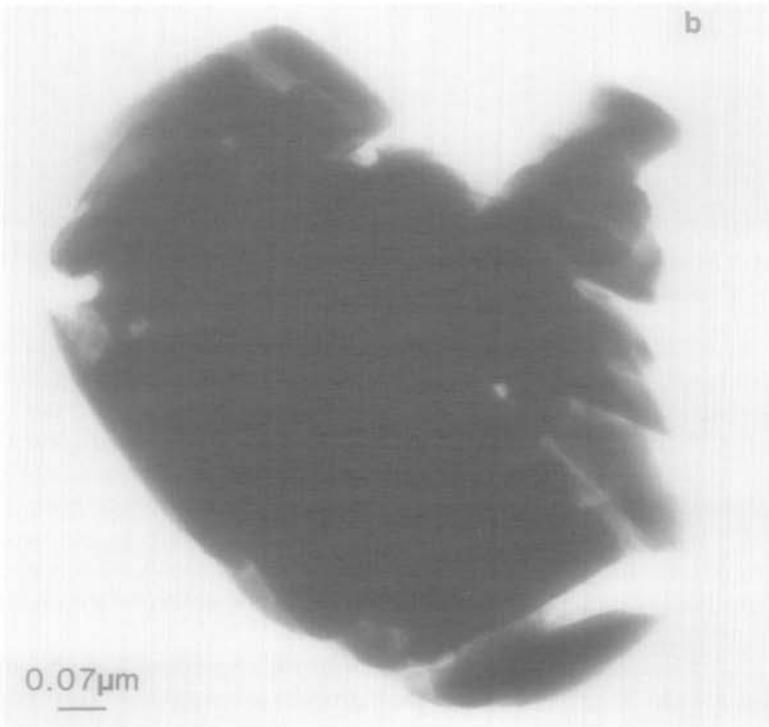
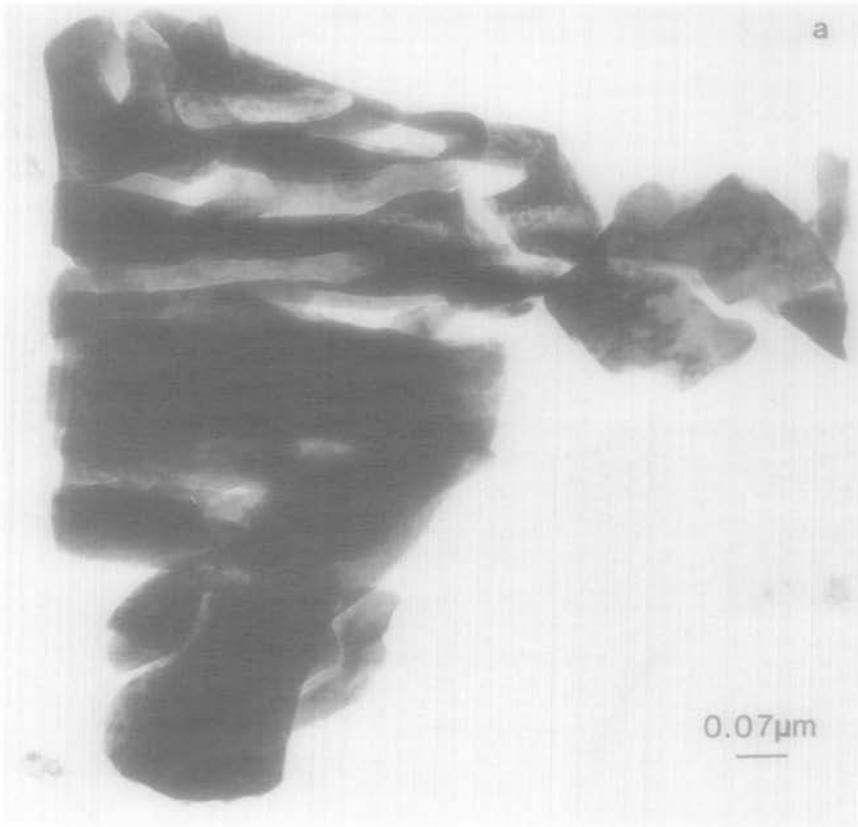


FIG. 3. An electron micrograph showing the final  $\text{PrO}_2$  remaining after leaching. (a) The water-acid-leached  $\text{PrO}_2$  product. (b) The acid-leached  $\text{PrO}_2$  product.

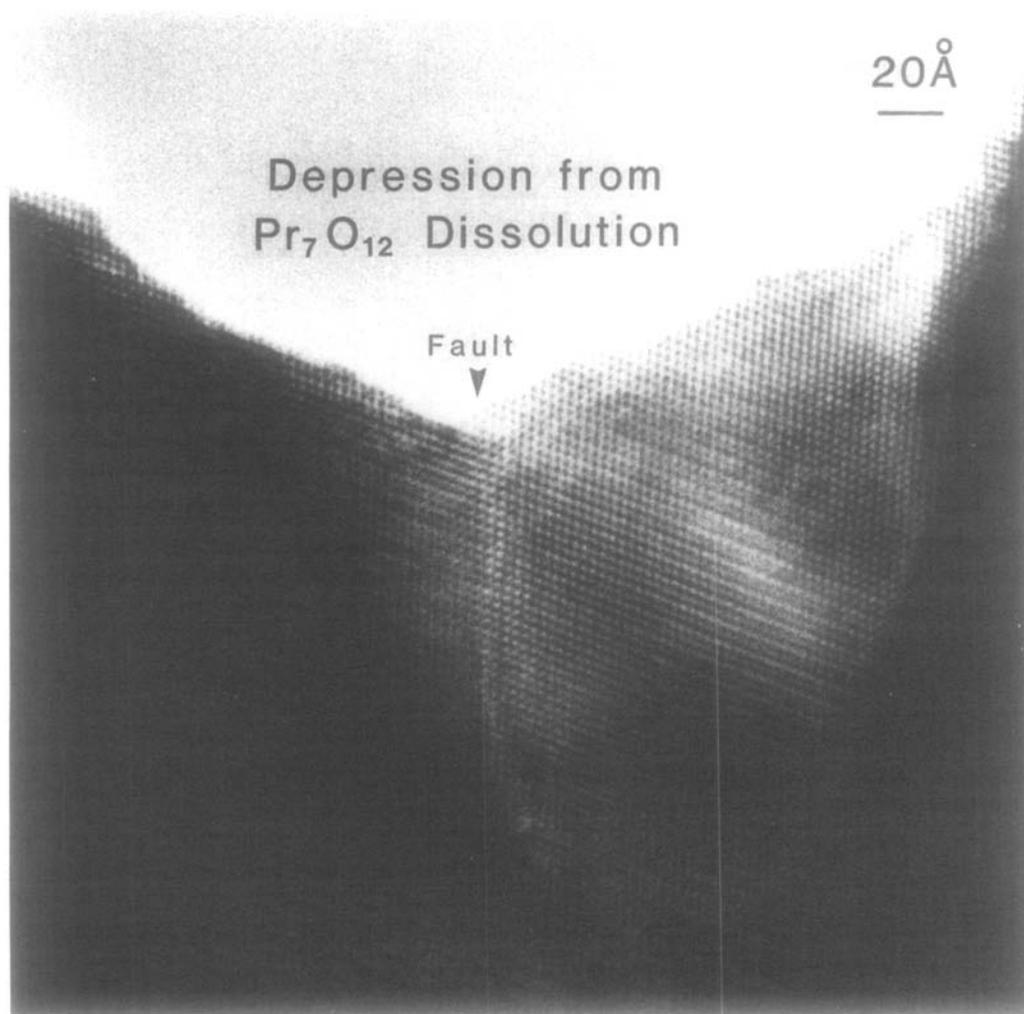


FIG. 4. A  $\langle 110 \rangle$  high-resolution electron micrograph along  $\langle 110 \rangle$  of a reacted crystal showing the excessive removal of material from a faulted region near the surface.

profiles of the tips of the penetrating fingers are approximately  $35$  or  $60^\circ$ . These angles are close to that between  $[110]$  and  $[111]$  planes suggesting that in this case as well as in the original material the  $[111]$  planes are more stable (8).

Diffraction contrast images of the original particles of  $\text{PrO}_x$  indicate plentiful dislocations that usually intersect the surface at an angle. A leached crystal reveals the nature of the regions yielding to the attack. In Fig. 4 it is apparent that material has been

removed from the vicinity of a distorted or dislocated volume of the crystal. The faulted region perpendicular to the surface may be located by looking at a low angle along various atomic rows in the photograph. It seems likely that such dislocations are reaction sites and that the reaction follows these defects forming the re-entrant fingers.

In Fig. 5 several aspects of the leaching process are revealed. This image was taken of a crystal after being stirred 8 days in 5%

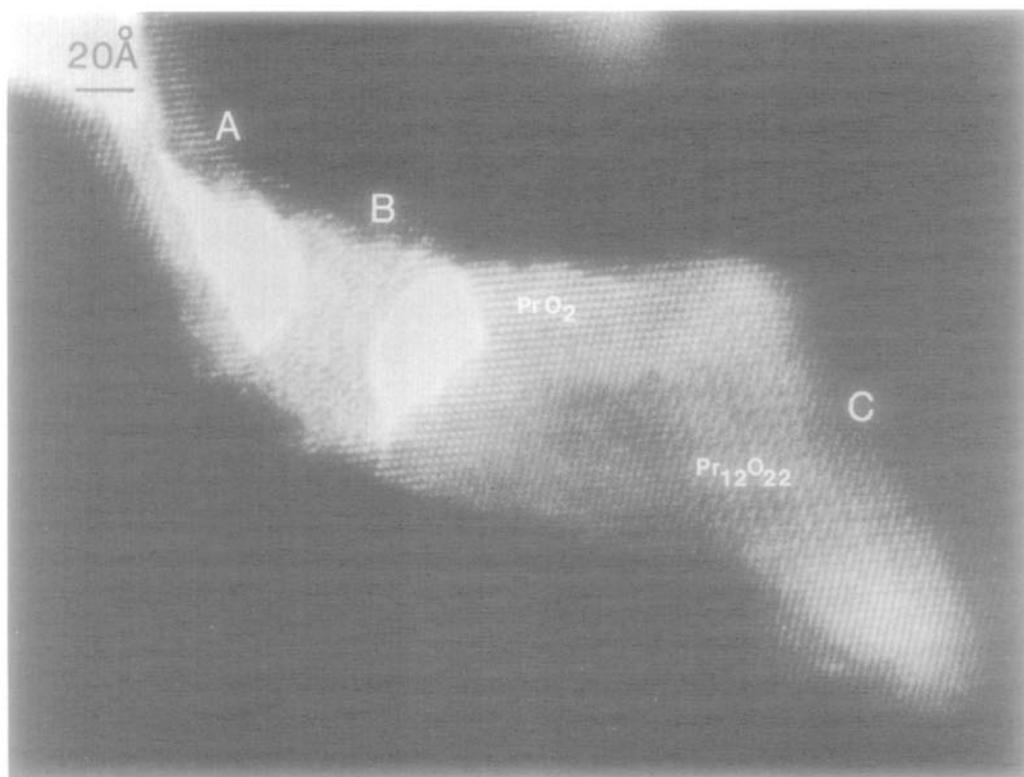
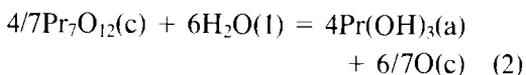


FIG. 5. A  $\langle 110 \rangle$  high-resolution electron micrograph along  $\langle 110 \rangle$  of a reacted crystal showing a remnant of the reaction including a residue of  $\text{PrO}_2$  at A, an amorphous region at B, and a superstructure of  $\text{Pr}_{12}\text{O}_{22}$  set in a thin section of  $\text{PrO}_2$  at C.

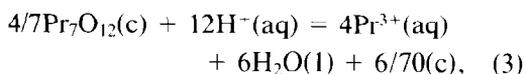
acetic acid and shows a residual thin region left when material was removed. Consider three features as follows: A thin bridge of  $\text{PrO}_2$  near the outside surface connects two thicker regions of dioxide. Further along the channel, a partially ordered bridge again links the two thicker regions. The fringes at the connecting edges clearly extend through the interface although they are rather irregularly spaced. The middle of the bridge appears nearly amorphous suggesting some reaction, perhaps hydration, during the reaction or when washing. The remaining thin region is primarily  $\text{PrO}_2$ ; however, there is clearly the periodicity of the intermediate phase ( $\text{Pr}_{12}\text{O}_{22}$ ) manifest in the superstructure. This clearly is an incompletely oxidized region.

### Discussion

The solvolytic disproportionation of  $\text{Pr}_7\text{O}_{12}$  may be represented as follows. At some point of attack the crystal is dissolved by the action of water followed by treatment with acid or more rapidly with acid directly. This is illustrated by the X-ray diffraction patterns of Figs. 2a and 2b that show the disappearance of the trivalent praseodymium from the fluorite-related phase.



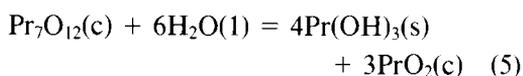
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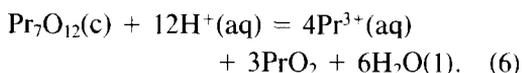
followed by a reaction in the interior as the oxygen is transported by diffusion along a gradient away from the reaction site,



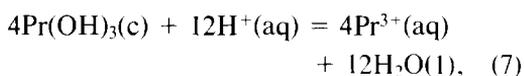
The overall reaction is, then,



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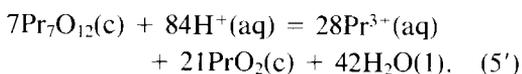
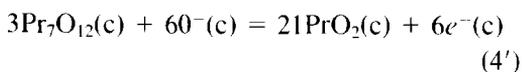
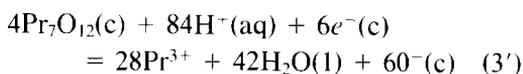


Reaction (5) is followed by the selective dissolution of  $\text{Pr}(\text{OH})_3$  using 10% acetic acid,



leading to the same final overall reaction as written in Eq. (6).

The oxidation state of the diffusing oxygen could be neutral as indicated in Eqs. (2), (3), and (4) or it could be either  $\text{O}^-$  or  $\text{O}^{2-}$ . In either of these last alternatives electrons would have to be transported in the opposite direction to anion flow. Any of these transport mechanisms are plausible since the oxide is both a good oxygen conductor and an electronic semiconductor (7, 8). Oxygen transport in either polycrystalline or single crystals of  $\text{Pr}_7\text{O}_{12}$  was found to be by neutral oxygen interstitials utilizing oxygen exchange studies and a point-defect model (9). For example, the reactions (3), (4), and (5) would become



None of the experiments described here aid in deciding the oxidation state of the diffus-

ing oxygen. The smaller uncharged oxygen might be the most mobile.

These reactions, although occurring here with  $\text{Pr}_7\text{O}_{12}$ , could occur with any of the intermediate mixed-valence oxides between  $\text{Pr}_2\text{O}_3$  and  $\text{PrO}_2$ . Furthermore, it is reasonable that there would be ordered phases temporarily formed as the lower oxide is oxidized toward  $\text{PrO}_2$  or reduced toward  $\text{Pr}_2\text{O}_3$ . An example of this is clear in Fig. 5 on the right side of the thin region where an ordered superstructure has been formed. This superstructure, with four praseodymium atoms in the cross section of the projected unit cell, is  $\text{Pr}_{12}\text{O}_{22}$ .

In this study, the electron microscope has revealed the actual course of the reaction by imaging the products. In Fig. 3a, for example, it is clear that the reaction with boiling water has proceeded preferentially along certain directions in the crystal, leaving behind the product hydroxide to be leached subsequently by the acetic acid solution. A similar morphology is indicated in the image shown in Fig. 3b when the crystal is leached with dilute acid. The conclusion to be drawn is that certain paths in the crystal are easy reaction paths and that these are almost certainly dislocations shown to be plentiful by dark-field imaging. The point of attack would be the point of emergence of the dislocation with the surface. Figure 4 shows the residue of dislocations in the reacted crystal and Fig. 5 shows the termination of a reaction at a fault along which it has presumably traveled.

It is to be expected that the reaction can proceed as the  $\text{PrO}_2$  formed becomes reducible by the exit of oxygen from the reaction region. This diffusion apparently occurs most easily along faults such as dislocations and the reaction terminates only when the specimen is oxidized completely to  $\text{PrO}_2$ . The skeleton of  $\text{PrO}_2$  remaining would then be the permanent record of the more dislocation-free regions of the original crystal.

Figure 5 would seem to have preserved a

record of the course of the reaction. The original Pr<sub>7</sub>O<sub>12</sub> is disordered as reaction proceeds by the invasion of OH<sup>-</sup>, H<sup>+</sup>, or anionic species on and into the acid-base sites of the crystalline surface accompanied by removal by the acid solution. This is suggested by the isthmus of disordered material in the middle of the thin region surrounded by PrO<sub>2</sub> on either side.

### Conclusion

The solvolytic disproportionation of Pr<sub>7</sub>O<sub>12</sub> occurs along preferred easy reaction paths that have dislocation complexes at their cores. This morphology is due to the fact that all the oxides involved are fluorite-related and a continuous framework of the dioxide remains even as the leached material has been removed along re-entrant fingers in several directions of easy reaction. The oxygen diffuses along dislocations in the solid, effectively transporting Pr<sup>3+</sup> to the reaction site for dissolution. It will be of interest to examine other examples of solvolytic disproportionation to reveal the path of reaction.

### Acknowledgment

Financial support from the NSF through Research Grant DMR-8516381 and Grant DMR-8306501 which supports the high-resolution facility is gratefully acknowledged.

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