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Twinning in $Pr_{24}O_{44}$: An Investigation by High-Resolution Electron Microscopy

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In the oxidation of Pr_7O_{12} to $Pr_{24}O_{44}$, the diminished number of defects within the crystal are structurally redistributed. Both structures have a direct relationship to the fluorite lattice for the arrangement of the metal and the oxygen atoms. The defect cluster in these structures consists of two vacancies within the oxygen sublattice that are paired along the [111] direction of the fluorite cell. The transition from one phase to the other is very often accompanied by twinning and also by the formation of antiphase boundaries. It is shown here that twin domains can be related to the loss of symmetry during transformation from the fluorite-related rhombohedral Pr_7O_{12} to the triclinic $Pr_{24}O_{44}$. The family tree for the rare-earth oxygen-deficient fluorite-related structures is used to explain the twinning observed in $Pr_{24}O_{44}$.

Introduction

Increasing attention is being given to relationships in cognate structures. Among the many reasons for this attention is the desire to know the course of chemical reaction in which one member of a family transforms into another. Few of the examples given in the literature have involved composition change in their transformations although this is certainly a valid application of the elegant group theoretical schemes that have been devised (*1, 2*).

The higher oxides of Ce, Pr, and Tb are structurally related to the fluorite CeO_2, PrO_2, and TbO_2 by an ordered or disordered arrangement of vacant oxygen sites. In this study twinning in $Pr_{24}O_{44}$ is used to rationalize the oxidation path followed in its formation from Pr_7O_{12}. Starting with a highly symmetrical structure called the aristotype (*3*) other related structures can be generated by symmetry reduction and the results represented in the form of a family tree (*2*).

In the rare-earth oxides of the homologous series R_nO_{2n-2} ($n \leq 4 \leq \infty$) the unit cells are known and the space groups have been suggested from X-ray (*4*), neutron (*5, 6*), and electron (*7*) diffraction patterns and from high-resolution electron microscope (HREM) images (*8, 9*). The space groups suggested are $R\bar{3}$ for R_7O_{12} (R = Pr (*4*), Tb (*10*), and Ce (*6*)), $P\bar{1}$ for the three compounds R_9O_{16} (R = Pr (*8*)), $R_{11}O_{20}$ (R = Tb (*10*), and Ce (*11*)), and $R_{24}O_{44}$ (R = Pr (*9*)). The structure and space group of $Pr_{40}O_{72}$ (n = 10) is less well established.

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Phase reactions involving both compositional and structural changes present a valuable opportunity for the application of group theory to transitions among the phases of the homologous series Pr_7O_{2n-2}. A powerful tool for this discussion of structural relationships is sub- and supergroups of the space groups of these phases. In this paper oxidation reactions are to be considered whereas reduction in the Pr_nO_{2n-2} and Tb_nO_{2n-2} systems have already been treated in a related way to some degree (*12*).

Symmetry Relationships in the Rare-Earth Oxide System

The group–subgroup relationships in oxidation among the members of the praseodymium oxide system, Pr_nO_{2n-2}, are shown as a family tree in Fig. 1. The family tree delineates the relationships between the anion-deficient structures related to the fluorite sublattice. The formalism used follows that proposed by Bärnighausen (*2*). In each reaction, arrows show the structural transition according to a maximal subgroup. Using these relationships and the indices of the particular transition one can predict the number and type of orientational twins that are produced in losing point-group symmetry. For example, the index t4 for the transition $Fm\bar{3}m$ to $R\bar{3}^{\frac{2}{m}}$ means that the transformation is classified as translationengleich. The new rhombohedral cell has only one-fourth the volume of the $Fm\bar{3}m$ cell and only one-fourth of the symmetry elements are kept. The index 4 also indicates quadruple twins are possibly

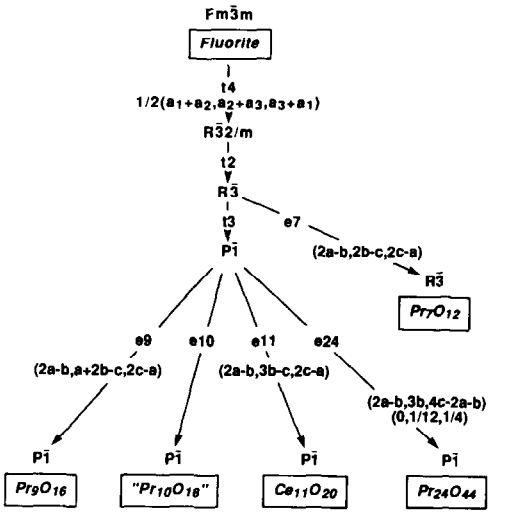


FIG. 1. Symmetry relationships in the praseodymium oxide system.

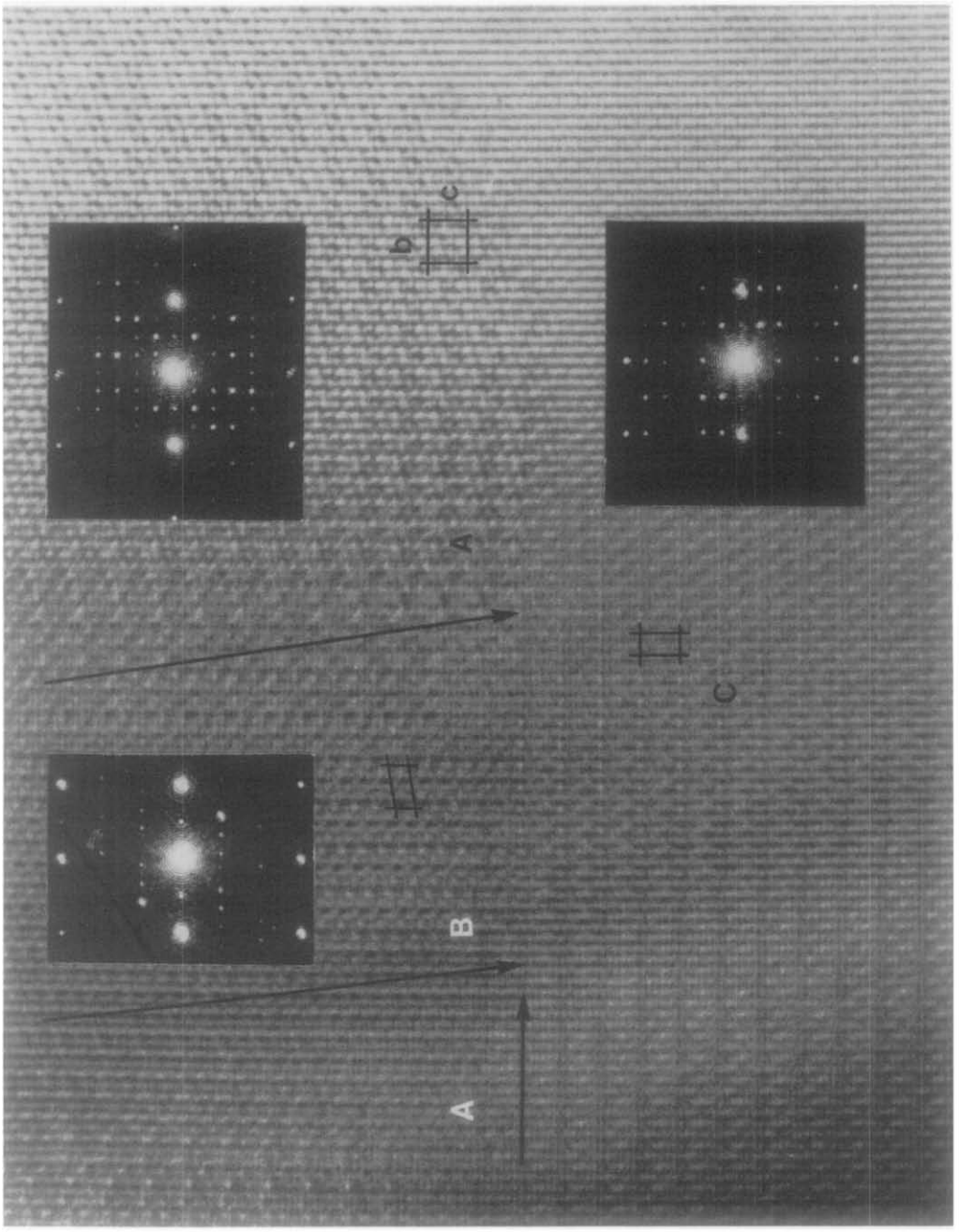
caused by the loss of the fourfold symmetry. An equivalent or isomorphous transition is indicated with an "e" and gives the number of antiphase domains to be expected from this transition.

In this study the Pr_7O_{12} ($R\bar{3}$) was produced by thermal reduction of higher oxides that are fluorite-related.

Experimental Part

The intermediate β phase $Pr_{24}O_{44}$ was prepared from a 99.999% pure oxide from Research Chemicals, Inc. The starting material, nominally "Pr_6O_{11}," was heated at 1000°C in a platinum dish for 24 hr in order to remove absorbed H_2O and CO_2, cooled to 200°C, and placed in a desiccator. The

FIG. 2. HREM image of $Pr_{24}O_{44}$. The cell is shown as a rectangle along the [100] direction in area A which corresponds to the [21$\bar{1}$] direction of the fluorite cell. Area B shows the $[1\bar{1}\bar{1}]_{120}$ rotation twin and area C is the $[100]_{180}$ rotation twin. Optical diffractograms are inset.


b
c
A
C
B
A

treatment at 1000°C in air produces Pr_7O_{12} which then reoxidizes to Pr_6O_{11} at 200°C. The dry decarbonated product was placed in a quartz tube and annealed at 350 Torr oxygen pressure for 2 days at 400°C to assure an annealed single-phased product with the composition $Pr_{24}O_{44}$, $\beta(1)$. An X-ray powder diffraction pattern confirmed that the product was the $\beta(1)$ phase.

A sample of this carefully prepared material was crushed, suspended in ethanol, and applied to a holey carbon film supported on a microscope grid. Electron micrographs were taken with a JEM 4000EX high-resolution electron microscope operated at 400 kV. The images were recorded at optimum defocus using a current density of about 5 A/cm^2. The thin crystal was oriented along the $[21\bar{1}]$ fluorite direction which is along the a-axis of the $\beta(1)$ cell. Along this shortest axis of the $\beta(1)$ structure (6.78 Å) the vacancies are aligned parallel to the electron beam. Optical diffractogram analysis was used to obtain Fourier transforms of the periodicities present in selected regions of the micrograph.

The image shown in Fig. 2 depicts a triple twin of $Pr_{24}O_{44}$. By comparing the inserted optical diffraction patterns with those calculated as illustrated in Fig. 3, the twins were identified with respect to their orientation in the fluorite lattice and the twin laws were determined. Area A shows a projection of $Pr_{24}O_{44}$ along the a-axis. The projected unit cell along this [100] direction is marked as a rectangle. The optical diffraction pattern shows this to be identical with one of the 12 independent $\langle 211 \rangle$ zones of the fluorite structure (Fig. 3). In fact, the whole crystal is oriented along one of the $\langle 211 \rangle$ zones. This confirms that the fluorite structure itself is only slightly modified and that the f.c.c. cation lattice is maintained throughout the crystal. However, three orientations of the superlattice, which depend on defects in the anion sublattice, are apparent. If the a-axis in $Pr_{24}O_{44}$ is said to be parallel to the $[21\bar{1}]$ fluorite direction the twin in area B has an a-axis parallel to $[\bar{1}12]$ and in area C an a-axis parallel to the $[2\bar{1}1]$ fluorite direction. The twin axis between A and B is the fluorite $[\bar{1}1\bar{1}]_{120}$ and the twin axis between A and C is the $[100]_{180F}$ direction.

The transformation matrices give the relationship between the unit cell of $Pr_{24}O_{44}$ and the fluorite cell for these twins as follows:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_F = 1/2\ (M) \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{24}$$

1. The relationship between twins A and B is given by the matrix M. The twin axis is the fluorite $[\bar{1}1\bar{1}]_{120}$.

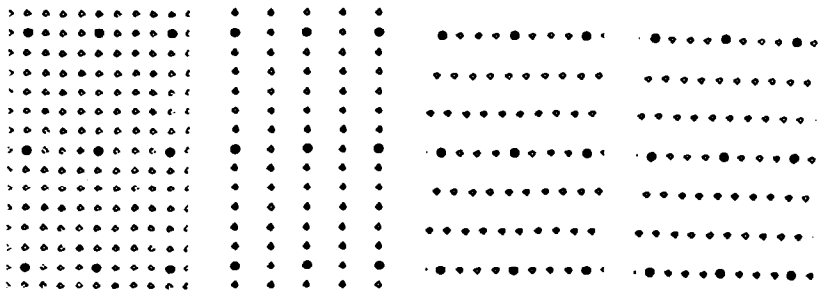


FIG. 3. Calculated diffraction patterns for $Pr_{24}O_{44}$.

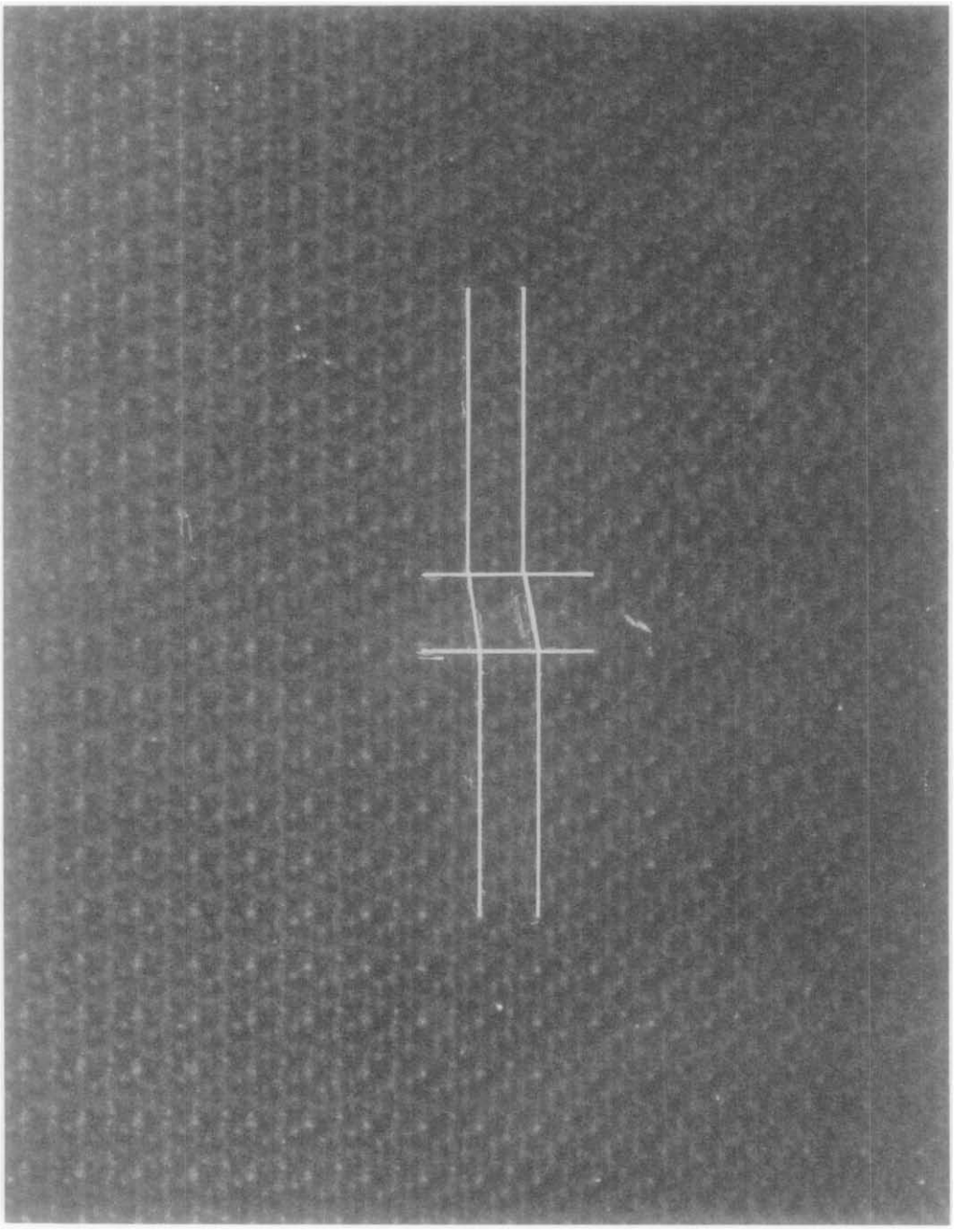


FIG. 4. Antiphase domains in $Pr_{24}O_{44}$.

$$\begin{pmatrix} 2 & 0 & \bar{2} \\ 1 & 3 & \bar{3} \\ \bar{1} & 3 & 3 \end{pmatrix} \text{----} \begin{pmatrix} \bar{1} & \bar{3} & \bar{3} \\ 1 & \bar{3} & \bar{3} \\ 2 & 0 & 2 \end{pmatrix} \text{----} \begin{pmatrix} \bar{1} & 3 & \bar{3} \\ \bar{2} & 0 & \bar{2} \\ \bar{1} & \bar{3} & 3 \end{pmatrix}$$

2. The relationship between twins A and C is given by the matrix M. The twin axis is the fluorite $[100]_{180}$.

$$\begin{pmatrix} 2 & 0 & \bar{2} \\ \bar{1} & 3 & \bar{3} \\ \bar{1} & 3 & 3 \end{pmatrix} \text{----} \begin{pmatrix} \bar{2} & \bar{0} & 2 \\ \bar{1} & \bar{3} & \bar{3} \\ 1 & \bar{3} & \bar{3} \end{pmatrix}$$

Relating these results to the family tree suggests that during the phase transition from Pr_7O_{12} to $Pr_{24}O_{44}$ the $[\bar{1}\bar{1}\bar{1}]$ rotation twin is produced by the loss of the threefold axis during the symmetry reduction from $R\bar{3}$ to $P\bar{1}$, and the [100] rotation twin is produced by the loss of the fourfold axis during symmetry reduction from $Fm\bar{3}m$ to $R\bar{3}^{\bar{2}}_{m}$ in the fluorite structure. In Fig. 4 one of the antiphase boundaries predicted by the e24 index in the family tree is presented.

Reduction of PrO_2 to form the successive intermediate phases $PrO_2 \rightarrow Pr_{24}O_{44} \rightarrow Pr_{11}O_{20} \rightarrow Pr_{10}O_{18} \rightarrow Pr_9O_{16} \rightarrow Pr_7O_{12} \rightarrow Pr_2O_3$ is more difficult to relate by group-maximal subgroup considerations. It is known that at least in some cases the transitions occur via a disordered state. For example, $Tb_{11}O_{20}$ or $Tb_7O_{12} \rightarrow TbO_x$ (disordered) $\rightarrow Tb_2O_3$ (*13*). It has also been observed that when the higher oxides of Pr or Tb are reduced by electron beam heating, domains of any of the intermediate phases can be observed to nucleate and grow without apparently going through the reduction sequence (*14*).

Conclusion

Group theoretical methods are useful tools when used in conjunction with high-resolution electron microscopy in studying systems undergoing phase reactions involving a compositional change. These combined techniques infer the history of a material as well as suggesting the mechanism of transition. In the interpretation of HREM images the symmetry relationships can explain possible twinning and the formation of antiphase boundaries.

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