THE SOLID STATE CHEMISTRY
OF RARE EARTH OXIDES

Final Report
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ADDENDUM TO FINAL REPORT

(Included separately)

*Reprints & Preprints
Removed*

Submitted and in Press

1. "The Binary Rare Earth Oxides," LeRoy Eyring, in "Handbook on the Physics and Chemistry of Rare Earths," L. Eyring, Ed., North-Holland Publishing Co.
2. "Calculated n-Beam Crystal Structure Images of Oxides Based on Fluorite and ReO_3 and the Interpretation of Observed Images," L. Eyring, A. Skarnulis and E. Summerville, J. Solid State Chem. (Title page and Abstract only)
3. "High Resolution Crystal Structure Images of Beta Phase ($\text{Pr}_{24}\text{O}_{44}$) in the Praseodymium Oxide System," E. Summerville, R. T. Tuenge and L. Eyring. (Title page and Abstract only)
4. "Nonstoichiometry, Order and Disorder in Fluorite-Related Materials for Energy Conversion." L. Eyring Advances in Chemistry Series 1977. (Title page and Abstract only)
5. "On the Nature of Extended Defects and their Ordering in Fluorite-Related Refractory Oxides," L. Eyring and R. Tuenge, Argonne National Laboratory Report. (Title page only)

Reprints

1. "The Crystal Structure of $\text{Pr}(\text{OH})_2\text{NO}_3$," M. Lundberg and A. J. Skarnulis, Acta Cryst. B32, 2944-2947 (1976).
2. "Oxygen Transport in Polycrystals and Single Crystals of $\text{Pr}_7\text{O}_{12 \pm \delta}$," K. H. Lau, D. L. Fox, S. H. Lin and L. Eyring, High Temperature Science 8, 129-139 (1976).
3. "The Structural Chemistry of Some Complex Oxides: Ordered and Disordered Extended Defects," LeRoy Eyring and Leung-Tak Tai, in "Treatise on Solid State Chemistry, Vol. III, N. B. Hannay, Ed., Plenum Publ., pp. 167-252 (1976).

ABSTRACT

Work under Contract E(11-1)-1109 and its antecedents has been primarily for the purpose of obtaining detailed thermodynamic, kinetic and structural information on the complex rare earth oxides of praseodymium and terbium. These systems exhibit homologous series of ordered phases, order-disorder transformations, wide-range nonstoichiometric phases, chemical hysteresis in two-phase regions and many other solid state reaction phenomena.

Fluorite-related materials of importance to ERDA occur as nuclear fuels, radiation power sources, insulators and solid electrolytes. The rare earth oxides serve directly as model systems for such similar materials and, in a more general sense, they serve as models of solids in general since they exhibit nearly the full range of solid state properties.

As the project comes to a close, the work in progress includes a study of chemical hysteresis using the technique of high resolution transmission electron microscopy to give structural details almost at the atomic level on ordered materials, materials with defects (including extended defects) and on materials undergoing reaction.

I
FINAL REPORT
ON
CONTRACT E(11-1)-1109

The forerunner of Contract E(11-1)-1109 titled "The Solid State Chemistry of Rare Earth Oxides" began in the fall of 1950 with A. E. C. support. At the beginning, compounds in which a rare earth atom was not trivalent were to be studied. Very soon, however, the obviously interesting complexity of the higher oxide systems of praseodymium and terbium usurped nearly our full attention. Although there have been a number of studies on formates, carbonates, halides and oxalates, etc. the past quarter century has been a progressive study of nonstoichiometry and extended defects in solids utilizing the oxides of praseodymium and terbium as model systems.

Nonstoichiometry in nonmetallic solids had been known for a long time in 1950, nevertheless, the frequency of occurrence of this phenomenon was little investigated and its structural and thermodynamic basis virtually unknown. Since that time there has been an explosion of knowledge in this area and today it is a primary subject of concern in solid state science. The work on this project

has elucidated a major system, the fluorite-related materials, and has played an important role in the evolving story.

We have just written a chapter on oxides for a handbook on the rare earths of which we are coeditor. This chapter, included with this report, reviews the physics and chemistry of the rare earth oxides, including our contributions, and might be consulted for details. In this space, we sketch our work only in the barest outline.

In the early years the phase diagrams were investigated using tensimetric techniques and compounds of curious stoichiometry such as $\text{PrO}_{1.714}$, $\text{PrO}_{1.778}$, $\text{PrO}_{1.833}$, $\text{TbO}_{1.714}$, $\text{TbO}_{1.818}$, etc. were prepared and analyzed and their heats of formation obtained by calorimetric measurements. At the same time, powder diffraction x-ray studies showed that the intermediate phases were not cubic (as are the end-member sesquioxides and dioxides) as had earlier been believed but rather were of lower symmetry. In addition, the oxides previously reported as having an oxygen content greater than in the dioxide were shown to be hydroxides or hydroxy carbonates.

It gradually became clear that these complex fluorite-related oxide systems (CeO_x , PrO_x and TbO_x) formed homologous

series of oxides with the generic formula $R_n O_{2n-2}$ ($4 \leq n \leq \infty$) and that these could disorder at higher temperatures and pressures into two truly nonstoichiometric phases of wide composition range; $R_2 O_{3+\delta}$ (σ phase, $0 \leq \delta \leq 0.4$) and $RO_{2-\delta}$ (α phase, $0 \leq \delta \leq 0.3$) with a narrow miscibility gap between. The phase diagram of the $PrO_x - O_2$ system is illustrated in Figure 1.

As indicated above, these are not only compositional homologues but are fluorite-related phases with close structural relationships. The end-members are isomorphous as C-type sesquioxides and fluorite dioxides. In addition, the intermediate compound $R_7 O_{12}$ is isomorphous in all three series and is, moreover, the structural prototype of the structural principle which relates the various homologues. The other intermediate phases, although compositionally analogous, do not, in general, have identical structures.

The fluorite-related materials are a vast category with many examples important to the ERDA programs. For example, $UO_{2 \pm \delta}$, ThO_2 and other actinide dioxides and intermediate oxides. In addition, there are many fast-ion conductors based on ThO_2 , ZrO_2 , HfO_2 and CeO_2 with admixtures principally of the alkaline

earth and rare earth oxides. These, as well as other fluorite-related systems of importance, are illuminated by the elaborated behavior of the rare earth oxides.

As the support of this program comes to an end, we are engaged in active programs to further clarify the accommodation of extended defects in materials. In particular, we are studying hysteresis in phase transformations and reactions which characterize most non-metallic systems where phase intergrowth is possible. These studies are pursued by careful thermodynamic and kinetic measurements. Figures 2a and 2b illustrate hysteresis in the $\text{TbO}_x\text{-O}_2$ system.

The new technique of high resolution transmission electron microscopy on crystals yielding images at about $3.5\text{\AA}$ resolution is being applied to a study of the structural basis of solid state reactions. It has been possible to obtain information on the structure of the intermediate phases. (Figure 3 shows the projection of many of the unit cells in the system and Figures 4 and 5 show observed and calculated images of two cases.) Of greater importance is the possibility of following solid state reactions at virtually the atomic level. Figure 6 demonstrates

this capability as $Tb_{11}O_{20}$ decomposes to Tb_7O_{12} + oxygen. The value of this cannot be overemphasized when one contemplates the laternative indirect methods available. At the least, it is a potent structure-determining tool to augment the powerful traditional diffraction techniques in deciding well-ordered structures and it has no peer in clarifying the nature of specimens with defects and/or undergoing reaction.

In short, the inquiry into the thermodynamic, kinetic and structural behavior of the rare earth oxides supported during the past twenty-seven years by the A. E. C. and ERDA has been a valuable factor in the emerging science of nonstoichiometric and defect rich materials destined to be of ultimate importance in the emerging new energy technologies. If that were not enough, these same studies have played and will continue to play a significant role in the development of the modern system of knowledge and theory of the defect solid state.

FIGURE LEGENDS

1. A projection of the PrO_x phase diagram. Metastable or assumed boundaries are dashed.
- 2a. Isobaric hysteresis loop for a) the reaction $2/7\text{Tb}_7\text{O}_{12} \rightleftharpoons \text{Tb}_2\text{O}_3 + 3/14\text{O}_2(\text{g})$. Dashed loop in the intrinsic hysteresis envelope, and b) the reaction $7/11\text{Tb}_{11}\text{O}_{20} \rightleftharpoons \text{Tb}_7\text{O}_{12} + \frac{4}{11}\text{O}_2$ (after Lowe and Eyring (1975)).
- 2b. Isobaric hysteresis loop for a) the reaction $2/7\text{Tb}_7\text{O}_{12} \rightleftharpoons \text{Tb}_2\text{O}_3 + 3/14\text{O}_2(\text{g})$. Dashed loop in the intrinsic hysteresis envelope, and b) the reaction $7/11\text{Tb}_{11}\text{O}_{20} \rightleftharpoons \text{Tb}_7\text{O}_{12} + \frac{4}{11}\text{O}_2$ (after Lowe and Eyring (1975)).
3. Projections of the unit cells of members of the homologous series along the common a axis $[21\bar{1}]$ fluorite.
4. Observed and calculated $\langle 100 \rangle_7$ lattice images of Pr_7O_{12} . The calculated image in the lower right corner is based on the known structure for a crystal of about $200\text{\AA}$ thick and about $800\text{\AA}$ underfocus.
5. Image of a thin edge of a crystal of $\text{Pr}_{12}\text{O}_{22}$. The calculated image based upon the proposed structure is shown as an insert at the bottom right. The white dots correlate with the projected vacancy rows which exist in the proposed structure.
6. An image of multiple-phased TbO_x down $[21\bar{1}]_F$. Specimen prepared by reduction of $\text{Tb}_{11}\text{O}_{20}$ in the microscope to one containing a large amount of Tb_7O_{12} . Integers indicate n in $\text{Tb}_n\text{O}_{2n-2}$ for cell projections. Mode of reaction regions at the boundaries is indicated in the darker regions.

Figure 1. A projection of the PrO_x phase diagram. Metastable or assumed boundaries are dashed.

Figure 2a. Isobaric hysteresis loop for a) the reaction $2/7\text{Tb}_7\text{O}_{12} \rightleftharpoons \text{Tb}_2\text{O}_3 + 3/14\text{O}_2(\text{g})$. Dashed loop in the intrinsic hysteresis envelope, and b) the reaction $7/11\text{Tb}_{11}\text{O}_{20} \rightleftharpoons \text{Tb}_7\text{O}_{12} + \frac{4}{11}\text{O}_2$ (after Lowe and Eyring (1975)).

Figure 2b.

Isobaric hysteresis loop for a) the reaction $2/7\text{Tb}_7\text{O}_{12} \rightleftharpoons \text{Tb}_2\text{O}_3 + 3/14\text{O}_2(\text{g})$. Dashed loop in the intrinsic hysteresis envelope, and b) the reaction $7/11\text{Tb}_{11}\text{O}_{20} \rightleftharpoons \text{Tb}_7\text{O}_{12} + \frac{4}{11}\text{O}_2$ (after Lowe and Eyring (1975)).

Figure 3. Projections of the unit cells of members of the homologous series along the common a axis $[21\bar{1}]$ fluorite.

Figure 4.

Observed and calculated $\langle 100 \rangle_7$ lattice images of Pr_7O_{12} . The calculated image in the lower right corner is based on the known structure for a crystal of about 200 Å thick and about 800 Å underfocus.

Figure 5.

Image of a thin edge of a crystal of $\text{Pr}_{1.2}\text{O}_{2.2}$. The calculated image based upon the proposed structure is shown as an insert at the bottom right. The white dots correlate with the projected vacancy rows which exist in the proposed structure.

Figure 6.

An image of multiple-phased TbO_x down $[21\bar{1}]_F$. Specimen prepared by reduction of $\text{Tb}_{11}\text{O}_{20}$ in the microscope to one containing a large amount of Tb_7O_{12} . Integers indicate n in $\text{Tb}_n\text{O}_{2n-2}$ for cell projections. Mode of reaction regions at the boundaries is indicated in the darker regions.

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