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A Disordered Intermediate Stage in the Reduction of $Tb_{11}O_{20}$ or Tb_7O_{12} to C-Type Tb_2O_3 in the Electron Microscope

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A thin crystal of $Tb_{11}O_{20}$ with a patch of Tb_7O_{12} has been observed to reduce in the high-resolution electron microscope to Tb_2O_3 (C-type). In both cases the reduction occurred through a disordered intermediate stage which was of fluorite structure. The Tb_2O_3 was observed to grow into this disordered region in patches previously termed *cooperative emergence* in a nucleation controlled ordering process. Whereas transformation (reaction) between $Tb_{11}O_{20}$ and Tb_7O_{12}, for example, would be expected to be cooperative and displacive, the transformation to a C-type structure would be reconstructive and, thus, the intermediate stage of disorder is not unexpected. Direct observation of this intermediate stage in the reduction by high-resolution electron microscopy is an accomplishment unique to this powerful technique. © 1988 Academic Press, Inc.

Introduction

High-resolution electron microscopy provides the experimental conditions that allow the direct observation of discrete stages in some chemical reactions. This unique capability permits the determination of stages in the mechanism of reactions that have lifetimes at least of the order of a second. The image itself, as well as the optical diffraction pattern of the small area of interest, gives information concerning the homogeneity of the region being studied. Homogeneity is of greatest importance in the instance of the occurrence of disordered phases since these could easily be masked by intermixed ordered phases.

The TbO_x–O_2 system, under conditions of importance here, consists of the following phases: Tb_2O_3 (C-type), Tb_7O_{12} (ι), $Tb_{11}O_{20}$ (δ), and TbO_2. This represents the composition region $TbO_{1.50}$–$TbO_{2.00}$. Although oxidation as well as reduction can occur during imaging conditions in the microscope (*1*, *2*) we apparently are only observing reducing conditions in the experiments to be reported here. Figure 1 shows the projections of the unit cells of the phases of our concern. The dots along the lines of the images in the thin edges correspond to the dots in Fig. 1 representing columns of Tb atoms. It may require some magnification to see these dots along the horizontal lines of the images.

In an earlier study (*1*), the incomplete reduction of Tb_7O_{12} to Tb_2O_3 was observed. In this earlier work because of the rapid

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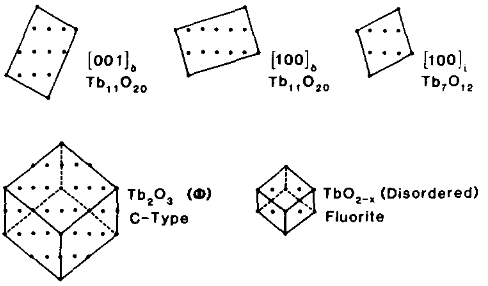

FIG. 1. A sketch along $[21\bar{1}]_F$ of the projected unit cells of the ι, δ, fluorite, and ϕ phases of TbO_x. The horizontal rows of black dots in the thin regions of the crystal imaged in Fig. 2 correspond to the dots representing columns of metal atoms in this illustration.

reduction there was a serious lack of time resolution so that the details of the reduction were not apparent. The same can be said of the observations on the reduction of Pr_7O_{12} and Pr_9O_{16} in this same paper. Relevant conclusions in this earlier study were that disorder is probably a prerequisite to reduction since the C-type sesquioxide requires a reconstructive transformation from the ordered R_7O_{12}, R_9O_{16}, $R_{11}O_{20}$ (R = Pr, Tb). The C-type oxide appeared to nucleate on the surface of the crystal at any possible site and spread laterally and deepen to give patches that were not coherent when grown to impingement, as would be expected of random nucleation. This process was termed "cooperative emergence."

We emphasize again that, whereas the transformation between $Tb_{11}O_{20}$ and Tb_7O_{12} is expected to be cooperative and displacive (*3*), the transformation from either to the C-type would be expected to be reconstructive.

Experimental Part

Specimens of $Tb_{11}O_{20}$ were prepared by equilibrating hydrothermally grown crystals of TbO_x (*4*) with 200 Torr oxygen pressure at 400°C for 16 hr followed by a rapid cooling to 200°C and removal to a desiccator. The crystals were then evacuated and sealed in quartz tubes until used in the experiments.

$Tb_{11}O_{20}$ crystals were ground in a mortar under 100% alcohol, and the resulting powder was suspended by sonication in the alcohol and picked up on holey carbon grids by dipping in the suspension and drying.

Small crystals with thin edges projecting into the holes of the carbon support were studied by means of the top-entry JEOL 4000EX microscope operated at 400 kV. The results reported here are from a through-focus series of exposures (Δf = −300 to −650 Å) taken over a minute or two. The techniques used are described by Smith (*5*).

Results

The results are discussed in terms of Fig. 2, consisting of images of TbO_x, which is fluorite-related, taken along $[211]_F$ (F = fluorite). The separate images (a) through (d) requiring a few seconds each to record are from a through-focus series taken within a minute or two. In interpreting these images the apparent superstructure of each phase is readily identified from the projection of Fig. 1. Since there is no thickness change during the experiment the unit cell projection would not change in a qualitative way.

The images are placed in Fig. 2 such that, by use of the coordinates, reference can be made to corresponding regions in each image. The series captures changes that are already occurring when the first image was taken.

In Fig. 2a several patches of structure can be identified. At region (A,5–8) is a well-ordered patch of δ phase ($Tb_{11}O_{20}$) in the [001] orientation (see Fig. 1). The specimen was prepared as the $Tb_{11}O_{20}$ composition. The core of a region of ι phase (Tb_7O_{12}) is (B–D,3–5). An orientational

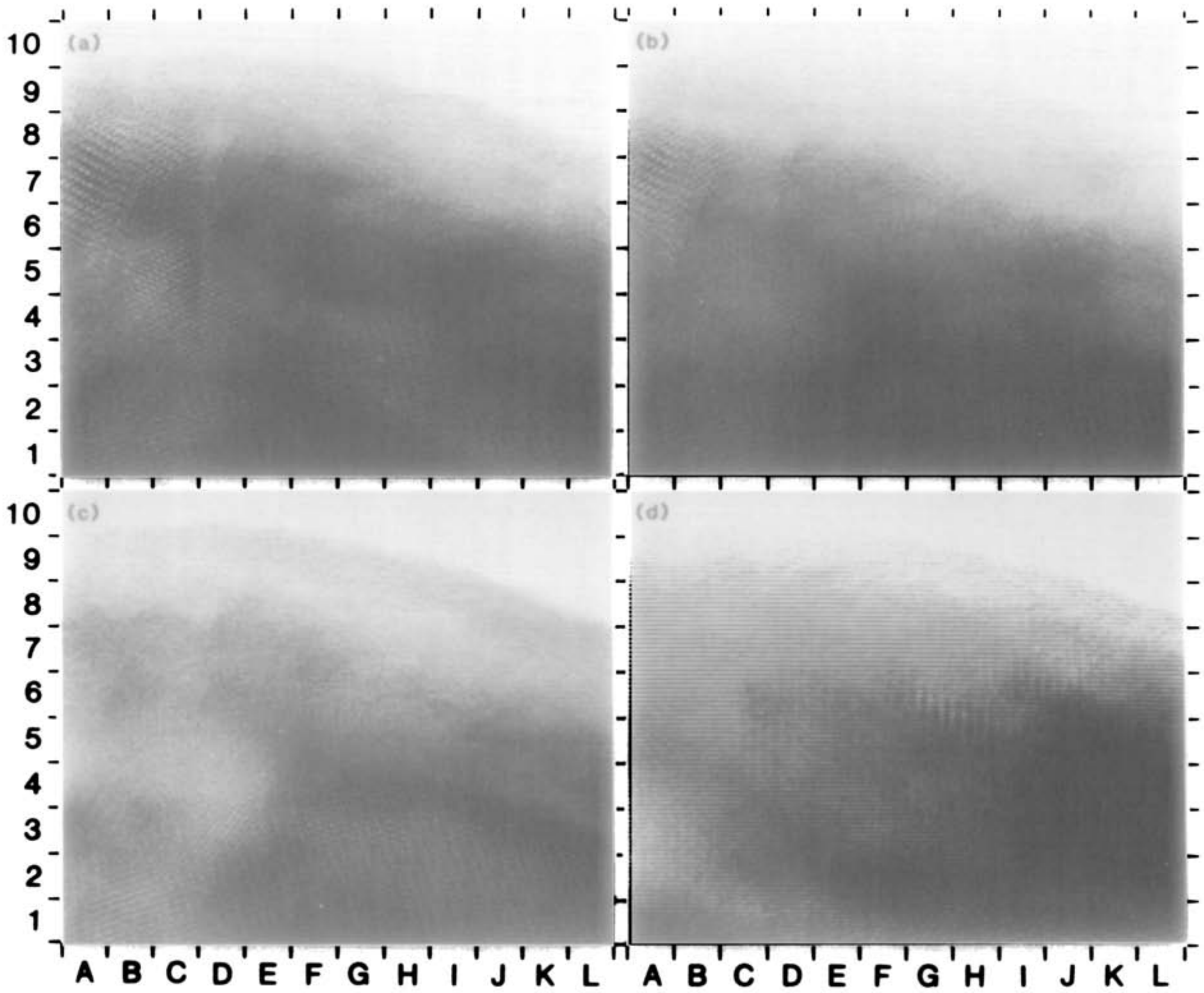

FIG. 2. Four images of terbium oxide taken at intervals of about 30 sec showing the progressive reduction of an original crystal, initially containing ι and δ phase material, that at first disordered then began to order into the C-type Tb_2O_3.

variant of the $Tb_{11}O_{20}$ [100], representing the main body of the crystal, is to be found at (A–L,0–3). The remainder of the figure (C–L,3–9) consists almost entirely of an image of the fluorite TbO_x structure with no superstructure. Each black dot in this thin region of the crystal corresponds to a column of Tb atoms. The composition of this region is unknown but is almost certainly between Tb_7O_{12} and Tb_2O_3 since ordered regions of C-type Tb_2O_3 are observed to emerge in this area at a later time.

In a matter of about 30 sec Fig. 2b was taken. Already changes can be observed. Region (A,5–8) [001] δ has reduced in both size and degree of order. The greatest change is in ι phase (B–D,3–7). A disordered fluorite structure has replaced the highly ordered ι in this region. There is a faint indication of the ordering of the C-type Tb_2O_3 at (B–C,4–6). A small area near (C,3) remains unchanged. The [001] δ phase in the thicker region has changed very little.

The reduction reaction has progressed significantly in Fig. 2c. A minute or so after Fig. 2b was taken, the disordered fluorite-like TbO_x had completely invaded the [001] δ phase (previously at (A,5–8)) but still had left the [100] δ at the bottom almost unchanged. Partially ordered C-type Tb_2O_3 occupies much of the region (A–G,4–5) in Fig. 2c.

Finally in Fig. 2d we see that the disordered fluorite material has replaced the [100] δ phase almost to the bottom of the figure. The C-type Tb_2O_3 is very prominent in the central region of the figure. In some parts the order is quite complete, for example, at (H–K,5–7).

The thin edge of the crystal was the first to reduce. The Tb_7O_{12} was the first to disappear, followed by the $Tb_{11}O_{20}$ nearest the edge, and finally the thicker part of the crystal consisting of $Tb_{11}O_{20}$. As these phases disappear they are replaced first by a disordered TbO_{2-x} in which patches of Tb_2O_3 nucleate at random and grow.

Discussion

As just mentioned, it is clear that under imaging conditions the original specimen of $Tb_{11}O_{20}$ has reduced to give first a disordered fluorite-type region with random oxygen vacancies. The disordered phase, probably with a composition near $TbO_{1.5}$, then begins to order into the C-type Tb_2O_3. This shows that the transformation from lower to higher symmetry goes through a high-symmetry, thoroughly disordered, intermediate structure. Previous observations of the reduction of Pr_9O_{16} or Pr_7O_{12} to C-type Pr_2O_3 under similar conditions (*1*) failed to show the formation of any ordered intermediate phases. This experience agrees with the observations made here where, under conditions where the C-type Tb_2O_3 would be the stable composition under the oxygen pressure and temperature of the microscope, intermediate structures do not form. Rather the vacancies, ordered in $Tb_{11}O_{20}$ and Tb_7O_{12}, first disorder and then reorder as the C-type final product. When the conditions of temperature and oxygen pressure are higher (as in equilibrium experiments made on bulk samples) the intermediate phases appropriate to these conditions are indeed formed.

The C-type Tb_2O_3 nucleates and grows independently in the disordered intermediate material as indicated by the lack of coherence between the patches of Tb_2O_3 at (I–L,3–4) and (H–J,6–7), i.e., the unit cell boundary is not coincident. This same phenomenon was observed previously (*1*).

Reconstructive transformations are expected to occur between two crystalline phases separated by some disordered region (a few atomic distances thick) through which atoms can move and rearrange. In the present case, we have shown that the transformation occurs differently. An intermediate disordered phase exists for seconds or even minutes between the initial ordered arrangement and the final one. Apparently, the disordered phase is not especially unstable.

We must note that the disordering only involves oxygen and not rare earth atoms; thus, a generalization of what is observed here cannot be made to all kinds of reconstructive transformations. Moreover, a big composition change occurs within the disordered structure during reduction and, except for Tb_7O_{12}, ordered structures corresponding to the composition range between Tb_7O_{12} and $TbO_{1.5}$ are rarely observed in the microscope. These two points are consistent with the relative stability of the disordered structure.

Conclusions

Evidence is presented that shows the disordering of $Tb_{11}O_{20}$ and Tb_7O_{12} to a fluorite-like structure, TbO_x, with random oxygen vacancies as a definite stage in the reduction of these compounds with well-ordered oxygen vacancies to another ordered structure that requires a reconstructive change. The symmetries first increase in the disordered material, then decrease somewhat to the C-type Tb_2O_3. The disordered structure has been found to be relatively stable in these experiments.

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