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# Structures and structural defects in colloidal particles altered *in situ* in HREM

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## Abstract

In the past, equilibrium tensimetric studies made on the mixed $Pr_yTb_{1-y}O_x$–$O_2$ system revealed a marked decrease in the stability, or total absence, of the ordered intermediate phases belonging to the homologous series $R_nO_{2n-2}$ known in the binary Pr and Tb oxides. The early X-ray studies did, however, indicate that ordered intermediate phases are observed in rapidly cooled samples. The work reported here was designed to obtain a better resolution of the structures of any intermediate phases formed in quite homogeneously mixed specimens. $Pr_{0.9}Tb_{0.1}O_x$ cooled from 1100 °C in He then observed *in situ* in HREM showed a well-ordered new structure unknown in the binary constituent oxides. $Pr_{0.5}Tb_{0.5}O_x$ obtained *in situ* in HREM from the electron beam-induced decomposition of $Pr_{0.5}Tb_{0.5}OHCO_3$ exhibited a superstructure that suggests one or more of the monoclinic structures with a composition with $n$ equal to or greater than 10. This apparent oxidation in the electron beam has also been reported in the binary oxides. Unfortunately, these results still do not provide information on the structures existing at equilibrium at higher temperatures.

## 1. Introduction

The phase diagrams of the higher oxides of Pr and Tb are dominated at lower temperatures and oxygen pressures by the existence of a homologous series of oxygen-deficient, fluorite-related phases that can be represented by the formula $R_nO_{2n-2}$ [1,2]. Known structures in the Pr–O system include $n=4$, 7, 9, 10, 11, 12, 16 and infinity. In the Tb–O system $n=4$, 7, 9, 12, and infinity are known. Corresponding members of the two series, although isocompositional, anion-deficient and fluorite-related, frequently are not isostructural [3]. Without counting 4f electrons, Pr and Tb in their +3 and +4 oxidation states are isoelectronic. Their corresponding states have different radii due to the lanthanide contraction.

The properties of the binary oxides of Pr and Tb can be altered by random replacement of the cations. This introduces a further complication into an already complicated system yielding ternary compounds having atoms of mixed valence states and mixed sizes. In these oxide systems, the cation substructure is complete, face centered cubic and immobile at temperatures below 1200 °C, while the oxygen substructure contains vacant oxygen sites, depending on composition and thermal history, which are extremely mobile down to 300 °C [1]. It is desired to see the effect of arbitrary substitution of the immobile metal atoms of different radii and oxidation potentials on the structure of the phases obtained.

Thermodynamic observations of oxygen pressure, temperature and composition for the mixed ternary systems are quite different over the same range of conditions studied for the two binary oxides [4]. Figure 1 shows the tensimetric studies of these systems covering compositions from pure $PrO_x$ at the top through the mixed oxides to pure terbium oxide at the bottom [4]. The

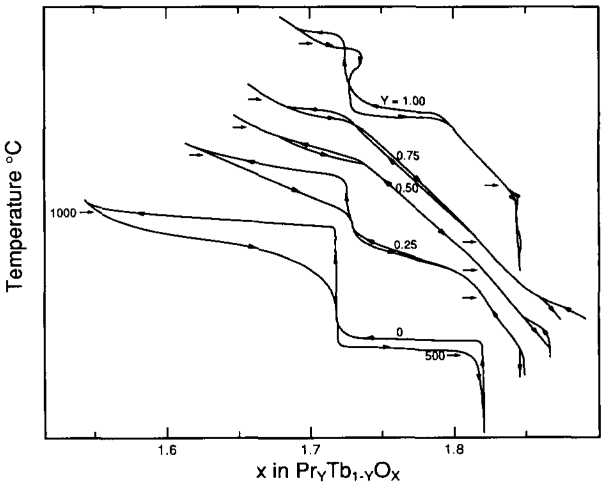

Fig. 1. Composite $T, x$ curves for the Pr–Tb and $Pr_yPb_{1-y}O_x$–$O_2$ systems after Kordis and Eyring [6].

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most striking difference is the muted appearance or absence of evidence of the ordered intermediate series in the mixed oxides. That is, the only region showing a strong tendency for order is near the iota-phase ($R_7O_{12}$) for the mixture $Pr_{0.25}Tb_{0.75}O_x$. Otherwise, the behavior resembles that of the praseodymium, and presumably that of terbium oxides at higher temperatures and oxygen pressures where only the widely non-stoichiometric $\alpha$ and $\sigma$-oxides exist. The early X-ray studies [5] on this mixed oxide system indicated ordered intermediate oxides in rapidly cooled samples. We report here experiments that probe the structural behavior of these ternary oxides in greater detail.

## 2. Experimental details

Monodisperse colloidal spheres of the mixed oxides have been prepared by homogeneous precipitation of the hydroxycarbonate from mixed chloride solutions containing urea under a controlled temperature of 90 °C [6].

Nanospheres only about 50 nm in diameter were lifted on holey carbon microscope grids from sonicated suspensions to be studied either on the JEOL 4000EX or the Akashi 002B top entry, high-resolution electron microscopes, capable of essentially atomic resolution. Recordings were made of the reactions utilizing a Gatan low-light video system at TV rates of frame acquisition of 1/30 s.

Analyses were then made utilizing a frame-accurate editing system with software capable of providing computer analysis of images and diffraction patterns.

## 3. Results and discussion

The results from a study of two specimens are reported here. The first was a sample of $Pr_{0.9}Tb_{0.1}O_x$ that was

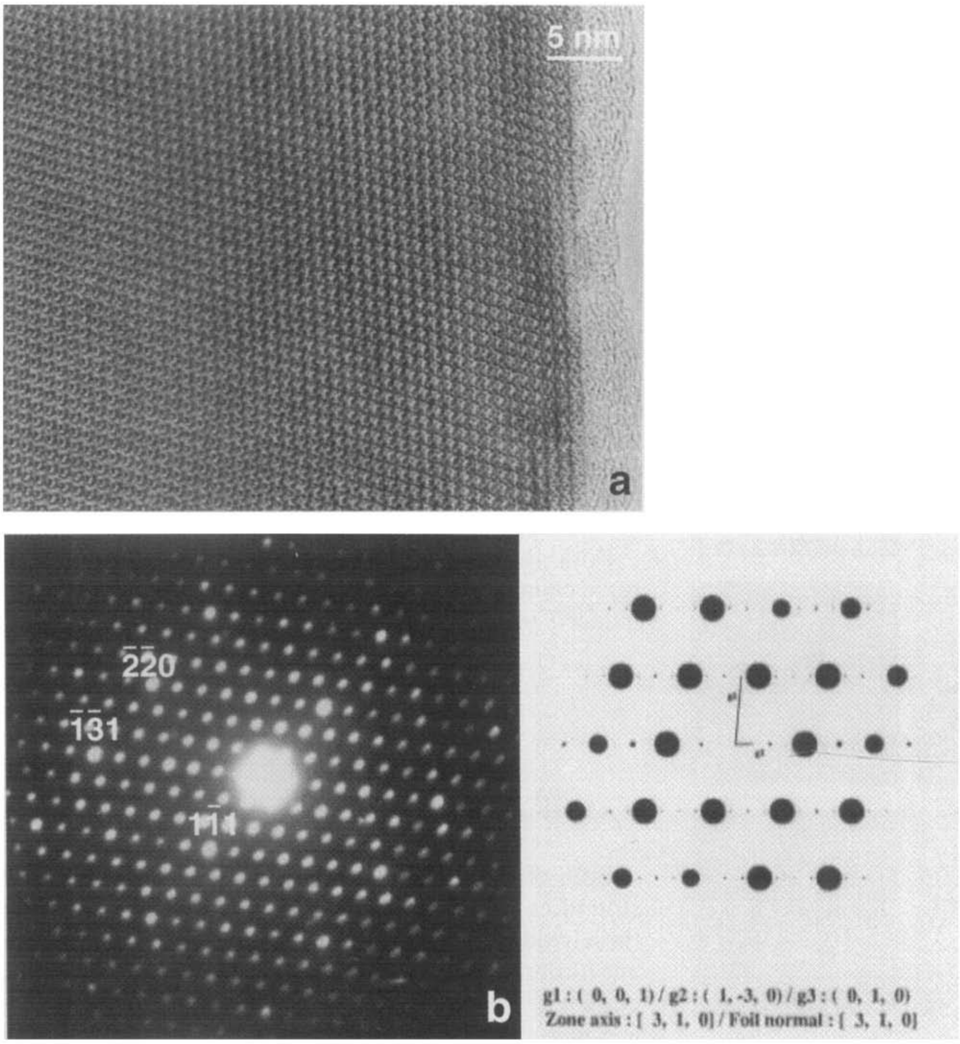

Fig. 2. (a) A high-resolution image of a new phase in $Pr_{0.9}Tb_{0.1}O_x$. (b) A selected area electron diffraction pattern of the new phase shown in (a). (c) The calculated diffraction pattern for the [3 1 0] zone of the $\beta(1)$ phase of $Pr_{24}O_{44}$.

formed from the hydroxycarbonate colloidal spheres by thermogravimetric (TGA) treatment in a He atmosphere to a final temperature of 1100 °C which would be expected to yield the sesquioxide in either of the binary systems. The other specimen was $Pr_{0.5}Tb_{0.5}O_x$ formed *in situ* in the microscope by beam heating without insertion of a condenser aperture. The latter sample was shown to be an intimate mixture of Pr and Tb using a 1-nm diameter probe (see the paper in this volume by Tong *et al.*). On the basis of these observations, the former sample is also assumed to be homogeneously mixed.

### 3.1. $Pr_{0.9}Tb_{0.1}O_x$

This sample was imaged in the JEOL 4000EX with electron beam intensities that would normally leave the specimen unchanged during structural identification. Most of the particles gave diffraction patterns typical of a disordered α-phase, however one provided a diffraction pattern (Fig. 2(b)), indicating a well-developed superstructure of the fluorite structure, and a through-focus series of images one of which is shown in Fig. 2(a), confirming the diffraction pattern. The superstructure is a 7 by 21 net in a ⟨2 1 1⟩ fluorite zone pattern that has never been found in either series of binary oxides. (The $n = 7$ members of the praseodymium and terbium binary oxide series are isostructural and different from this structure.) The composition of this mixed phase has not been established.

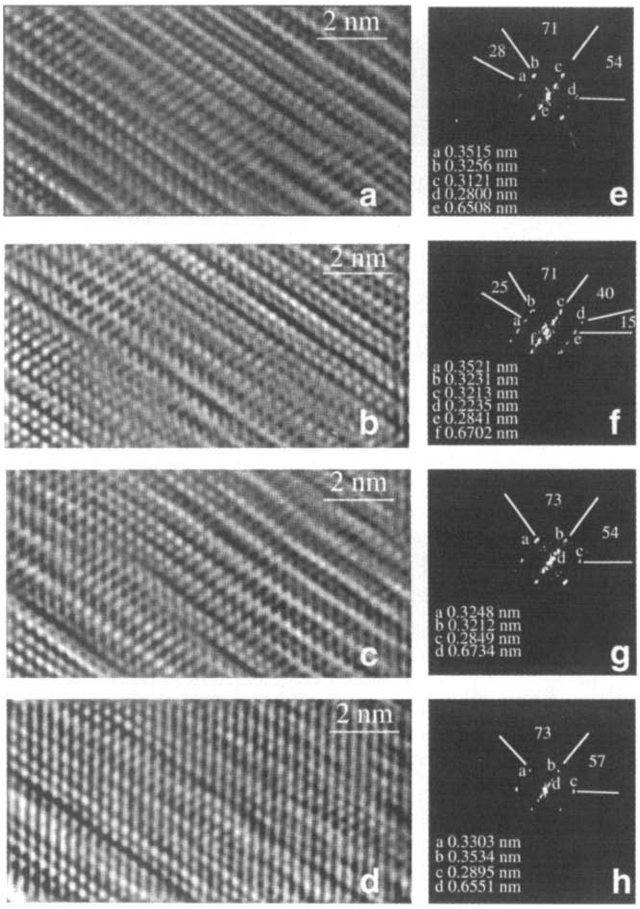

Fig. 3. An analysis of single-frame images taken at intervals of 24 s, 10 s and 26 s of a specimen of $Pr_{0.5}Tb_{0.5}O_x$. Diffractograms of the corresponding images are to the right of each.

### 3.2. $Pr_{0.5}Tb_{0.5}O_x$

An oxide definitely showing superstructure was produced by the electron beam-induced decomposition of a hydroxycarbonate colloidal sphere *in situ* in the Akashi 002B microscope. The details of its preparation and analysis are given in the paper by Tong *et al.* in this volume. The results of a video-frame analysis are provided in Fig. 3. The individual frames were taken at time intervals of 24 s between a and b, 10 s between b and c, and 26 s between c and d. The sharp spots repeated in each diffractogram correspond to the substructure which is the ⟨1 1 0⟩ zone of the f.c.c. fluorite structure. The spots a and b of Fig. 3(h) correspond to the {1 1 1} planes and the spot c corresponds to the {2 0 0} planes of the fluorite substructure.

A calculation of the diffraction patterns of the possible intermediate phases indicate that superstructure streaking and spots along the ⟨1 1 1⟩ fluorite direction occurs in many of the series phases with $n = 10$ or greater, for example, the [3 1 0] zone of the β(1) phase of praseodymium oxide (Fig. 2(c)). This structure has not been observed in the binary $TbO_x$ system although the β(3) structure in the binary $TbO_x$ system would give superstructure spots in the same direction for the [6 1 0] zone axis but with different relative intensities.

Both the images and the diffractograms do show rapid changes in these time intervals. Apparently, beam-induced oxidation occurs in this instance.

## 4. Conclusions

Both of the specimens studied here exhibit oxidized structures induced by the electron beam; most often these oxidized structures are disordered of the α-type but ordered, oxidized intermediate phases are also observed. The ordered phase in the $Pr_{0.9}Tb_{0.1}O_x$ system is a new structure not observed in either of the binary systems or in the $CeO_x$ system. The ordered phase in the $Pr_{0.5}Tb_{0.5}O_x$ system could correspond to one of several monoclinic phases observed in the binary phases. The disordered $\alpha$-phase frequently found here is commonly observed in the $PrO_x$ system and is assumed to exist, but has never been seen, in the $TbO_x$ system.

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