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Nanoanalytical characterization of $Pr_{0.5}Tb_{0.5}O_x$ obtained from *in situ* video observation in the high resolution electron microscope

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Abstract

This paper illustrates the capability, with the high resolution electron microscope and associated techniques, of characterizing a material with lateral resolution near the atomic level, temporal resolution at 1/30 s, and chemical analysis of volumes no more than 2 nm wide perpendicular to the electron beam. $Pr_{0.5}Tb_{0.5}(OH)CO_3$, in the form of an amorphous colloidal sphere, is transformed through $(Pr_{0.5}Tb_{0.5}O)_2CO_3$ to the oxide, $Pr_{0.5}Tb_{0.5}O_x$. Chemical analysis through the various stages of decomposition establishes essentially random dispersal of the rare earths. Structural analysis of video frames at time intervals of a few 1/30 s permit progressive characterization of the material as it changes. This is relevant to the promulgation of mechanisms of solid state reactions at the atomic level.

1. Introduction

It is frequently desired to characterize nanoparticles or ultrathin films of materials at high spatial and temporal resolution. The characterization could include chemical, structural, and textural analysis during chemical or physical change. High resolution electron microscopy (HREM) coupled with video recording and single-frame analysis of the video record, enables *in situ*, atomic level analysis of a product or, in favorable cases, the promulgation of the mechanism of a solid state reaction [1]. These analyses can also reveal the atomic dispersion of the elements within the sample at the atomic level.

In the synthesis of ternary compounds, it is necessary to determine the phase composition and the chemical homogeneity of each single phase. This is particularly true for compounds where arbitrary replacement of the metal atoms is possible.

It is sometimes of interest to study mixed-valent compounds which can have properties of scientific and practical importance. Indeed, such compounds can be altered in subtle ways using anomalous replacement of the constituent atoms. Such possibilities exist in the rare earth oxides where anomalous replacement is expected to be the rule.

The phase constitution and structures of the complex binary higher oxides of the rare earths (*i.e.* those of Ce, Pr and Tb) have been rather thoroughly studied [2–5]. Thermodynamic and other studies have been made of the mixed valent higher oxides of the praseodymium–terbium oxide system [6]. Here we illustrate some nanocharacterization techniques possible in the HREM study of such mixed systems.

2. Experimental part

The precursors of the specimens studied by HREM were prepared as colloidal spheres by homogeneous precipitation of a mixed hydroxycarbonate from a warm urea solution containing equal molar Pr and Tb ions [7]. Figure 1(a) shows a collection of spheres from the preparation. The monodisperse colloidal spheres produced were suspended in ethanol by sonication and applied to holey carbon grids for HREM study using a top entry Akashi 002B electron microscope.

The elemental nanoanalyses for Pr, Tb, and O were carried out using an HB-501 scanning transmission electron microscope equipped with a windowless energy-dispersive X-ray detector and a 1-nm probe [8].

The decomposition of the mixed hydroxycarbonate to the mixed oxide was video-recorded at high resolution by means of a Gatan low-light video camera system. The 0.5 inch VHS tape was copied to 0.75 inch U-MATIC format for frame capture and analysis in a video editing system [9]. Single-frame analysis was conducted by means of the Gatan Digital Micrograph program.

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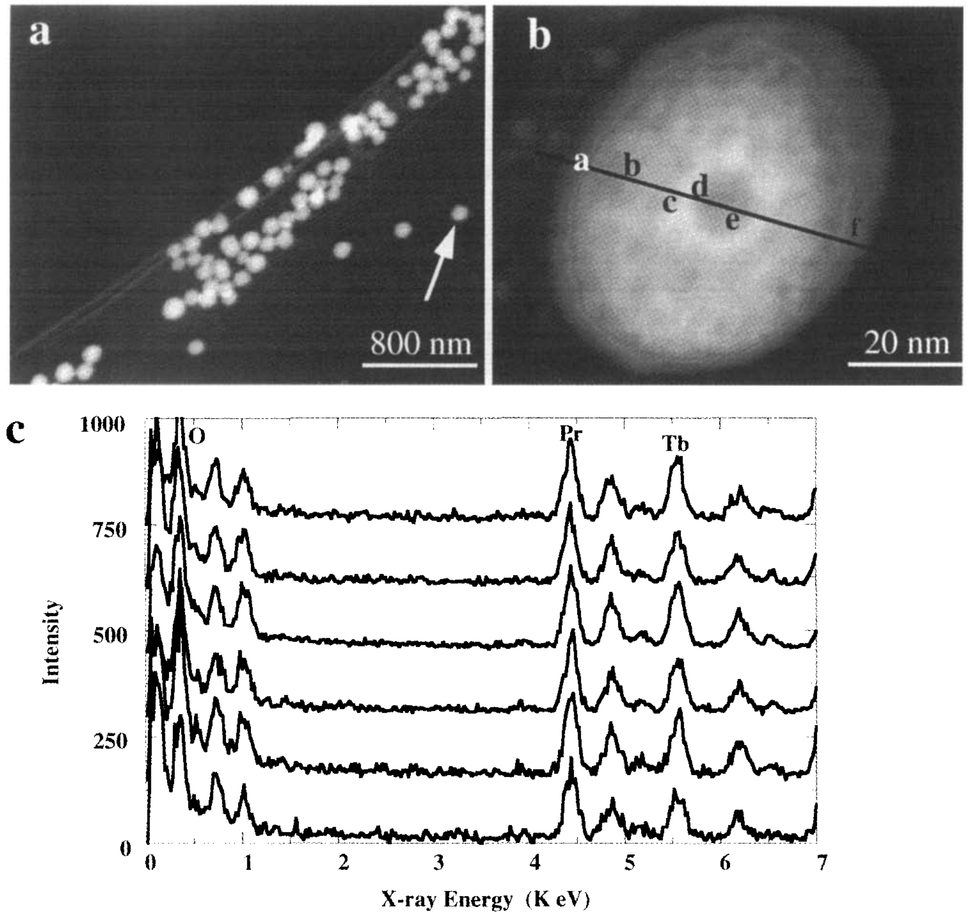

Fig. 1. (a) Freshly prepared $Pr_{0.5}Tb_{0.5}OHCO_3$ colloidal spheres. (b) A spherical particle from (a) that has been under an imaging beam for 25 min following many structural changes. (c) EDS spectra taken with a 1-nm electron probe from positions a–f in b), shown in order bottom to top.

3. Results and discussion

3.1. The chemical analyses

The chemical analyses of the elements in volumes conservatively estimated as being 2 nm in diameter perpendicular to the beam were obtained by EDS in the HB-501. The analyses were carried out at six stages of decomposition of the amorphous hydroxycarbonate to the final crystalline oxide. (1) The average composition of a single colloidal sphere was taken after 12 min of beam irradiation of suitable intensity for imaging then again after 25 min in a more intense beam. (2) The composition of the same particle was determined near the center, part way out, and at the very edge. (3) Analysis was made at two regions between the center and edge of a particle heated by the electron beam with no condenser apertures. (4) A particle heated by the direct electron beam that had clearly crystallized was examined in four regions on a line from top to bottom. (5) A particle, heated in the direct electron beam for 20 min, shown in Fig. 1(b), was analyzed at six locations as indicated by the letters from a to f. The analytical curves obtained are given in Fig. 1(c) in alphabetical order from bottom to top. (6) Finally seven analyses at selected regions were made of a particle that had been annealed at 600 °C for 12 h under an oxygen pressure of 6 Torr. The analytical curves shown in Fig. 1(c) are typical of every analysis made. The ratio of the Pr and Tb peaks remains a constant but the relative variation in the oxygen peak suggests different oxygen compositions of the particular volumes analyzed. We conclude that the homogeneous precipitation of the cations is indeed homogeneous at the level of 2 nm and does not change under the range of conditions imposed in these experiments.

3.2. The structural analysis

Video-recorded images show the condition of a specimen, at high resolution and at TV rates of 30 frames per second. Since each frame is an interlace of two fields, each formed from alternate line raster patterns they can be de-interlaced (separated) to produce 60 field images per second if desired. Reactions that proceed at comparable rates can be analyzed to reveal the mechanism of change at the atomic level.

The *in situ* decomposition of a hydroxycarbonate during HREM study goes through the dioxycarbonate to the oxide by loss of H_2O and CO_2 [9]. These reactions can all be studied by the techniques described here. The analysis of the captured frames yields information on the state of a particular small region at 1/30 s. It must be realized that the region analyzed may be of uncertain thickness, may not be perfectly aligned and of imperfectly known defocus hence the interpretations cannot be rigorously proved. Nevertheless, the chemical state may be adequately represented.

In the concluding paragraphs, we present results (Fig. 2) that illustrate observations and analyses on a sample of $Pr_{0.5}Tb_{0.5}(OH)CO_3$ that had been strongly beam heated *in situ* in the microscope after most, if not all, of the volatile decomposition products had been lost. The images a, c, and e were grabbed from the tape at 2- or 3-s intervals. The diffractograms of each image are shown as b, d, and f, respectively. (Silicon is used as a calibration standard.) It is obvious from either the images or the diffractograms that there is a progressive development of the sample during these 4–6 s. (The differences between the images can most easily be seen by viewing them at a low angle while rotating in the plane of the page.) These differences are primarily due to changes in the structure and/or the tilt of the zone axis. The strong spots of the diffraction pattern are approximately those from the [1 1 0] zone of a face centered cubic unit cell. In an aligned crystal, the spot b in pattern b of Fig. 2 would be indexed as −2 0 0, the spot at a would be −1 −1 1, and c would be −1 1 −1. The C-type sesquioxide and any disordered or ordered intermediate phases in this mixed oxide system is expected to be fluorite (RO_2)-related with a complete f.c.c. metal atom substructure but with between 0.25 and 0.00 vacant oxygen sites depending on the oxygen composition. The [1 1 0] zone axis pattern would have 54.7° between the (2 0 0) and the (1 1 1) planes. The corresponding d-spacings of the (2 0 0) and the (1 1 1) planes would be 0.3176 nm and 0.2750 nm, respectively for a lattice parameter of 0.5500 nm. This is approximately true for all the frames as can be seen from the calculated d-spacings displayed on the diffraction patterns.

If no change occurs, one could apply a cross-correlation to obtain average results. Cross-correlation is a method to judge whether or not two images have the same pattern. This has been done and image g is the sum of a and c, and h is the diffractogram of g. The image i corresponds to the sum of e and g, and j is the diffractogram of i. The cross-correlation treatment of the results of the experiment is clearly not correct but confirms rather the change observed simply by looking at the images. This suggests that the actual evolution of the specimen is the main cause of the observed discrepancies.

There is no hint of a superstructure to the diffractograms, especially in those of the summed images. This suggests that the sample has the fluorite structure and hence has a composition greater than $RO_{1.72}$ and is disordered (*i.e.* it is in an α-phase region of the phase diagram) [2].

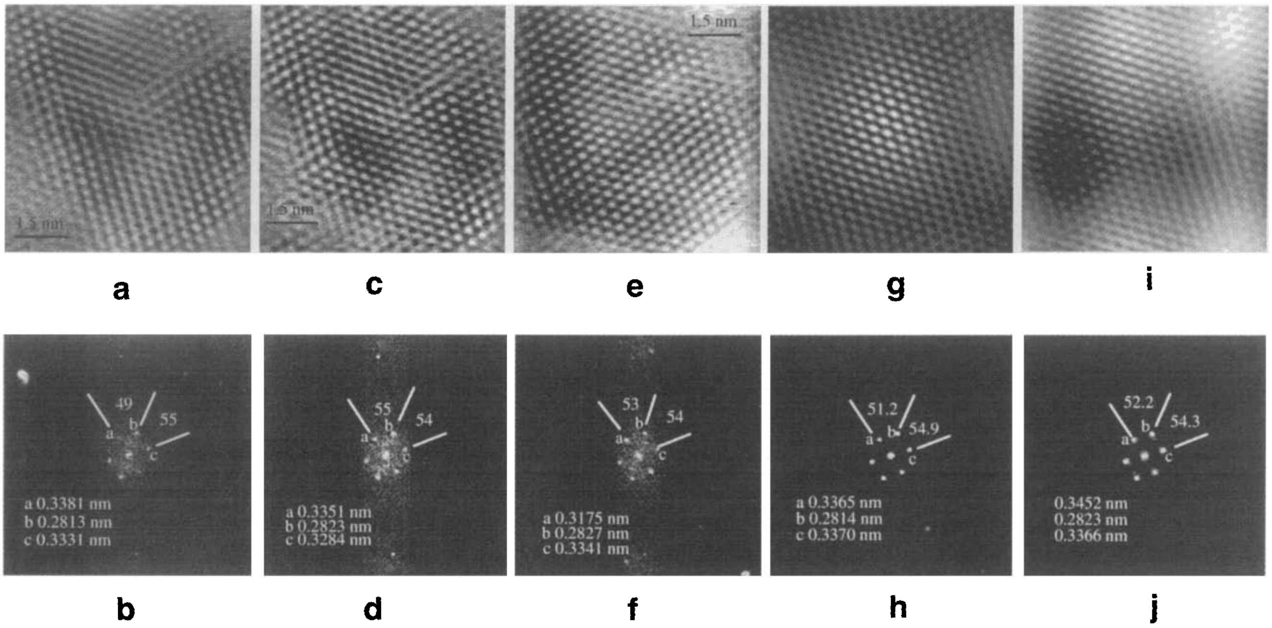

Fig. 2. Three single-frame images of a particle of $Pr_{0.5}Tb_{0.5}O_x$. Images of a, c and e were captured from the videotape at intervals of 2 or 3 s. Image g is the sum of a and c, while i is the sum of e and g. The diffractograms are from the images above them.

4. Conclusions

In the broader sense, these experiments have confirmed that the frame-by-frame analysis of video-taped HREM observations can reveal structure, defect structure and structural changes as a function of time using information collected at 1/30 s. Furthermore, it is possible to determine the average composition in regions as small as 2 nm across as a function of sample preparation and treatment. These techniques and their improved and extended successors can make possible the illumination of solid state reactions at the atomic level.

It is observed that the oxide end-product of the *in situ* decomposition of $Pr_{0.5}Tb_{0.5}(OH)CO_3$ is not the C-type sesquioxide as would be expected from earlier studies on the binary compounds. Nanochemical analysis provides evidence that the product is not ordered with respect to the metal atoms. The images and the calculated diffraction patterns indicate no ordering of the vacant oxygen sites, *i.e.* there is no evidence of a superstructure. These observations are consistent with the thermodynamic measurements that show markedly less evidence for ordered intermediate phases as the ratio of the mixed cations in the system approaches one. These observations are also consistent with the problems of order when there is a fixed, perhaps random, mixture of cations of different radius and electronic condition.

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