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OPTICAL DETERMINATION OF THE OXYGEN STOICHIOMETRY OF NANOPHASE METAL-OXIDE MATERIALS*

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OPTICAL DETERMINATION OF THE OXYGEN STOICHIOMETRY OF NANOPHASE METAL-OXIDE MATERIALS

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Introduction

Nanophase metal-oxide ceramics have gained considerable notoriety^{1,2} as a consequence of their interesting and potentially useful physical and chemical properties. In the case of nanophase TiO_2 , with grain sizes in the range 2 - 20 nm, ductility, enhanced sinterability^{3,4}, extensive plastic deformation⁵, and high atomic diffusivities^{6,7} have all been observed in these cluster consolidated materials. These unique or enhanced properties of cluster-assembled TiO_2 and other nanophase metal-oxides can be used in a host of applications in current and future commercial technology. However, in order for these materials to be commercially viable, their synthesis must be controlled and highly reproducible. In the case of gas-phase condensed clusters, the synthesis of a metal-oxide is achieved by first creating metal clusters which are subsequently oxidized in an oxygen gas atmosphere or by sublimation of an oxide precursor to form metal-oxide clusters directly^{6,8,9}. Although the clusters are highly reactive, due to the large percentage of surface atoms, complete oxidation of the material during cluster synthesis is often incomplete. There are also some cases where the resulting material phase can be adjusted by the rate at which oxidation takes place⁶. Although there are a variety of characterization techniques being used to study nanophase materials, none of these techniques has demonstrated a strong sensitivity to the oxygen stoichiometry.

Quite often the physical properties of metal-oxide ceramics are highly dependent on the metal/oxygen ratio and stoichiometry, and slight deviations can have substantial effects. For example, it has been observed that the mechanical wear characteristics¹⁰ and electrical and optical properties¹¹ of TiO_2 can be significantly affected by deviations in the oxygen stoichiometry. To achieve a high degree of reproducibility of nanophase metal-oxides, it is of the utmost importance that identification of the material stoichiometry be made by a simple, nondestructive measurement.

In this paper we present an overview and assessment of the use of optical techniques, primarily Raman scattering, for analyzing the composition and stoichiometry of nanophase metal-oxide ceramics. Raman scattering has been shown to be a useful technique for evaluating the oxygen stoichiometry of some metal oxide materials¹²⁻¹⁴. However, it is essential for nanophase materials that grain size effects are considered since their ultrafine grain sizes can produce large shifting and broadening of the Raman spectrum^{15,16}.

Experimental

The nanophase metal-oxide ceramic samples used in this study were produced by the gas-phase condensation technique which is described in elsewhere^{6,9}. For this study, TiO_2 and ZnO samples were prepared, but for each case the precursor materials and method were quite different. TiO_2 samples were made by evaporation of Ti metal in a helium atmosphere, followed by a subsequent rapid oxidation of the metal clusters thus produced. The ZnO samples were

made by subliming ZnO powder in a helium atmosphere (ZnO has a low melting temperature and high vapor pressure). However, during sublimation the ZnO clusters became oxygen deficient and needed to be further oxidized in subsequent oxidation steps. The collected clusters were consolidated into a disk-shaped compact under vacuum (ca. 10^{-6} Pa). The as-consolidated compacts were 9 mm diameter by ca. 0.2 - 0.4 mm thick and contained grains of about 12 nm average diameter in the case of TiO_2 and 5-6 nm in the case of ZnO. The Raman spectra of the nanophase metal oxide samples were obtained with a Jobin-Yvon, U-1000 Raman spectrometer and a Coherent Innova 70 Ar^+ ion laser operating at 514.5 nm. Further details are described elsewhere¹³.

Results and Discussion

In the gas-phase condensation process, as presently exercised, the rapid backfill of oxygen gas into the processing chamber to oxidize the clusters does not usually result in complete oxidation, even in the case of ZnO powder which starts out stoichiometric and later becomes oxygen deficient after sublimation. In order to achieve complete oxidation of the clusters to a fully stoichiometric value, a post oxidation process is needed whereby the lightly compacted clusters are heated in an O_2 atmosphere^{6,15}. The process is time consuming and a quantitative assesment of the stoichiometry of the sample during oxidation is not easily obtainable.

Figure 1a shows the Raman spectrum of an as-consolidated nanophase TiO_2 sample which had no other processing other than the initial oxidation via a rapid backfill of O_2 and consolidation. As can be seen, the spectrum exhibits four distinctive peaks and a broad underlying continuum which tails off at higher Raman shifts. The peaks at 610 cm^{-1} and 220 cm^{-1} are attributed to the rutile phase of TiO_2 and the peaks at 154 cm^{-1} and 424 cm^{-1} are attributed, respectively, to the anatase and rutile phases of TiO_2 , although they are broadended and shifted relative to the peaks of bulk TiO_2 material^{12,16}. The Raman spectrum of a fully oxidized sample (annealed in air at 600°C) is shown in Figure 1(b) and exhibits much sharper spectral features and has peak positions that are in excellent agreement with bulk TiO_2 material. It is worthwhile to note that even to the naked eye it is obvious that the as-consolidated material is oxygen deficient since it has a black or "gun-metal" blue color, as opposed to a fully oxidized sample which is white.

Previous experimental Raman scattering results on metal-oxide ceramics have shown¹²⁻¹⁴ that peak shifting and broadening can be related to an oxygen deficiency in the material. However, in the case of nanophase materials, the shifting and broadening of the spectral peaks may, in principle, also be due to grain size effects since it has been shown¹⁶ in studies on laser-induced crystallization of amorphous silicon that grain size effects (in the 1 - 100 nm range) produce similar shifting and broadening. X-ray diffraction and TEM measurements on the TiO_2 sample shown in Figure 1 indicate that some grain growth does occur with the oxidation step (the 12 nm grain size in the as-compacted sample increases to ca. 20 nm after oxidizing for 1 h at 600°C); however, the spectral shifting is much larger than that witnessed for the grain size effects seen in nanocrystalline silicon¹⁶.

Although some grain growth does occur during oxidation (ca. a factor of 2), a grain size dependence of the Raman spectrum can be ruled out based on two experimental observations¹³ which are exhibited by the peak position versus annealing temperature data shown in Figure 2. First, no spectral changes are observed when the samples are annealed at 200° , 400° and 600°C in an Ar atmosphere where some grain growth will be expected³ at 600° . As can be seen, spectral changes take place during annealing in an oxygen atmosphere. Second, an oxygen

reduction of the fully oxidized samples (achieved by annealing them at 600°C in a dynamic 10^{-4} Pa vacuum) shifts the spectrum back toward that of the as-consolidated state, as can be seen by the filled square symbol in Figure 2 which represents the data for the vacuum reduced sample. The grain size would not be expected to shrink upon oxygen reduction. Both of these experiments clearly rule out grain size effects and are consistent with earlier Raman results¹⁷ on nanophase TiO_2 which attribute the grain-size independent line broadening to intragrain defects.

From the experimental evidence discussed above, it becomes apparent that the relationship between the nanophase TiO_2 (really TiO_x) oxygen stoichiometry and the Raman spectral features can be determined. This was done by progressively measuring the oxygen intake (weight gain) of an as-consolidated sample using a TGA microbalance (during cycles at temperatures in the range 300°-650° C in an O_2 atmosphere) and measuring the corresponding Raman spectrum (peak position and broadening)¹⁴.

The calibration curves plotted in Figure 3 show the peak position of the rutile 447 cm^{-1} vibrational mode and the peak position and full width at half maximum (FWHM) of the anatase 143 cm^{-1} vibrational mode, all as a function of the material's O/Ti ratio. The calibration of the Raman spectrum of nanophase TiO_2 as a function of O/Ti ratio clearly demonstrates that the oxygen stoichiometry can be quantitatively and nondestructively assessed by Raman scattering.

Concurrent with the changes in the peak positions of the Raman spectrum, large changes were observed in the sample's optical properties and Raman scattering intensity during the oxidation. The as-consolidated samples typically have a dark blue color due to defect structures that contribute to a large absorption background¹¹. Upon oxidation, the samples lighten to a pale blue color and the intensity of the Raman scattered light increases. At an O/Ti ratio of 1.99, the samples develop a pale yellow color which progressively changes to white as oxidation continues to 2.0. However, in this same region the Raman spectrum (peak positions and scattered light intensity) changes very little. It is not unusual that the intensity of the Raman scattered light changes as the optical properties of the material change, since the scattering cross section is dependent on the material's optical constants¹⁸. However, the fact that the optical properties change more visibly than the Raman spectrum for O/Ti ratios greater than 1.99 suggests that a quantitative assessment of the optical constants might be a more sensitive probe of the O/Ti ratio in this range.

To demonstrate that the sensitivity of the Raman scattering technique is ubiquitous to other Raman active, nanophase metal-oxides, the Raman spectra of nanophase ZnO were measured at three stages, (i) as-consolidated, (ii) partially oxidized, and (iii) fully oxidized and are shown in Figure 4 a,b, and c, respectively. The evolution of the spectra with oxidation shows a change in relative intensity of the 438 cm^{-1} mode relative to the structure between $515 - 530\text{ cm}^{-1}$. Unlike TiO_2 , there is little peak shifting, however, calibration of the oxidation state as a function of relative intensity can be made in a manner similar to that performed in Ref. 12. Much like the TiO_2 samples, the ZnO sample color change with oxidation is quite similar, again indicating that optical constant measurements may also be an effective means of characterizing the samples.

Conclusions

We have demonstrated that the oxygen stoichiometry of nanophase metal-oxide materials can be measured using optical techniques, primarily via Raman scattering. Although a quantitative assessment was made for only the Raman data, optical constants measurements

(i.e., complex refractive index) can also be employed. The Raman technique, however, has two very distinct advantages over optical constant measurements: (i) Raman scattering is not highly sensitive to surface roughness, and (ii) the Raman microprobe (discussed in Ref. 12) can be employed to examine microscopic sample areas as small as 1 mm in diameter.

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Figure 1. The Raman spectra of nanophase TiO_2 in the (a) as-compacted state and (b) the fully oxidized state.

Figure 3. The variation with O/Ti ratio of the peak position of (a) the rutile mode and (b) the strongest anatase mode.

Figure 2. The peak position of the anatase "144 cm^{-1} " as a function of annealing temperature in various atmospheres. The arrows indicate the sample history.

Figure 4. The Raman spectrum of nanophase ZnO in three stages (a) as-consolidated, (b) partially oxidized, and (c) fully oxidized.

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