

**STUDY OF NANOPHASE TiO<sub>2</sub> GRAIN BOUNDARIES  
BY RAMAN SPECTROSCOPY\***

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**ABSTRACT**

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Raman spectra have been recorded for as-consolidated nanophase TiO<sub>2</sub> samples with differing grain sizes and on samples annealed in air at a variety of temperatures up to 1273 K. The nanophase samples with the smallest grain size, about 12 nm average diameter, could have 15-30% of their atoms in grain boundaries; nevertheless, the strong Raman-active lines representative of the rutile structure were found to dominate all of the observed spectra, independent of grain size and annealing treatment. These lines were quite broad in the as-consolidated nanophase samples, equally in 12 nm and 100 nm grain-size compacts, but sharpened considerably upon annealing at elevated temperatures. The Raman data give no indication of grain-boundary structures in nanophase TiO<sub>2</sub> that are significantly different from those in conventional polycrystals. However, defect structures within the grains, which anneal out at elevated temperatures, are evidenced by changes in the Raman spectra.

**INTRODUCTION**

The average grain sizes of nanophase materials synthesized to date [1-3] are typically about 5 to 10 nm, although samples with both larger and smaller grain sizes can be made. With such small grains, the fraction of atoms in these materials that lie in or very near grain boundaries is large and, hence, the grain-boundary structure in these materials is expected to play a significant role in determining their properties. For example, a nanophase material with a 5 nm average grain diameter would have from about 30 to 60% of its atoms associated with grain boundaries, taking a grain-boundary thickness of about 0.5 nm [4] to 1 nm [5]. This percentage would drop to about 15-30% for a 10 nm grain size, and would be quite small (around 1-3%) for a 100 nm grain size. Therefore, the structures of the grain boundaries in nanophase materials need to be elucidated. This is particularly so in the light of the rather surprising suggestion by Gleiter and coworkers [2, 5], based upon the results of a variety of experiments, that the grain-boundary structures in nanocrystalline metals exhibit neither short-range nor long-range order and are thus "gas-like" in nature.

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In the present work, Raman spectroscopy was employed to probe the local structure of the grain boundaries in nanophase TiO<sub>2</sub>, a material already investigated by a number of complementary techniques [6]. The Raman spectra of both single-crystals and conventional coarse-grained polycrystals of TiO<sub>2</sub> are rather well known [7-12] and provide a basis for comparison with the results on nanophase TiO<sub>2</sub>. Furthermore, Raman spectroscopy is a sensitive probe of the local structural units in a material, and can thus be used effectively in ultrafine-grained nanophase TiO<sub>2</sub> to investigate its grain-boundary structure. The present paper is only a brief report of our Raman spectroscopy investigation; a more complete report will appear elsewhere.

## EXPERIMENTAL PROCEDURES

Nanophase TiO<sub>2</sub> samples 9 mm in diameter and about 0.2 to 0.3 mm thick were synthesized via the gas-condensation of titanium powders followed by their oxidation and in situ consolidation in a 10<sup>-5</sup> Pa vacuum under a piston pressure of 1.4 GPa [3, 6]. The grain size distributions in the as-consolidated samples were determined by transmission electron microscopy. Altogether, four samples were investigated by Raman spectroscopy in their as-compacted state and after various annealing treatments in air at elevated temperatures. The results for only two of these samples are reported here, one with an initial average grain size of about 100 nm and the other with an initial average grain size of 12 nm. This latter sample was successively annealed in air for 0.5 h at 573, 773, 973, and 1273 K, with Raman spectra measured after each anneal.

The Raman spectrometer used in these measurements consisted of a SPEX Industries Model 1403 double monochromator with an RCA No. C31034 photomultiplier tube detector and a SPEX SCAMP data collection and analysis system. Sample excitation was effected by a Coherent Model CR6 argon-ion laser using the 514.5 nm line at power levels between 80 and 120 mW. The laser beam was incident on the sample at an angle of about 60° with respect to the surface normal. The scattered light was collected in a direction perpendicular to the incident beam.

## RESULTS AND DISCUSSION

Raman spectra for two of the nanophase TiO<sub>2</sub> samples investigated are shown in Figures 1 and 2. They are typical of our observations. As can be clearly seen in Fig. 1(a) and (b) and Fig. 2, both the 12-nm and 100-nm average-grain-size as-compacted samples yielded rather similar Raman spectra above 200 cm<sup>-1</sup> that are dominated by readily distinguishable bands at 600 ± 7 cm<sup>-1</sup> and 418 ± 10 cm<sup>-1</sup>. These two bands, although significantly (and similarly) broadened for both of these samples, are known [7, 8, 11, 12] to originate from the A<sub>1g</sub> and E<sub>g</sub> Raman-active zone-center (k=0) phonons of the TiO<sub>2</sub> rutile structure. In addition to the strong rutile bands at "600" and "418" cm<sup>-1</sup>, a weak incipient band at 240 ± 10 cm<sup>-1</sup> was also observed in the as-compacted samples, which intensified with annealing, concomitant with the sharpening of the "600" and "418" cm<sup>-1</sup> bands, as shown in Fig. 1. A band at 144 ± 8 cm<sup>-1</sup>, which was observed

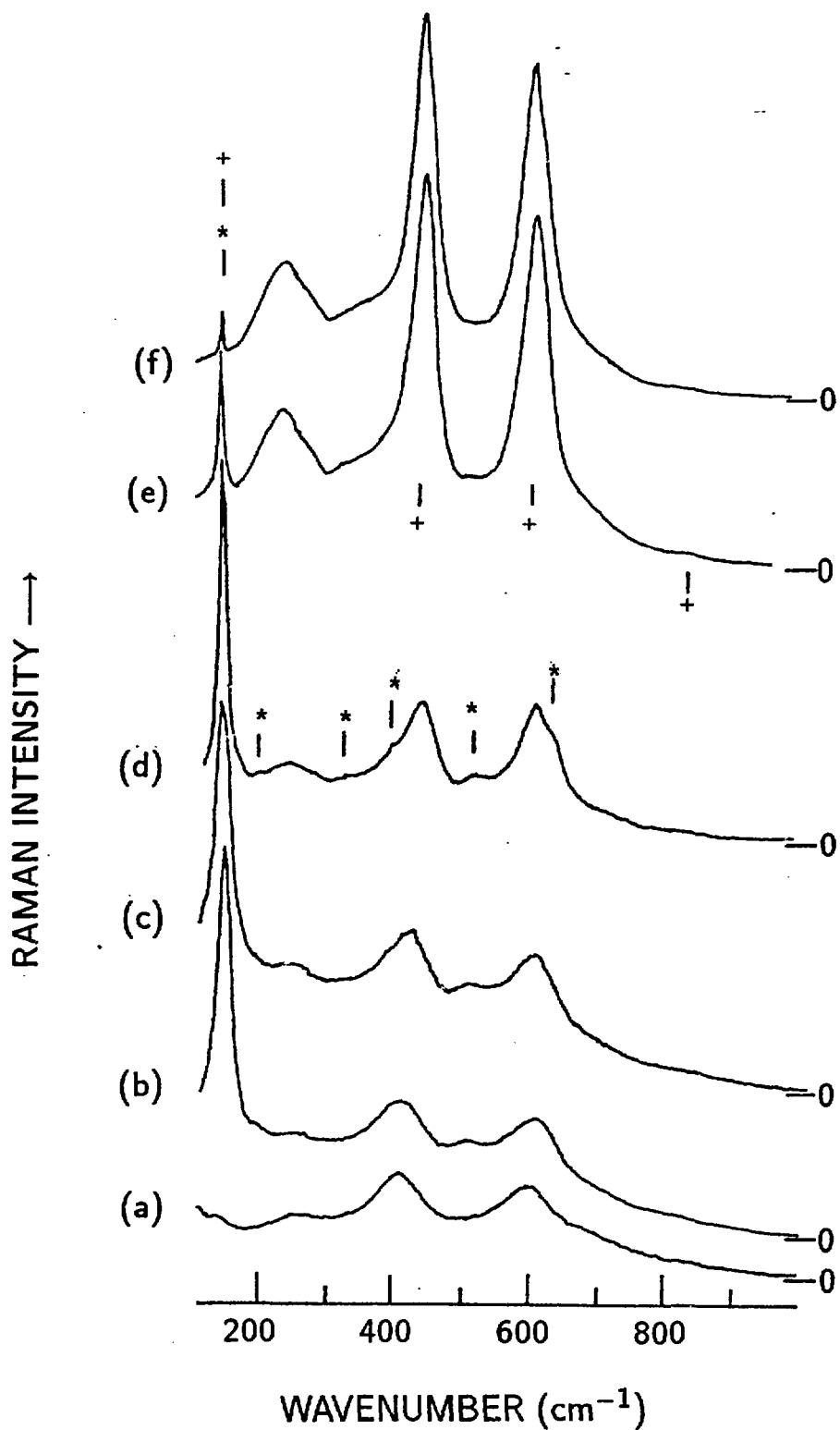


Figure 1. Raman spectra of two areas (a) and (b) of an as-compacted nanophase TiO<sub>2</sub> sample, with a 12 nm average grain size, compared with spectra for area (b) after successive annealing in air for 0.5 h at 573 K (c), 773 K (d), 973 K (e), and 1273K (f). (\* indicates anatase k=0 phonon; + indicates rutile k=0 phonon)

in sporadic regions of the samples, can be attributed to the anatase form of  $\text{TiO}_2$  [9]. The relative intensity of this latter band in the Raman spectra of the present samples indicates the presence of only a small quantity ( $< 5\%$ ) of the anatase phase in these sporadically detected regions, when the work of Exarhos et al. [9, 10] is used as a guide. Nevertheless, most of the Raman spectra recorded were taken from these regions for their additional interest regarding the anatase-to-rutile phase transformation.

The presence of the "600" and "418"  $\text{cm}^{-1}$  Raman bands in the as-compacted samples indicates that the basic structural unit in this nanophase  $\text{TiO}_2$  is that of rutile. This conclusion is consistent with the results of previous electron microscopy investigations of essentially identical material [6]. Furthermore, since both the intensity and broadening of these bands are found to be uncorrelated with the grain sizes in the nanophase materials, even ranging over a factor of  $\sim 10$ , it can be concluded that the grain-boundary structures present in these samples give rise to no Raman scattering which is clearly distinguishable from that of the grains themselves. This is further emphasized by the lack of any new structure in the Raman spectra for the as-compacted nanophase  $\text{TiO}_2$  with a 12 nm grain size, which does have a significant grain-boundary volume fraction (around 15-30% depending upon the grain boundary thickness). It appears, therefore, that there is no evidence from the present data on a nanophase oxide to support the contention by Gleiter and coworkers [2, 5] of unique nanocrystalline grain-boundary structures having neither short-range nor long-range order. On the contrary, the measured Raman spectra indicate rather clearly that as-compacted nanophase  $\text{TiO}_2$  is composed of both grains and grain boundaries which are comprised completely of the structural units of rutile (either short-range or long-range ordered), with the exception of sporadically distributed, very small quantities of the anatase form of  $\text{TiO}_2$ .

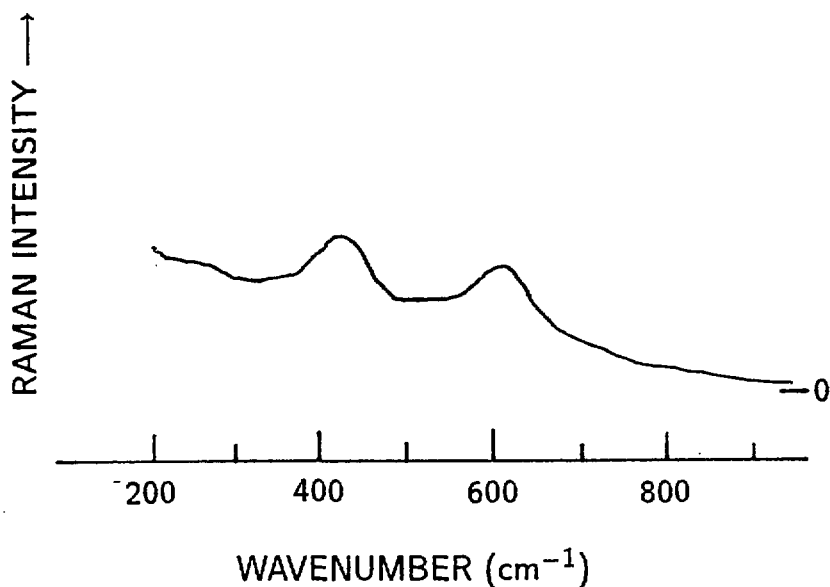


Figure 2. Raman spectrum from an as-compacted nanophase  $\text{TiO}_2$  sample with an 100 nm average grain size.

What then is the reason for the broadening of the "600" and "418"  $\text{cm}^{-1}$  Raman bands in the as-compacted samples, which is removed with annealing at elevated temperatures in air? It appears that this broadening is due to significant concentrations of defects within the rutile grains, since it occurs for as-compacted nanophase  $\text{TiO}_2$  samples having a wide range of grain sizes. Studies of the defect structure of conventional coarse-grained  $\text{TiO}_2$  [13, 14] have indicated the presence of planar defects in slightly reduced rutile, and these have also been seen by transmission electron microscopy in nanophase  $\text{TiO}_2$  (rutile) samples [15] synthesized in the same manner as those in the present study. The atomic displacements and relaxations around these oxygen-deficient defects apparently give rise to the observed broadening in the "600" and "418"  $\text{cm}^{-1}$  Raman bands. Indeed, similar Raman-band broadening has also been observed in amorphous  $\text{TiO}_2$  coatings [10]. Upon annealing the present nanophase samples in air at elevated temperatures, as demonstrated clearly by the sequence of spectra shown in Fig. 1, these bands narrow and intensify while maintaining the peak frequencies (or wavenumbers) representative of the  $A_{1g}$  and  $E_g$  zone-center phonons of the  $\text{TiO}_2$  rutile structure.

Two additional phenomena which result from the annealing of these samples are evident in the sequence of spectra shown in Fig. 1. One is the transformation at elevated temperatures of the sporadically-occurring anatase in the present samples to the rutile form of  $\text{TiO}_2$ , evidenced by the reduction of the intensities of the anatase  $k=0$  phonon bands upon annealing at 973 K and above [compare spectra (d) and (e) in Fig. 1]. The other is the development with annealing of the band at "240"  $\text{cm}^{-1}$ . The observed reduction in the intensity of the "144"  $\text{cm}^{-1}$  band of anatase at 973 K, followed by its almost complete removal at 1173 K, is consistent with prior Raman spectroscopy observations [7, 10] that the anatase-to-rutile transformation occurs in the 1023 - 1123 K temperature range. The "240"  $\text{cm}^{-1}$  band, which is always observed to some degree in Raman spectra of single-crystal and polycrystalline rutile  $\text{TiO}_2$  [7, 11, 12], but is not due to one of the four Raman-active zone-center phonons of rutile [7, 8, 11], is observed in Fig. 1 to gain intensity with annealing as the "600" and "418"  $\text{cm}^{-1}$  rutile bands intensify and undergo narrowing. It is clear from this response to annealing in air that the "240"  $\text{cm}^{-1}$  band is not associated with intracrystalline disorder in rutile, as previously suggested [12], but is more likely connected with either a second-order scattering processes [11] or latent anharmonicity. In any case, the exact source of this band requires further investigation that is beyond the scope of the present work.

In summary, the study of nanophase  $\text{TiO}_2$  by Raman spectroscopy has shown that these samples in their as-consolidated state are comprised of material, both grains and grain boundaries, having only the structural units of rutile; the sole exception being trace amounts of sporadically distributed anatase. The rutile Raman spectra are significantly broadened by the presence of intragrain defects that are removed at elevated temperatures, leading to spectra commonly found in coarser-grained rutile. No evidence was found for the "gas-like" grain-boundary structures that have been suggested for nanocrystalline metals, even though sufficient grain-boundary volumes were present to have yielded spectral information about their local atomic structures.

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