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Raman Spectra of Titanium Dioxide

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First-order Raman spectra have been recorded at room temperature for the anatase and rutile phases of polycrystalline titanium dioxide using an argon ion laser as exciter. The high-temperature rutile phase was found to be stabilized at temperatures below 450°C. Anatase transforms to rutile phase at ~750°C. All the Raman active fundamentals predicted by group theory are observed.

Introduction

Titanium dioxide is known to exist in three crystalline modifications: rutile (tetragonal), brookite (orthorhombic), and anatase (tetragonal). In addition, there are two high-pressure phases, TiO_2-II, which has the α-PbO_2 structure (*1–4*), and TiO_2-III (*5*). The rutile form has a space group D_{4h}^{14} ($P4_2/mnm$) and the lattice constants a = 0.4594 and c = 0.2958 nm. The Raman spectrum of rutile was first recorded by Narayanan (*6*). Since then, a number of papers have appeared in the literature concerning the lattice dynamics of the rutile phase (*7–10*) and the assignment of the observed Raman bands in this structure (*11–14*). There has not been agreement among the several authors concerning phonon frequencies and symmetries. In large measure, these disagreements arise from the relatively strong two-phonon processes in TiO_2. High-pressure Raman spectra of rutile have been investigated (*15–18*) and it is reported that the many new Raman bands that appear at about 26 kbar are due to the high-pressure phase, TiO_2-II, with the space group D_{2h}^{14} ($Pbcn$) having four molecules of TiO_2 in a unit cell. The rutile-to-TiO_2-II transformation is sluggish, occurs over a wide pressure range, and is irreversible. Recently Mammone *et al.* (*5*) reported the TiO_2-II-to-TiO_2-III phase transition occurring at a pressure of 372 kbar. From their Raman spectral data Mammone *et al.* (*5*) suggested that the primitive cell of TiO_2-III phase contains at lest four formula units of TiO_2.

The brookite form of TiO_2 has a more complicated crystal structure. It has eight molecules in its unit cell with the lattice dimensions a = 0.9184, b = 0.5447, and c = 0.5145 nm and all the atoms are in general positions of the simple orthorhombic space group D_{2h}^{15} ($Pbca$). No investigations on brookite regarding its optical and dielectric properties have been reported in the literature.

Anatase belongs to the space group D_{4h}^{19} ($I4_1/amd$) with an elongated cell having a = 0.3783 and c = 0.951 nm. Raman spectra of both natural and synthetic crystals of anatase were investigated at room temperature and the mode assignments

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were made (*19, 20*). The long-wavelength optical phonons in this phase have been worked out on the basis of a rigid-ion model by Krishnamurthi and Haridasan (*21*). The effects of hydrostatic pressure on the Raman spectra of anatase and the occurrence of a pressure-induced phase transition at room temperature have been investigated by Ohsaka *et al.* (*17*). Anatase inverts to another modification, α-anatase, when heated to about 640°C and on further heating this phase changes to rutile at about 1000°C (*22*). Brookite is inverted into rutile at ~750°C (*23*). Anatase and brookite transform irreversibly and exothermically to rutile phase (*24, 25*). The rates of transformation are markedly influenced by the nature and amount of impurities present (*24, 26*). A study by Shannon and Pask (*26*) of the crystallography of the transformation using single crystals of anatase indicated that the rutile phase was nucleated on the surface and then spread into the anatase. The enthalpies of transformation of brookite and anatase to rutile were reported by Mitsuhashi and Kleppa (*27*).

According to Ohsaka *et al.* (*17*) the commercial anatase powder which was heated at 800°C for 4 hr showed only the Raman bands due to anatase phase, indicating that in powder samples the anatase-to-rutile transformation does not occur even at 800°C. Previous work on rutile was done with single crystals where the spectra were obtained for different polarizations to show all the allowed Raman bands. Sample orientation is important in single-crystal experiments. Porto *et al.* (*14*) have shown that for a D_{4h} crystal, to which TiO_2 belongs, an error in proper determination of the a axes (x–y plane orientation) can result in incorrect assignments of two fundamental modes of vibration.

What we report here is the stabilization of the rutile phase at temperatures below 450°C. It is also shown that anatase transforms to rutile at ~750°C. In the present experiments, the Raman spectra of powder samples are recorded using an argon ion laser as exciter and the observed spectra are compared with the published single-crystal spectra. The Raman spectra of solids are often observed using single crystals. Burns and Scott (*28*) have shown the similarity in the Raman spectra of a single-crystal and a polycrystalline material.

Experimental

Titanium dioxide powders were prepared by slow evaporation of tetraisopropyl titanate solution (Tyzor, Dupont Co.) to a rigid, transparent, uniformly colored polymeric glassy state which was subsequently heated to a series of high temperatures to 1000°C. The samples were placed in capillary tubes and supported by a sample holder for the backscattering geometry. Radiation (488 nm) from a Coherent Radiation Laboratories Model 52 argon ion laser served as the excitation wavelength. The scattered light was analyzed by a Jarrell–Ash 25-300 Raman spectrophotometer equipped with an ITT FW-130 (S-20) photomultiplier and an Ortec 9302 amplifier/discriminator. Photon counting was performed by a minicomputer (24K minicomputer, Alpha LSI-2/10G, Computer Automation, Inc.). The laser beam was focussed on the capillary tube by a lens system, and the Raman scattered radiation was collected by an F 1.2 objective lens and focussed into the monochromator. An interactive graphics terminal (4010-1, Tektronix, Inc.) facilitated spectral analysis, such as rapid and accurate determination of peak positions. The spectra in Figs. 1 and 2 were run with a scan rate of 4 cm^{-1}/sec and a slitwidth of 2 cm^{-1} and the spectrum in Fig. 3 was run with a slower scan rate (1 cm^{-1}/sec). Each sample was scanned as many as ten times and the summed spectra were stored on a floppy disk.

Results and Discussion

Rutile Phase

The rutile structure has two TiO_2 molecules in the unit cell with the space group D_{4h}^{14} ($P4_2/mnm$). There are six atoms in the unit cell, implying a total of 15 (= $3N - 3$) vibrational modes. From a group theoretical analysis (*6*) it can be shown that these 15 modes have the following irreducible representations: $A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + 2B_{1u} + E_g + 3E_u$. Further, group theory reveals that four modes, $A_{1g} + B_{1g} + B_{2g} + E_g$, are Raman active and four modes, $A_{2u} + 3E_u$, are infrared active. The other three modes, $A_{2g} + 2B_{1u}$, are neither Raman active nor infrared active.

The Raman spectrum of TiO_2 powder (rutile) heated to 750°C in air for 5 hr is shown in Fig. 1. This spectrum is in good agreement with the single-crystal spectra of Porto *et al.* (*14*) and Beattie and Gilson (*19*). The frequencies of the Raman bands observed at room temperature are 144, 235, 320–360, 448, 612, and 827 cm^{-1}. Our assignment of the Raman bands in this phase are given in Table I.

Rutile exhibits an anomalously strong, broad band at about 235 cm^{-1}. This band shows considerable structure under high resolution. Largely because of its strength, several investigators have assigned this band to a fundamental process (*29, 30*). But the polarization values measured by Narayanan (*6*), using a single crystal for this broad band, did not coincide with that theoretically anticipated for any of the fundamental modes allowed by symmetry in this phase. Porto *et al.* (*14*) attributed this to a combination band. But none of the combinations of the fundamental modes allowed by the selection rule has this energy level. On the basis of Raman and neutron diffraction experiments, Hara and Nicol (*18*) proposed that the rutile lattice is disordered and that this strong band is disorder induced. They have also noted that the intensity of this band decreases with increasing pressure, and this decrease might be due to increased ordering. It should be pointed out that the scattering due to multiphonon processes is more intense in TiO_2 due to large anharmonicities in the TiO_6 octahedra (*5, 31*). The second-order spectrum of $SrTiO_3$, where the Ti is also octahedrally coordinated, is also very strong (*32, 33*). The enormous scattering power might result in the appearance of the second-order spectrum as a broad band at 235 cm^{-1}. In addition to this, there is yet another weak, broad band in the region 320–360 cm^{-1}. This band was also observed by Narayanan (*6*) and Porto *et al.* (*14*) but was left out of their discussions. Like the 235-cm^{-1} band, this band might also be either disorder induced or due to second-order scattering. A study of the spectrum at different temperatures may help to make

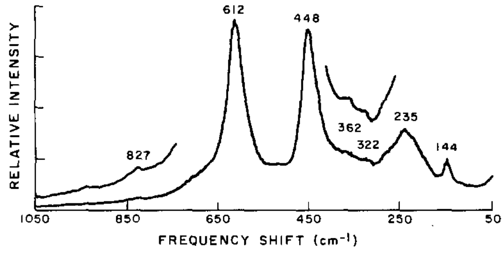

FIG. 1. Raman spectrum of TiO_2 powder heated to 750°C in air (rutile).

TABLE I

ASSIGNMENT OF THE RAMAN BANDS FOR THE RUTILE PHASE

Observed energy shift (cm^{-1})	Assignment	Published work[a] (cm^{-1})
144	B_{1g}	143
235	—	235
320–360	—	300–380
448	E_g	447
612	A_{1g}	612
827	B_{2g}	826

[a] Porto *et al.* (1967).

proper assignment of these bands. The mode assignments for the rest of the bands (Table I) are carried out with the use of available polarization data for each band from the single-crystal measurements reported in the literature (*11, 14*). The scattering intensity of the B_{2g} mode is relatively weak (*16*) and so this particular band appears as a weak band at 827 cm^{-1}.

There was no change in the spectrum of the rutile structure as the powder samples were heated to 1000°C and above. This indicates that the anatase-to-rutile transformation occurred at ~750°C as compared to the value of 915°C (*22*) and 1040°C (*27*) reported for single crystals. This reduction in transformation temperature may be due to the fine crystallite size used in this investigation. The Raman spectrum of the TiO_2 sample heated to 500°C which was previously heated to 750°C (rutile phase) showed only the bands due to rutile structure and this indicates that anatase transforms irreversibly to rutile phase (*24, 25*).

Anatase Phase

The conventional crystallographic unit cell is body centered (space group D_{4h}^{19}, $I4_1/amd$) and contains two primitive unit cells, each of which contains two formula units of TiO_2. According to the factor group analysis (*34*), six modes, $A_{1g} + 2B_{1g} + 3E_g$, are Raman active and three modes, $A_{2u} + 2E_u$, are infrared active. One vibration, B_{2u}, will be inactive in both infrared and Raman spectra. All of these modes account for the 15 normal modes of vibration.

TABLE II

ASSIGNMENT OF THE RAMAN BANDS IN ANATASE PHASE

Observed energy shift (cm^{-1})	Assignment	Calculated value[a]	Published work[a]
147	E_g	144	144
198	E_g	197	197
398	B_{1g}	400	399
515[b]	A_{1g}, B_{1g}	507, 519	519
640	E_g	640	639
796	First overtone of B_{1g} at 398 cm^{-1}	796	796

[a] Ohsaka *et al.* (1978).

[b] This band is a doublet of A_{1g} and B_{1g} modes.

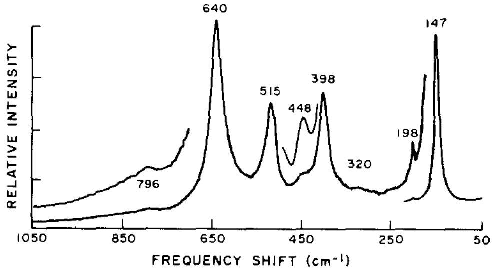

FIG. 2. Raman spectrum of TiO_2 powder heated to 450°C in air (anatase).

The Raman spectrum of anatase obtained by heating the glassy precursor to 450°C is given in Fig. 2. The frequencies of the Raman bands observed are 147, 198, 320, 398, 448, 515, 640, and 796 cm^{-1}. The 147-cm^{-1} band is the strongest of all the observed bands in anatase. The frequency of this band in anatase, 147 cm^{-1}, is nearly equal to that of the B_{1g} mode in rutile (144 cm^{-1}). The three bands at 147, 198, and 640 cm^{-1} are assigned to the E_g modes and the band at 398 cm^{-1} to the B_{1g} mode. The band at 515 cm^{-1} is a doublet of the A_{1g} and B_{1g} modes. The weak band at 796 cm^{-1} is the first overtone of the B_{1g} mode which is expected at that energy level. The 515-cm^{-1} Raman band which occurs at room temperature in anatase is shown to split into two bands centered at 519 and 513 cm^{-1} at low temperature (73 K) (*20*). The weak, broad band centered at 320 cm^{-1} which is also present in the rutile phase is either disorder induced or due to second-order scattering. It should be pointed out here that a Raman band is observed around 320 cm^{-1} by some of the earlier investigators

(*19, 20*). The frequencies of the Raman band, the mode assignment, the calculated values of the frequencies (*20*) on the basis of a short-range force model, and the published single-crystal data (*20*) are given in Table II.

The observed frequencies of the Raman bands in the powder sample heated at 450°C are in agreement with those reported by Ohsaka *et al.* (*17*) on commercial anatase heated to 800°C except for the presence of bands at 448 and ~320 cm^{-1} in the present investigation. The weak band at 448 cm^{-1} is the E_g mode found in the rutile phase. In order to see whether the strong A_{1g} mode (612 cm^{-1}) of the rutile phase is also present in the spectrum of the sample heated to 450°C, the sample was scanned at a slower scan rate (1 cm^{-1}/sec) in the region 250–750 cm^{-1} (see Fig. 3). The shape of the band centered at 640 cm^{-1} indicated that there could be a shoulder to this band at the lower frequency side. In the computer-controlled laser Raman spectrophotometer used in this work, there is an ancillary program which handles curve resolutions of overlapping peaks having either pure Gaussian or pure Lorentzian lineshapes, or any desired combination of these two functions. The computerized Raman spectrophotometer is described in detail in the literature (*35*). The three "pure" Raman bands at 515, 612, and 640 cm^{-1}, as shown in Fig. 4, were determined using a 10% Gaussian and 90% Lorentzian combination for the curve fitting. The cumulative curve containing the 612-cm^{-1} band generated by the computer is shown in Fig. 5. The weak band at 448 cm^{-1} and the band at 612 cm^{-1} are found to be present even in the spectrum of the samples heated to 400°C—however, the overall quality of the Raman spectrum improves markedly if the samples are heated at 450°C or higher. The intensities of the 448- and 612-cm^{-1} bands increased as the powder samples were heated to higher temperatures. The Raman spectrum of the sample heated to 600°C is given in Fig. 6. This spectrum contains the bands at 147, 198, 235, 321, 398, 448, 515, 612, 640, and weak bands at 799 and 825 cm^{-1}. The presence of the bands at 612 and 448 cm^{-1},

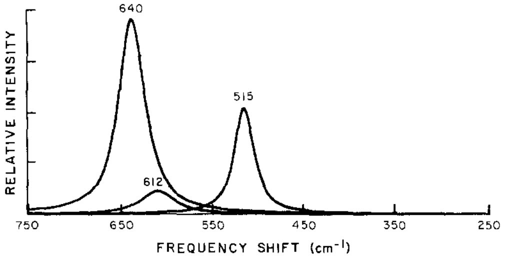

FIG. 4. Three "pure" Raman bands at 515, 612, and 640 cm^{-1} generated using a combination of 10% Gaussian and 90% Lorentzian function for the curve fitting for the TiO_2 sample heated to 450°C in air.

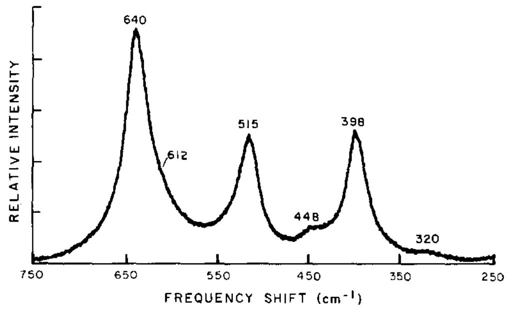

FIG. 3. Raman spectrum of TiO_2 powder heated to 450°C in air (anatase) scanned at a slower rate (1 cm^{-1}/sec) in the region 250–750 cm^{-1} to reveal the band at 612 cm^{-1}.

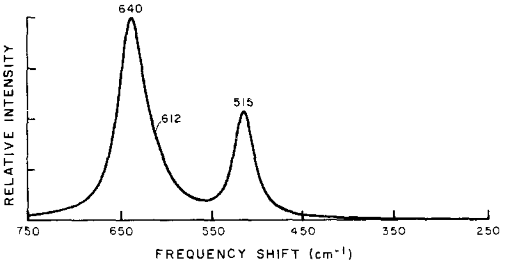

FIG. 5. The cumulative curve containing the bands at 515, 612, and 640 cm^{-1} generated using a 10% Gaussian and 90% Lorentzian combination for the TiO_2 sample heated to 450°C in air.

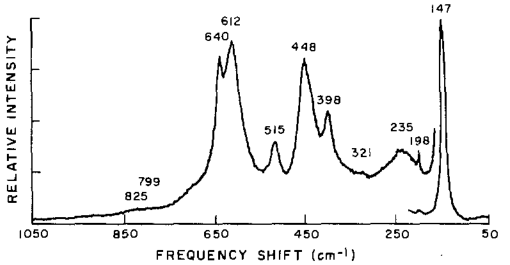

FIG. 6. Raman spectrum of TiO_2 powder heated to 600°C in air showing the strong bands due to anatase and rutile phases.

corresponding to the A_{1g} and E_g modes of the rutile phase in the spectrum of the samples heated at 450°C, suggest that rutile phase is stabilized at temperatures below 450°C, i.e., at temperatures much lower than the bulk transformation temperature of anatase to rutile. Filipovich and Kalinina (*36*) showed in a general way that the high-temperature polymorphs of a crystal could be stabilized at temperatures below its normal transformation temperature at some critical crystallite size if the high-temperature polymorph had a reduced surface free energy with respect to the low-temperature structure. The stabilization of the high-temperature modification (rutile phase) of TiO_2 at temperatures much below the transformation temperature is in agreement with the recent publication of Eror *et al.* (*37*) concerning the stability of hexagonal phase of $BaTiO_3$ at temperatures below 700°C and that of Garvie (*38*) concerning the phase transformations in ZrO_2. This stabilization of rutile phase at low temperatures might be the cause for the observed transformation temperature of 750°C as compared to the single-crystal transformation temperature of 900–1040°C (*22, 27*).

Conclusions

The first-order Raman spectra were recorded at room temperature for the anatase and rutile phases of polycrystalline titanium dioxide. The broad bands observed in rutile at 235 and 320–360 cm^{-1} are attributed to either second-order or disorder-induced scattering. The first overtone of the B_{1g} mode is observed at 796 cm^{-1} in anatase. The rutile phase was found to be stabilized at temperatures below 450°C. It was observed that anatase transforms irreversibly to rutile at ~750°C, i.e., at temperatures much lower than the bulk transformation temperature. The powder samples exhibited spectral features similar to those of single crystals and the measured peak frequencies were also in full agreement with those of the single crystals. This is in agreement with the results of Burns and Scott (*28*) in the system $PbZr_xTi_{1-x}O_3$, which states that "although there is no alternative to the wealth of information that can be obtained by single crystal studies, in some systems much of the same information can be realized from the powder method."

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