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The optical absorption edge of brookite TiO_2

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Abstract

The optical absorption edge of brookite TiO_2 was measured at room temperature, using natural crystals. The measurements extend up to 3.54 eV in photon energy and 2000 cm^{-1} in absorption coefficient. The observed absorption edge is broad and extends throughout the visible, quite different from the steep edges of rutile and anatase. No evidence of a direct gap is seen in the range measured. The spectral dependence of the absorption strongly suggests that the brookite form of TiO_2 is an indirect-gap semiconductor with a bandgap of about 1.9 eV.

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1. Introduction

Titania, TiO_2, occurs naturally as the minerals rutile, anatase, and brookite. The rutile and anatase forms have been intensively studied and have significant technological uses, owing, in large measure, to their optical properties: both are transparent in the visible and absorb in the near ultraviolet. Rutile is the world's most important white pigment in paint and has other everyday uses as a whitener in toothpaste and the UV absorber in sunscreens. The rutile (110) surface serves as a prototypical model for basic studies of oxide surfaces [1,2]. Anatase, in nanocrystalline form, is a photocatalyst and is the active component in self-cleaning cement [3]. It serves as the dye-supporting electron-transporting substrate in a promising class of solar cells [4,5]. Recent interest has developed in transparent anatase [6] and rutile [7] cobalt-doped films that are ferromagnetic at room temperature.

Relatively little is known about the brookite form of TiO_2. While large synthetic crystals of rutile and anatase have long been available, this is not the case for brookite. The brookite phase does occur in synthetic thin films of titania under certain conditions [8,9], and nanoparticle aqueous suspensions have also been studied photovoltaically [10]. For rutile and anatase, single crystal optical-absorption studies have shown that the transparent region in the visible is ended at an absorption-edge threshold located at a photon energy which (putting aside subtle details involving selection rules and exciton effects) is close to the interband direct gap E_0 [11–13]. At room temperature, E_0 is 3.06 eV for rutile [11] and about 3.3 eV for anatase [13]. E_0 is not known for brookite. Band-structure calculations have been reported that suggest that brookite has a direct gap [14]. Our experiments, however, as reported here, indicate that this is not the case.

Brookite is intermediate in density between rutile (densest) and anatase. It is of lower symmetry, orthorhombic, versus tetragonal for the other two. Its short-range order is less regular; in brookite, all six nearest-neighbor Ti–O bond lengths are different and the values span a larger range than in the tetragonal forms [15]. Studies of amorphous TiO_2 suggest a closer relation to brookite than to other crystal forms of titania [16].

In this paper, we report results of optical-absorption measurements on natural brookite crystals. The measurements extend from 2.1 to 3.54 eV in photon energy. No evidence for a direct gap is found in this range. Throughout the visible, the form of the dependence of optical absorption on photon energy suggests the presence of an indirect gap at about 1.9 eV.

2. Experimental

Brookite crystals, originating from the vicinities of Tremadoc, Wales and Bourg d'Oisans, France, were studied.

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The samples were transparent and pale brown in color. In contrast to rutile and anatase, brookite does not occur in colorless form [17,18]. Raman-scattering measurements, made with a JY-Horiba HR-800, showed prominent lines at 127, 152, 246, 319, and 639 cm^{-1}, in good agreement with reported spectra for brookite [19,20], whose Raman signature is distinctly different from that of both rutile and anatase [8].

Optical transmission measurements with unpolarized light [21] were carried out at room temperature, using a scanning prism-grating double monochromator system described elsewhere [22]. This spectrometer possessed resolution and stray-light-rejection characteristics known to be suited for the measurement of steep absorption edges [23]. Polished slabs of several thicknesses were prepared using fine-particle alumina slurries, and thicknesses were measured using a carbide-stylus spindle-displacement instrument (Mitutoyo 543-521).

3. Results: the optical absorption edge

The optical transmission results are shown in Fig. 1. The data are normalized to the transmission at 1.5 eV, where brookite is transparent. Five sample thicknesses were used, in order to cover a wide range of absorption coefficient. For the thinnest sample thickness, the small sample area necessitated the use of an aperture mask about 1 mm in diameter, and the low transmitted intensity at higher photon energies tested the stray-light limit of the instrument. Thus, the apparent leveling off of the transmission for this sample (above 3.55 eV) is treated as an artefact and not used for determining the absorption coefficient.

Standard methods [24] were used to determine the optical absorption coefficient from the relative transmission and the sample thickness. The results are presented in Fig. 2. The data extend from 2.14 to 3.54 eV in photon energy $h\nu$ and from about 20 to about 2000 cm^{-1} in absorption coefficient α. The overlap for different thicknesses is reasonable. The absorption spectrum exhibits, throughout the visible, a systematic increase in α with increasing $h\nu$.

While optical absorption measurements in bulk brookite have apparently not been reported earlier, we should note that

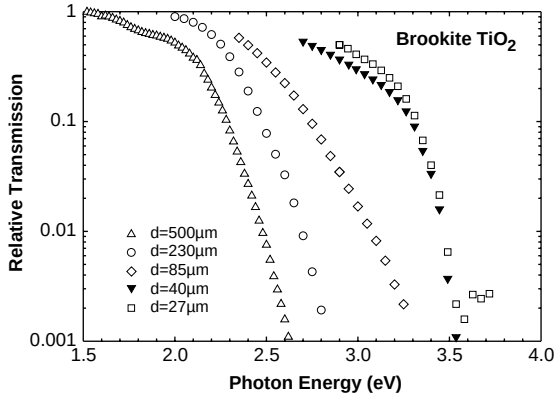

Fig. 1. The optical transmission of brookite samples for five thicknesses. The data are normalized relative to the transmission at 1.5 eV.

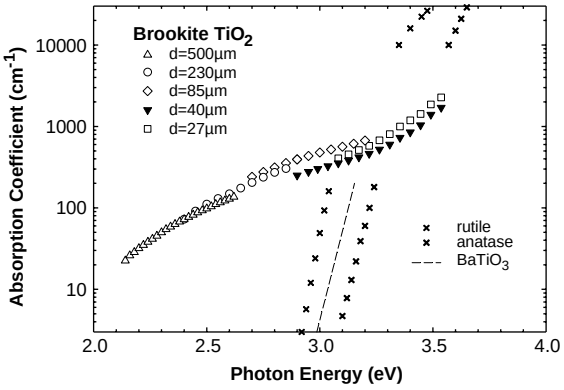

Fig. 2. The optical absorption edge of brookite TiO_2. Included for comparison are reported results for the absorption edges of rutile, anatase, and $BaTiO_3$ [13, 25–28].

qualitative mineralogical observations [17,18] support the presence of substantial absorption throughout the visible. The nanoparticle-suspension studies of Koelsch et al. [10] also support this. While those authors were able to observe visible transmission through undiluted suspensions of rutile and anatase, brookite suspensions required substantial dilution. Those authors attribute the pronounced difference in transmission to greater optical scattering by brookite, but brookite's refractive index in the visible is similar to that of rutile and anatase. The results we present here indicate that the effect observed by those authors is caused by brookite's greater optical absorption in the visible.

4. Discussion: direct and indirect gaps

In Fig. 2, we have included what we believe to be the most reliable reported results for the room-temperature absorption edges of the rutile and anatase forms of TiO_2, as well as for $BaTiO_3$. The low-α edges are from transmission measurements on bulk crystals: Ref. [13] for rutile and anatase, Ref. [25] for $BaTiO_3$. The high-α edges are from reflection ellipsometry measurements: Ref. [26] for rutile, Refs. [27,28] for anatase. The polarization shown is $E \perp c$ which is the first (lower $h\nu$) edge in each case. (For rutile, the $\alpha(h\nu)$ curves for the two polarizations are experimentally indistinguishable at room temperature [13]). All three materials (rutile, anatase, $BaTiO_3$) have steep absorption edges characteristic of direct-gap semiconductors. Below the edge, throughout the visible, each crystal is very transparent.

The optical absorption edge of brookite is seen to be quite different from that of rutile and anatase. The edge is broad and gradual, and it extends throughout the visible. It uneventfully passes through the steep edges of the other crystals. We see no evidence of a direct gap in the region spanned by our data and conclude that for brookite, the lowest direct gap is larger than 3.54 eV. Fig. 2 provides direct evidence that E_0 is significantly larger for brookite than it is for rutile and anatase.

The extended absorption-edge spectrum of brookite suggests the possibility of indirect transitions. While the definitive test for an indirect absorption edge is the presence, in

Table 1
Comparison of the brookite absorption edge to the indirect-transition absorption edges of crystalline Si, GaP, and AgCl

Crystal	Quadratic range for $\alpha(h\nu)$		Slope ($cm^{-1/2}$/eV)	E_{extrap} (eV)	E_G (eV)	Refs.
	$h\nu$ (in eV)	α (in cm^{-1})				
Si	1.25–2.00	10–2000	55	1.19	1.16	[24]
GaP	2.25–2.50	15–700	85	2.20	2.26	[29,30]
AgCl	3.05–4.00	30–6000	78	2.98	3.0	[31–33]
TiO_2 (br.)	2.15–2.85	25–350	19	1.94	–	This work

Aside from the Si data, which is for 77 K, room-temperature results are given.

low-temperature measurements, of distinct steps (at low absorption levels) associated with thresholds for phonon-emission and phonon-absorption processes [24], our room-temperature measurements can also address this issue. The basis for this is the empirical observation that at higher temperature and absorption levels, an indirect edge is generally well approximated by a linear relationship between $\alpha^{1/2}$ and $h\nu$. This holds true for Si, GaP, and AgCl, three very well-documented indirect-gap semiconductors [24,29–33]. An approximately quadratic increase in absorption with energy-above-threshold can be theoretically justified for indirect transitions assuming parabolic bands [24,29], but the point for the present discussion is primarily the empirical basis provided by well-studied indirect-gap semiconductors. Table 1 shows the characteristics of the observed quadratic dependences for Si, GaP, and AgCl. When the lowest direct gap lies well above the indirect gap E_G, the quadratic behavior extends over a wide photon-energy range (0.75 eV for Si, 0.95 eV for AgCl). Table 1 includes the slope and the extrapolated zero-absorption intercept (E_{extrap}) of the observed linear $\alpha^{1/2}$-versus-$h\nu$ dependence. E_{extrap} is within 0.1 eV of the actual indirect gap E_G in each case.

In Fig. 3, we show a plot of $\alpha^{1/2}$ versus $h\nu$ for brookite TiO_2 up to about 2.9 eV. Over the substantial photon-energy range of 2.15 to 2.85 eV, the measurements are reasonably well represented by a straight line. The best-fit parameters are given in Table 1. Based on the discussion given above and the observed value of E_{extrap}, we identify brookite TiO_2 as an indirect-gap semiconductor with a room-temperature bandgap of about 1.9 eV.

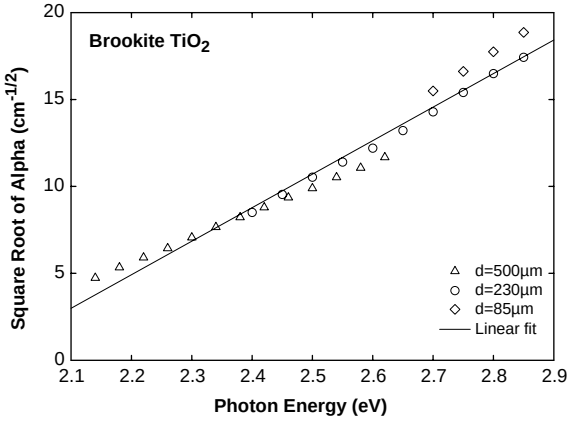

Fig. 3. Square-root plot for the brookite absorption edge.

5. Summary

We have measured the room-temperature optical absorption edge of brookite TiO_2, using natural crystals. The observed edge (Fig. 2) is broad and extends throughout the visible, quite different from the steep edges of rutile and anatase. No evidence of a direct gap is seen up to about 3.5 eV. The spectral dependence of the absorption (Fig. 3 and Table 1) strongly suggests that the brookite form of TiO_2 is an indirect-gap semiconductor with a bandgap of about 1.9 eV.

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