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# THE ABSORPTION SPECTRA OF THORIUM DIOXIDE

J. LAMBERT BATES

JULY, 1967

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THE ABSORPTION SPECTRA OF THORIUM DIOXIDE

By

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Ceramics and Graphite Research Section  
Materials Department

July, 1967

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QUESTION

1. A  
2. B  
3. C  
4. D

ANSWER



## THE ABSORPTION SPECTRA OF THORIUM DIOXIDE

J. Lambert Bates

INTRODUCTION

The purpose of this study was to determine the ultraviolet, visible, and infrared spectra of single crystal and polycrystalline  $\text{ThO}_2$ . Previously reported measurements have been limited to small single crystals<sup>(1)</sup>, to reflectance measurements<sup>(2,3)</sup> or to powder in organic films<sup>(4,5)</sup> and alkali halides.<sup>(6,7)</sup> Reported values for the forbidden energy gap vary from 3.3 to 3.9 eV, with a reported variation being due to different annealing conditions.<sup>(1)</sup>  $\text{ThO}_2$  also undergoes color changes when it is annealed under reducing or oxidizing conditions.<sup>(1)</sup>

Knowledge of the absorption properties of  $\text{ThO}_2$  is needed in order to better understand its electrical, thermal, and other physical properties. This paper describes measurements of the characteristic absorption edge of  $\text{ThO}_2$  and the visible and ultraviolet spectral changes resulting from heat treatments in air and in hydrogen.

SUMMARY

The absorption spectra of single crystal and polycrystalline  $\text{ThO}_2$  have been determined for the spectral range 0.247 to 13  $\mu$ . Complex changes in the ultraviolet and visible spectra occur when the oxide is heated in hydrogen or air. Absorption bands at 0.71  $\mu$  and 0.403  $\mu$  are observed when  $\text{ThO}_2$  is annealed in hydrogen at 1700 °C. Annealing  $\text{ThO}_2$  in air at 1000 °C removes these bands and produces an intense band at 0.306  $\mu$ . The absorption in the infrared range is the same for both single crystal and polycrystalline  $\text{ThO}_2$ , and is independent of the annealing conditions. The characteristic absorption edge is 5.02 eV.

## EXPERIMENTAL RESULTS

### SAMPLE PREPARATION

Polycrystalline wafers, 0.007 cm thick and 1.27 cm in diameter, were cut from large, high density compacts prepared by cold pressing  $\text{ThO}_2$  powder and sintering it at 1750 °C in commercial hydrogen. The specimens were first cut from the sintered compact and then annealed in air at 1000 °C for 4 hours. The final density of the  $\text{ThO}_2$  was  $9.5 \text{ g/m}^3$  (95% T.D.).

Single crystal specimens, 0.025 to 0.25 cm thick, were cut from crystal boules which had been grown during arc-fusion. Prior to its cutting, the crystal was annealed in hydrogen for 8 hr at 1700 °C. After the wafers had been cut from the large crystal their flat surfaces were polished. The specimens were of irregular shape with a maximum surface area on each flat side of approximately  $0.5 \text{ cm}^2$ .

After annealed in hydrogen, the single crystals were light blue in color. But after heated in air at 1000 °C for 16-64 hr, they were light tan.

The spectrographic analysis of the  $\text{ThO}_2$  is given in Table I.

### ABSORPTION MEASUREMENTS

The absorption spectra were measured by using (1) a Cary Model 14 spectrophotometer (spectral range 0.2 to  $2.65 \mu$ ), and (2) a Perkin-Elmer spectrophotometer Model 521 (spectral range 1.5 to  $15 \mu$ ). All measurements were made at room temperature, and no corrections were made for reflectance.

The polished sections of  $\text{ThO}_2$  were placed over a hole cut in a rigid, opaque plate. The plate supported the thin sections and masked the detector from extraneous radiation.

## RESULTS AND DISCUSSION

The infrared spectrum of  $\text{ThO}_2$  single crystals over the range 2.0 to  $13 \mu$  is shown in Figure 1. The single crystal spectrum exhibited broad weak bands at  $2.2 \mu$  (0.56 eV),  $2.7 \mu$  (0.46 eV),



4.9  $\mu$  (0.25 eV), and 8.5  $\mu$  (0.15 eV), with an intense band at 9.8  $\mu$  (0.13 eV). Another band was resolved at 11.4  $\mu$  (0.11 eV) very close to the edge of an intense absorption band above 13  $\mu$ . The presence of this intense band prevented measurements to longer wavelengths.

The absorption spectrum of the polycrystalline ThO<sub>2</sub> agrees with the spectrum of single crystal ThO<sub>2</sub> having strong bands at 9.7  $\mu$  and 11.6  $\mu$  (Figure 2). However, the increase in the optical density at the shorter wavelengths--undoubtedly due to the scattering of grains, as well as to the grain boundaries and porosity--prevented resolution of the bands at the shorter wavelengths.

*TABLE I. Spectrographic Analysis of Thorium Oxide Specimens*

Element	Impurities, ppm		Element	Impurities, ppm	
	B-39 (Crystal)	B-16 (Sinter)		B-39 (Crystal)	B-16 (Sinter)
Ag	<0.2	---	Mn	<4.0	1.0
Al	5.0	5.0	Mo	<2.0	---
B	<0.5	0.1	Na	---	500.0
Be	0.05	---	Ni	2.0	10.0
Bi	---	10.0	Pb	10.0	0.5
Ca	100.0	---	Si	---	<10.0
Cd	<10.0	---	Sn	---	0.5
Cr	<1.0	---	Ti	0.2	---
Cu	4.0	0.2	V	<1.0	---
Fe	5.0	<50.0	Y	50.0	---
Mg	50	10.0	Zn	<20.0	---
			Zr	1.0	---

The data are also in fair agreement with the limited reported data in this wavelength range (Table II). Terada and Tsuboi<sup>(5)</sup> reported a broad absorption band at approximately 27.5  $\mu$  with the shorter wavelength edge at 16  $\mu$ . This

is different from the  $13 \mu$  observed in this study. However, this difference may be related either to the significantly lower density of the  $\text{ThO}_2$  in the polyethylene film used by Terada and Tsuboi or to the high optical densities of the single crystals used in this study.

The infrared spectrum for  $\text{ThO}_2$  is very similar to the spectrum for  $\text{UO}_2$ ,<sup>(10)</sup> which has absorption bands at  $2.47 \mu$ ,  $5.35 \mu$  and  $9.83 \mu$  and an intense absorption band at  $24.5 \mu$ .<sup>(5)</sup> This similarity would suggest that these bands are related to specific characteristics of the fluorite structures of the two oxides.

TABLE II. *Infrared Absorption Bands in Thorium Dioxide*

	<u>Wavelength of Absorption Bands (Microns)</u>					
$\text{ThO}_2$ Crystal (B-39)	2.2 bw	2.7 bw	4.9 bw	8.5 Sh	9.8 vs	11.4 Sh
$\text{ThO}_2$ Polycrystal (B-19)					9.7 m	11.5 m
$\text{ThO}_2$ Dispersed in Polyethyl- ene Film <sup>(5)</sup>		2.7 w	5.9 w		9.3 bm	

s = strong intensity

m = medium intensity

w = low intensity

b = broad

Sh = shoulder

v = very

Complex changes in the absorption spectra of a  $\text{ThO}_2$  single crystal were observed after it was heated in hydrogen or air (Figures 3 and 4). The hydrogen annealed crystal exhibited two absorption bands at  $0.71 \mu$  (1.75 eV) and  $0.403 \mu$

(3.08 eV), with a shoulder on the absorption edge at approximately  $0.306 \mu$  (4.05 eV). Annealing the crystal in air for 16 hr at 1000 °C altered its color from light blue to light tan and removed the bands at  $0.710 \mu$  and  $0.403 \mu$ . However, the absorption increased significantly near the absorption edge ( $0.247 \mu$ ), causing a large band at approximately  $0.306 \mu$  (4.05 eV). In the infrared region  $>2.0 \mu$ , no changes in the absorption spectra due to annealing in either hydrogen or air were observed. The crystal was annealed an additional 48 hr in air at 1000 °C with no further change in the spectrum.

Differences in the optical densities of the sample after it has been annealed in hydrogen and in air (Figure 5) show a strong absorption band at  $0.306 \mu$  near the absorption edge and suggest another band at approximately  $0.26 \mu$  ( $\sim 4.8$  eV). However, because of the high optical densities near the edge, the existence of this band may be questioned.

Weinreich and Danforth<sup>(1)</sup> have also reported that when  $\text{ThO}_2$  is heated in air and in a vacuum, complex changes occur in the absorption spectra: when heated in air at 1000 °C the crystal reddened, but when heated in a vacuum at 1000 °C the color disappeared; subsequent heating at 1800 °C in a vacuum produced a sharp absorption peak at about  $0.400 \mu$ . This agrees very well with the peak at  $0.403 \mu$  observed in this study. However, Weinreich and Danforth did not observe the peak at  $0.71 \mu$  and, after the crystal had been heated in air, its apparent color was different.

The optical energy gap for  $\text{ThO}_2$  is 5.02 eV ( $0.247 \mu$ ). This energy was the same for both the hydrogen- and air-annealed samples, and is significantly greater than the 3.3 eV reported by Vratny and Kikalas<sup>(2)</sup> and the 3.9 eV reported by Weinreich and Danforth.<sup>(1)</sup> The latter authors reported an apparent shift to a lower energy gap when the sample was heated in a vacuum. However, the formation of

an intense band at  $0.306 \mu$  ( $0.405 \text{ eV}$ ) after the sample was heated in air could cause an apparent shift to shorter wavelengths if the optical densities were so high that this band could not be resolved.

The absorption bands near  $0.40$  and  $0.71 \mu$  may be attributed to F-centers caused by a stoichiometric excess of thorium produced by annealing in vacuum at  $1800 \text{ }^\circ\text{C}$ <sup>(1)</sup> or in hydrogen at  $1725 \text{ }^\circ\text{C}$ . Electron spin resonance spectra<sup>(9)</sup> of single crystal  $\text{ThO}_2$  suggest that these F-centers result from trapped electrons near  $\text{O}^{+2}$  ion vacancies caused by a metal excess in the crystal lattice. The excess metal is easily removed by heating in an air atmosphere at  $1000 \text{ }^\circ\text{C}$ .

By similar reasoning, the absorption band at  $0.306 \mu$  may be attributed to V-centers caused by a stoichiometric excess of oxygen in the  $\text{ThO}_2$ . This peak is observed only after the oxide is heated in an oxidizing atmosphere.

The concept of F- and V-centers in  $\text{ThO}_2$ , as proposed above, is also consistent with the electron spin resonance spectra of  $\text{ThO}_2$  that has been irradiated with electrons,  $\gamma$ -rays, or x-rays.<sup>(9)</sup> Ionizing radiation, which produces both free electrons and holes, forms both F- and V-type centers. Subsequent radiation with light or heat generally causes these excited states to recombine, bleaching the absorption peaks related to the F and V color centers. In  $\text{ThO}_2$ , ionizing radiation produces an absorption peak near  $0.34 \mu$  (the F-center) and causes a shift in the apparent absorption edge from  $0.30$  to  $0.34 \mu$ .<sup>(9)</sup> This apparent shift was undoubtedly the long wavelength edge of the absorption band at  $0.306 \mu$  (the V-center). Both bands were readily bleached at room temperature, suggesting that there had been shallow trapping of the electrons and holes during irradiation.

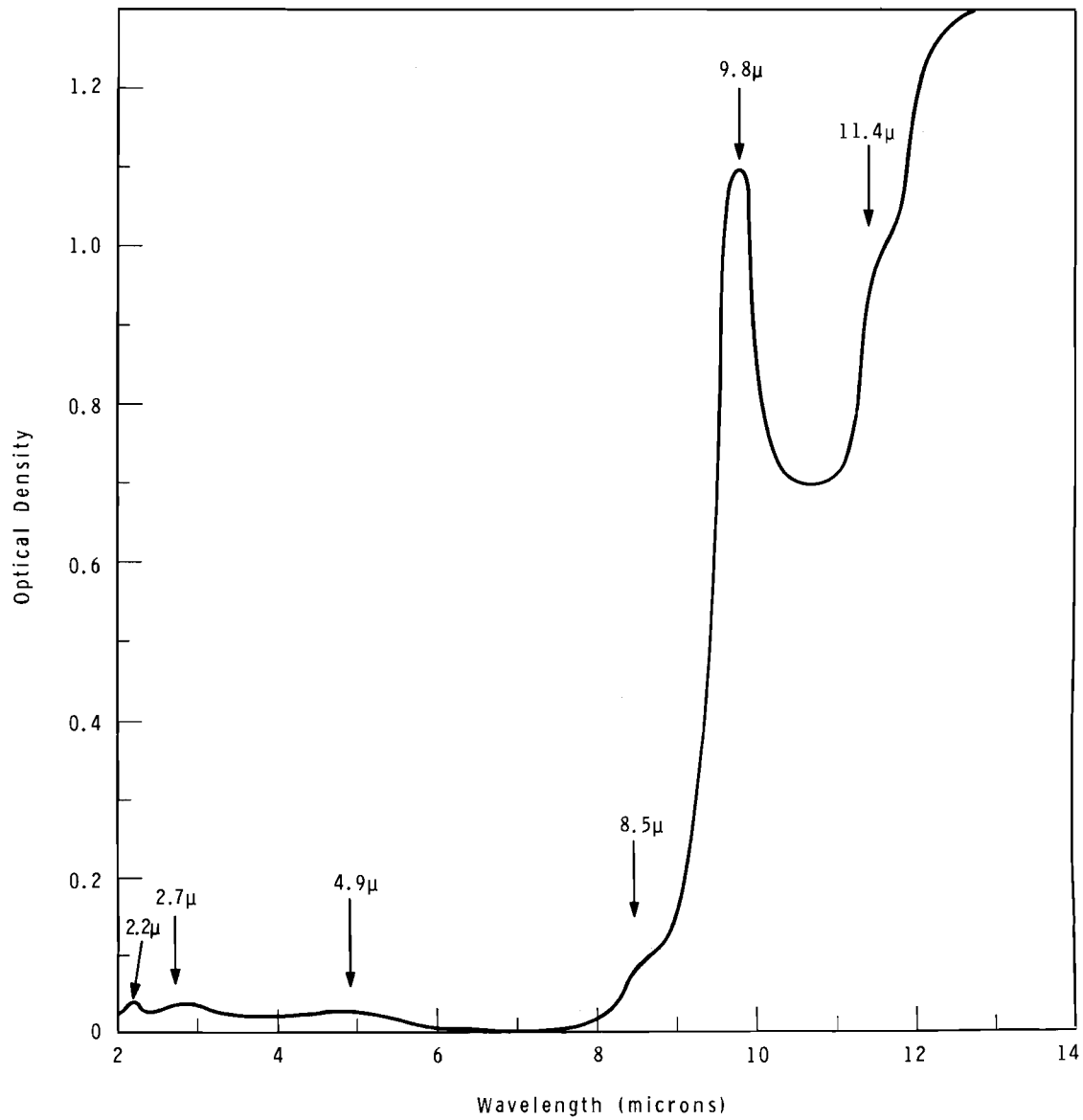


FIGURE 1. Infrared Absorption Spectrum of Single Crystal ThO<sub>2</sub> (B-39)

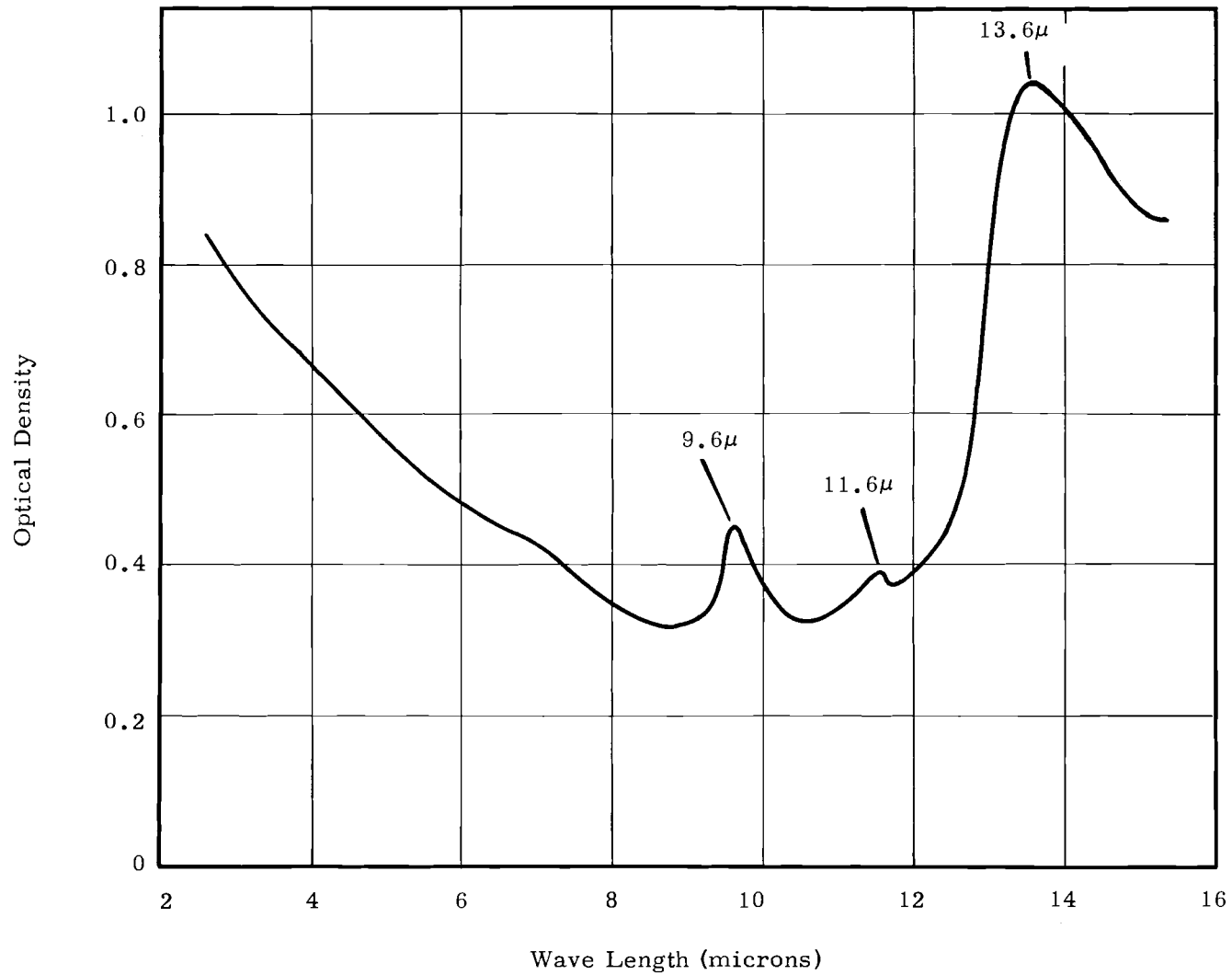


FIGURE 2. *Infrared Absorption Spectrum of Polycrystalline ThO<sub>2</sub> (B-19)*

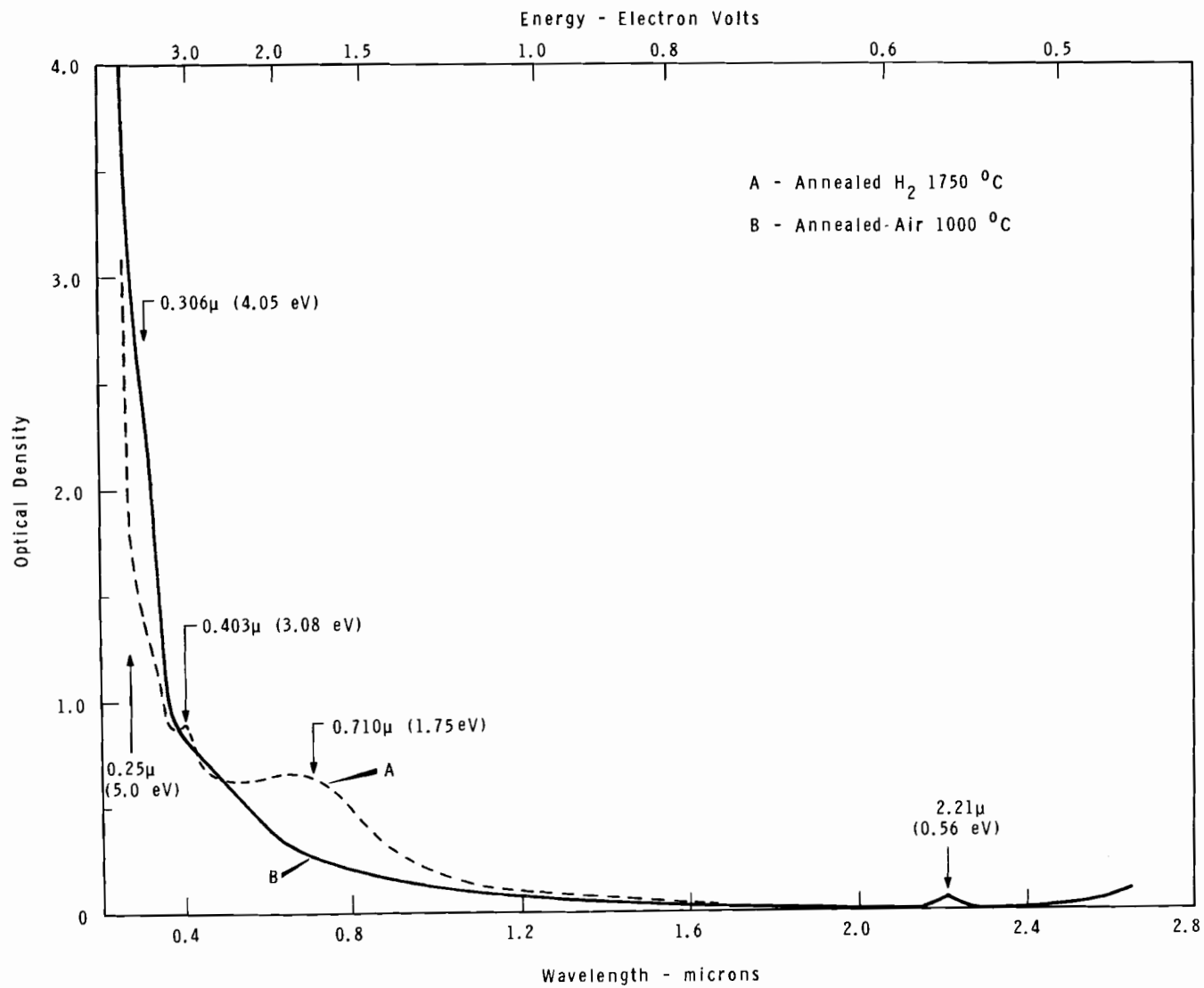


FIGURE 3. Ultraviolet, Visible, and Infrared Absorption Spectra of Single Crystal ThO<sub>2</sub> (Optical Density Versus Wavelength)

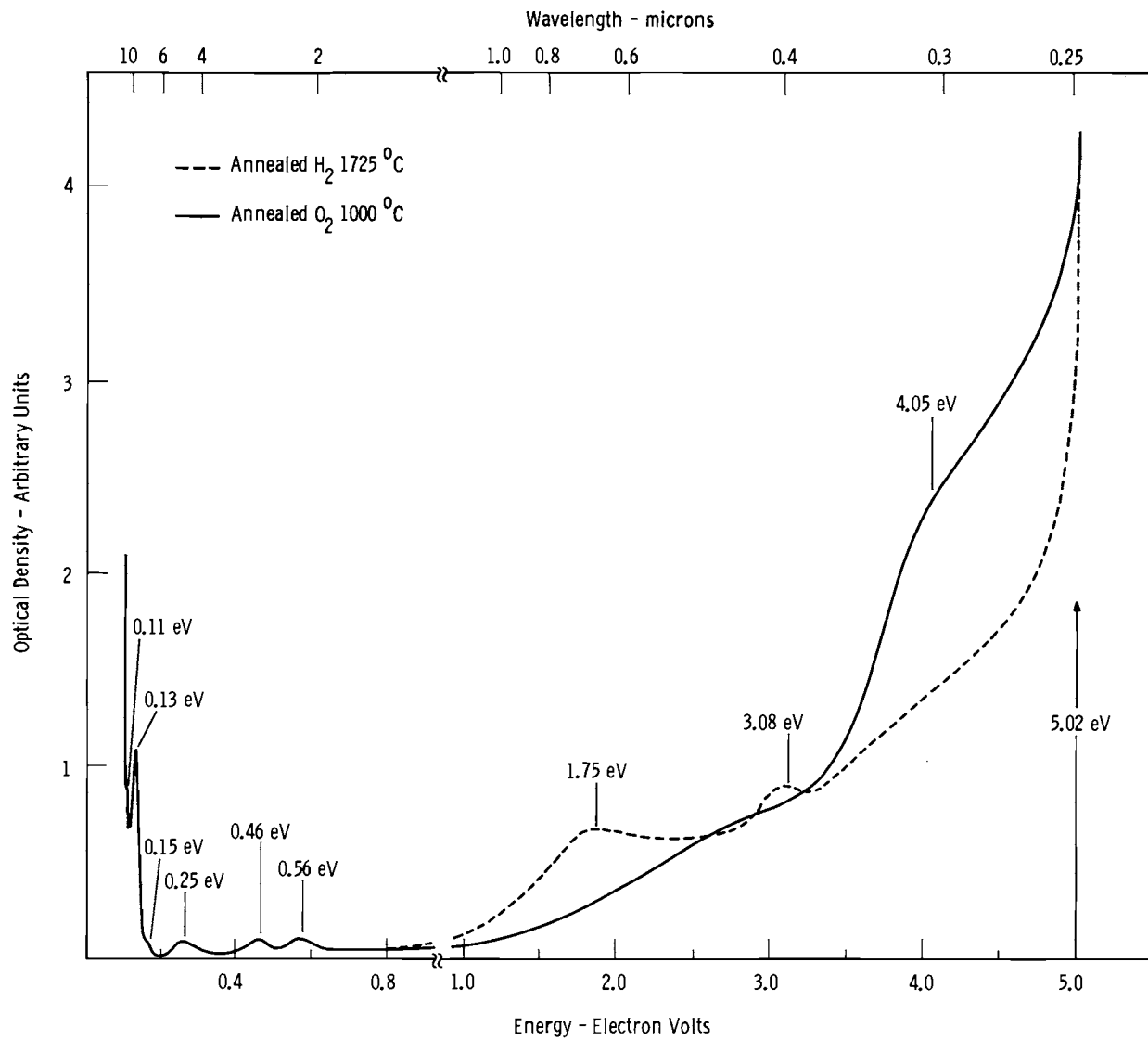
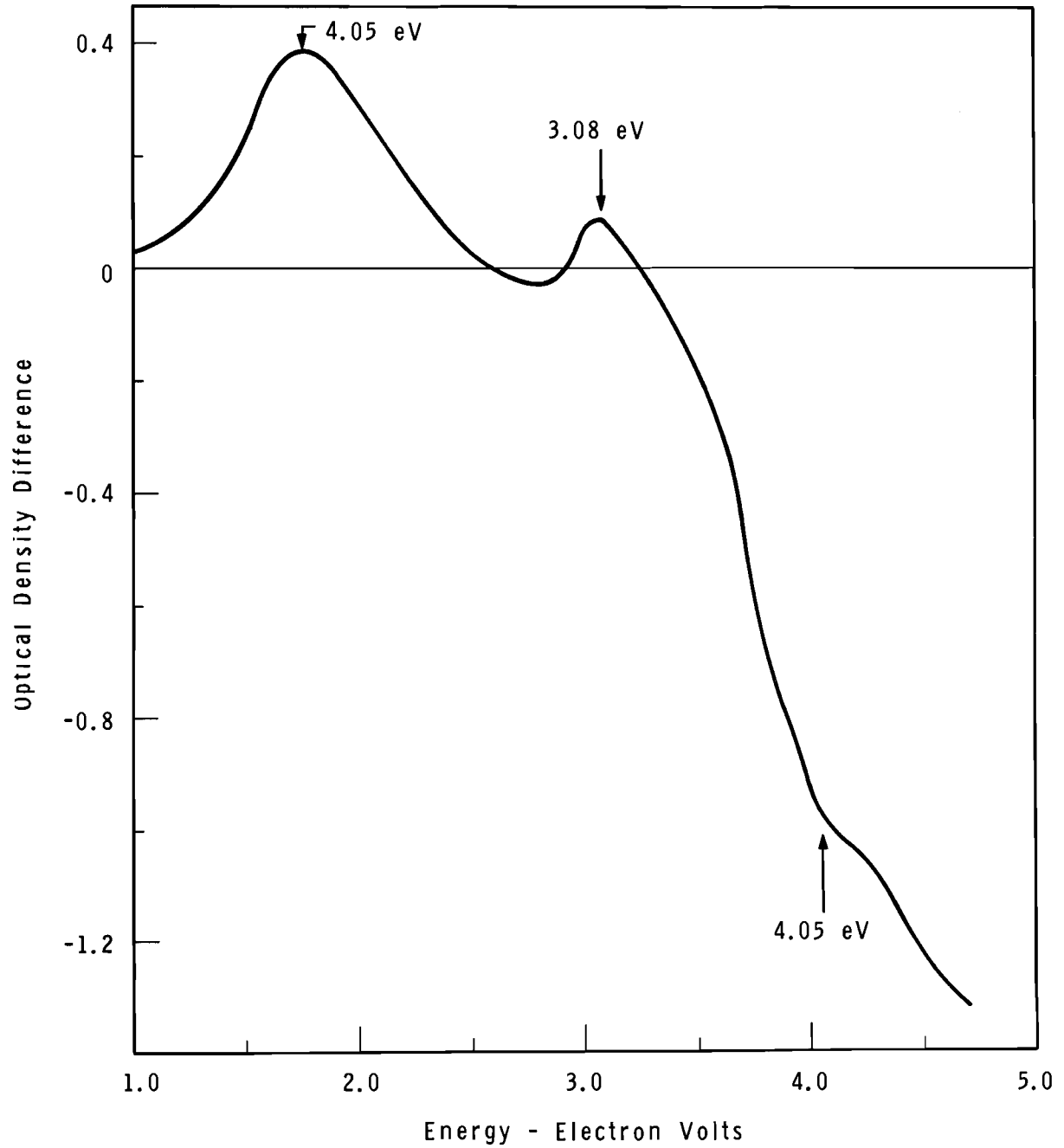


FIGURE 4. *Ultraviolet, Visible, and Infrared Absorption Spectra of Single Crystal ThO<sub>2</sub> (Optical Density Versus Wavelength)*





*FIGURE 5. Optical Density Difference Between Specimen Annealed in Hydrogen and in Air*

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