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VISIBLE AND INFRARED ABSORPTION SPECTRA
OF URANIUM DIOXIDE

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INTRODUCTION

The fundamental absorption properties of uranium dioxide, e. g., the forbidden energy gap and the absorption coefficient, are valuable in understanding the electrical, thermal, and other physical properties of UO_2 . However, comparatively little is known of the absorption characteristics of UO_2 . Measurements of the absorption spectra have been limited primarily to the study of thin films,^(1,2,3) and to powders contained in alkali halides⁽⁴⁾ or polyethylene.⁽⁵⁾ More recent studies have been made with polycrystalline thin sections^(6,7) and single crystal UO_2 ;⁽⁸⁾ but, measurements have been limited to a narrow wavelength range.

The purpose of this study was to determine the absorption spectra and absorption coefficients for single crystal and polycrystalline UO_2 . Preliminary results are described.

SUMMARY

The absorption spectra for single crystal and polycrystalline UO_2 have been measured between 0.6 and 15 μ at room temperature. The spectrum for UO_2 resembles that of a typical semiconductor, opaque in the visible but transparent over a large portion of the infrared. The absorption edge is located at approximately 0.6 μ (2.0 eV). A large optical window extends from 3 to 13 μ .

The absorption coefficient for single crystal UO_2 has been determined between 1.5 and 15 μ . A maximum value of 57 cm^{-1} was measured at 1.70 μ with minimum values of 6 cm^{-1} at 2.75 and 8 μ . The absorption coefficient of polycrystalline UO_2 at wavelengths less than 8 μ is estimated to be ten times larger than for single crystal UO_2 .

EXPERIMENTAL PROCEDURE

Uranium Dioxide Specimens

Sample thicknesses less than 0.03 cm were necessary to obtain satisfactory absorption spectra. Wafers of UO_2 were ground by hand on abrasive paper into thin sections 0.003 to 0.03 cm thick. Specimens less than 0.015 cm thick were thinned after the specimen was attached to a glass slide with a water soluble adhesive. The thinned sections were removed from the slide and the adhesive dissolved from the UO_2 before absorption spectra were measured. Final surfaces of all the thin sections were prepared with 600 grit metallographic paper. Sample areas as large as 2.5 cm^2 were used.

The absorption spectra for single crystals having overall O:U ratios between 1.96 and 2.001 were measured. Crystals with different orientations were also used. Polycrystalline samples were high density (97.5% TD) UO_2 that had been sintered at 1725 C in commercial hydrogen. The O:U ratio was 2.001.*

Absorption Measurements

The absorption spectra were measured with (1) a Cary Model-14 spectrophotometer (spectral range of 0.6 to 2.65μ), (2) a Perkin-Elmer Model-21 spectrophotometer with NaCl optics (spectral range 1.5 to 15μ), and (3) a Perkin-Elmer Model-237 grating spectrophotometer (spectral range 2.5 to 15μ). All spectra were measured at room temperature.

A thin section of UO_2 was placed over a hole or slit in a rigid, opaque plate. The plate supported the fragile specimen and masked the detector from extraneous radiation.

The absorption coefficient, α , was calculated from the differential optical density spectrum, measured in the double beam spectrophotometers, and the difference in sample thickness.** Because the surfaces of the crystals were prepared in an identical manner it is assumed that the surface scatter and reflection were the same for both specimens.

* The O:U ratios were determined by both oxidation and coulometric analyses.

** Sample thickness was measured to $\pm 0.0003 \text{ cm}$ with a micrometer and dial indicator.

Two methods were used to measure these differences in optical density while minimizing the effects of reflection and scattering.

- (1) The spectrum for each specimen was measured separately with the UO_2 in the sample beam and air in the reference beam. The optical density of the thicker sample was subtracted from the optical density of the thinner sample over the entire wavelength range (1.5 to 15μ).
- (2) A single differential spectrum was obtained by placing the thicker sample in the sample beam and the thinner sample in the reference beam of the double beam spectrophotometer.

The optical density differences between the two methods varied less than than the error of measurement.

RESULTS

The spectrum for UO_2 between 0.6 and 15μ is shown in Figure 1. A large optical window occurs in the infrared between 3 and 13μ . Two absorption bands at 9.83 and 5.35μ (0.248 and 0.127 ev) were observed in this window. These bands appear to be insensitive to the O:U ratio of the UO_2 .

FIGURE 1

Optical Density of Single Crystal Uranium Dioxide
(0.006 cm thick)

In the spectra for single crystal UO_2 , a number of sharp, overlapping bands were resolved between 0.6 and 2.65 μ (Figure 1). The energies and wavelengths of these bands are summarized in Table I. These bands appear to change with the stoichiometry of the crystal; the absorption increasing with an increase in O:U ratio.

TABLE I

ABSORPTION BANDS OF SINGLE CRYSTAL URANIUM DIOXIDE

Wavelength, μ	Photon Energy, ev
12.75	0.097
9.83	0.127
5.35	0.248
2.48	0.501
2.36	0.526
2.26	0.549
1.73	0.718
1.62	0.768
1.55	0.802
1.54-1.35*	0.805-0.920*
1.33	0.936
1.115	1.11
1.065	1.16
0.905	1.37
0.865	1.43
0.837	1.48
0.805	1.54
0.770	1.61
0.754	1.64
0.720	1.72
0.665	1.86

* A group of unresolved absorption bands were observed between these wavelengths and energies.

The band at 0.665 μ (1.86 ev) on the absorption edge appears to be the same as that observed by Kikuchi and Nasu.⁽⁶⁾ They suggest that this absorption band is characteristic of a point defect related to excess oxygen in uranium dioxide.

The spectrum for UO_2 resembles that of a typical semiconductor being opaque in the visible but transparent in a large portion of the infrared. The opacity at wavelengths less than 0.6μ may be caused by the excitation of electrons across a forbidden energy gap. The complex absorption between 0.6 and 3μ could result from impurities or stoichiometry variance in the oxide. The bands at longer wavelengths ($>3 \mu$) may be associated with other impurity absorption, reststrahlen or free-carrier absorption.

The apparent cut-off frequency (absorption edge) for single crystal UO_2 was observed near 0.6μ and is associated with a photon energy of approximately 2.0 ev . This value is very close to that reported at MOL, Belgium,⁽⁸⁾ (2.18 ev) and is significantly lower than the frequently reported values of 2.7 - 3.0 and 5.0 ev . However, Briggs⁽³⁾ suggests that this is the edge of a well-defined absorption peak at 0.6μ and would appear as an absorption edge because of the thicker UO_2 samples.

Values for the absorption coefficient between 1.5 and 15μ for single crystal UO_2 are shown in Figure 2. Minimum values of 6 cm^{-1} were observed near 2.75 and 8μ with a maximum value of 57 cm^{-1} at 1.70μ . This relatively low value of the absorption coefficient may be significant when analyzing heat conduction in UO_2 . It has been proposed^(9, 10) that radiation transfers a significant amount of heat in single crystal UO_2 at high temperatures. However for the radiation contribution to the thermal conductivity to be important, α should be less than 100 cm^{-1} . Although these data indicate α should be less than 100 cm^{-1} . Although these data indicate α for single crystal UO_2 to be significantly less than 100 cm^{-1} , the data were recorded at room temperature and may vary at higher temperatures where radiant energy transfer is important.

The translucent character of the thin UO_2 sections of single crystals makes possible the examination of UO_2 structure by transmission microscopy. The UO_2 is a brilliant red when viewed with transmitted white light. In some crystals, especially those with O:U ratios less than 2.00 , opaque centers are easily discernible by transmission microscopy.

FIGURE 2

Absorption Coefficient for Single Crystal UO_2

Some of these centers are caused by uranium metal inclusions. Other centers concentrate at the low angle grain boundaries in the single crystal and may result from impurity centers or dislocations.

Although not measured quantitatively, the absorption coefficient for polycrystalline UO_2 is estimated to be significantly larger than for single crystal UO_2 . The spectrum for a 0.006 cm thick section of sintered UO_2 is compared with the spectrum for a 0.015 cm thick single crystal* (Figure 3). (The O:U ratio of both specimens was 2.001.) It is evident that the absorption coefficient for the polycrystalline sample is larger at wavelengths less than 8 μ . At 4 μ , for example, the estimated absorption

* The UO_2 single crystal was annealed for 12 hr at 1725 C in commercial grade hydrogen.

coefficient for the sintered specimen is ten times larger than that of the single crystal. The higher optical density of the polycrystalline sample undoubtedly results from scattering of radiation at the grain boundaries.

FIGURE 3

Optical Density of Single Crystal and Polycrystalline UO₂

The present data represent the initial studies of the absorption characteristics of UO₂. Effects of purity, stoichiometry, and temperature are now being investigated.

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