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Application News

No.A460A

Spectrophotometric Analysis

Measurement of Band Gap of Titanium (IV) Oxide

Titanium dioxide (TiO_2) exhibits useful photocatalytic activity, and is widely used in antimicrobial products, pigments, cosmetics, etc. The fundamental physical property referred to as band gap (forbidden band) is often determined in research of the physical properties of titanium dioxide. In Application News A428, the determination of band gap in compound semiconductors was discussed, along with the calculation used in that analysis. However, the complexity of that calculation can make it difficult and time-consuming to complete the determination. To resolve this difficulty, we have developed a software approach utilizing an Excel macro, named "Band Gap Calculation Excel Macro,"[1)] which permits easy calculation of band gap. Here, using this same software, we introduce the calculation of band gap based on the diffuse reflectance spectra obtained from measurement of titanium dioxide using the UV-2600 ultraviolet-visible spectrophotometer.

Measurement and Result

We measured rutile and anatase, two different forms of titanium dioxide (TiO_2) manufactured by Wako Pure Chemical Industries, Ltd. The sample was pressed into a sample cup using a glass rod, and with the sample cup placed in the ISR-2600Plus integrating sphere attachment, the diffuse reflectance was measured. Fig. 1 shows the sample pressed into the sample cup, and Fig. 2 shows the compacted sample set in the integrating sphere. In addition, Fig. 3 shows the diffuse reflectance spectra of the samples measured using barium sulfate as the standard. The analytical conditions are shown in Table 1. It is clear from Fig. 3 that the wavelength positions of the absorption edges of the rutile and anatase forms are different. This difference represents a difference in the band gap.

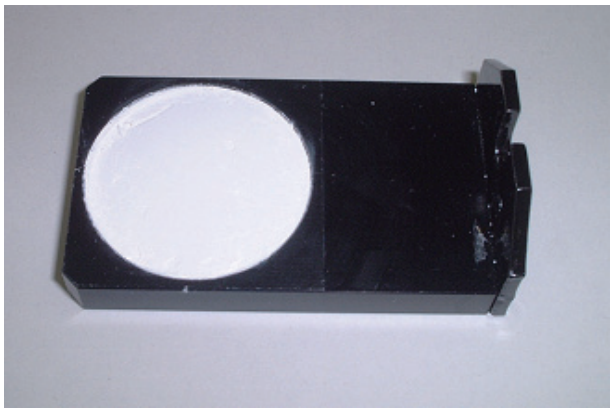

Fig. 1 Sample Pressed into Sample Cup

Fig. 2 Sample Set in Integrating Sphere

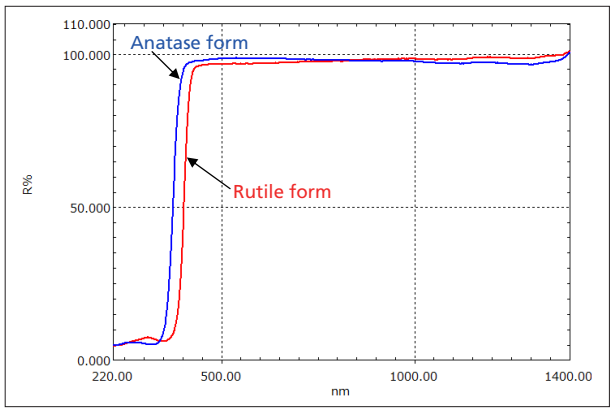

Fig. 3 Diffuse Reflectance Spectra (Red: Rutile form, Blue: Anatase form)

Table 1 Analytical Conditions

Instruments	: Shimadzu UV-2600 Ultraviolet-Visible Spectrophotometer ISR-2600Plus Integrating Sphere Attachment
Measurement Wavelength Range	: 220 nm – 1400 nm
Scan Speed	: Medium
Sampling Pitch	: 1.0 nm
Photometric Value	: Reflectance
Slit Width	: 5 nm
Detector Switching Wavelength	: 830 nm

Calculation Results

The band gaps of the rutile and anatase forms of titanium dioxide were calculated using the Band Gap Calculation Excel® Macro.

The procedure involves first saving the measured spectra in CSV format. The CSV data are then loaded into the macro using the file selection window shown in Fig. 4. The type of photometric value that was used (transmittance or reflectance) is selected in the photometric value area. The "value of n" corresponds to the type of sample transition process selected. "1/2" corresponds to Direct Allowed Transition, "3/2" is for Direct Forbidden Transition, "2" corresponds to Indirect Allowed Transition, and "3" is for Indirect Forbidden Transition.

Once the data are read into the macro, the spectrum is displayed at the upper part of the main window, as shown in Fig. 5, and the Tauc plot is shown at the lower part of the window. The Tauc plot is calculated by applying the Tauc plot approximation to the spectrum. The band gap value is determined by the point at which a tangent drawn at the inflection point of the Tauc plot intersects the horizontal axis (eV value). The tangent line is drawn using this software macro by applying an algorithm to an appropriately set range that can be regarded as approximately linear in the vicinity of the inflection point, and the tangent line is determined by applying the least squares method to that range. Fig. 6 shows an example using the spectrum of the anatase form of TiO_2. With the linear range set to 3.55 eV – 3.7 eV, the band gap for the anatase form was determined to be 3.49 eV. Similarly, that for the rutile form was determined to be 3.20 eV. The band gap for both samples was calculated as "direct allowed transition."

Thus, the band gap can easily be determined using this software macro. For details regarding the actual calculation, please refer to Application News A428 "Measurements of Band Gap in Compound Semiconductors."

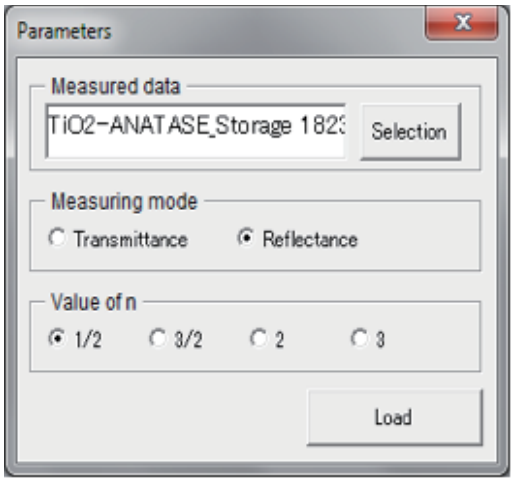

Fig. 4 Window for Selecting a File

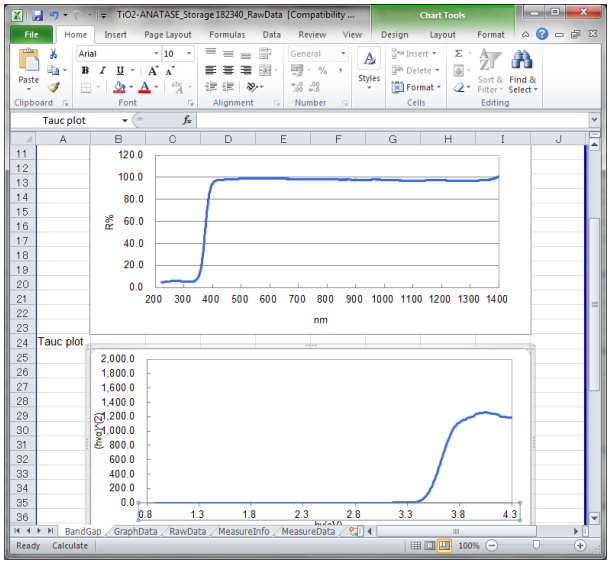

Fig. 5 Main Window

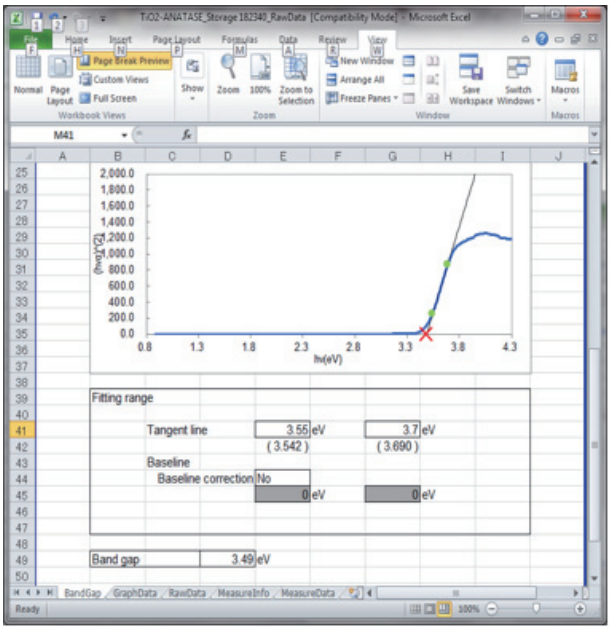

Fig. 6 Main Window (Band Gap Calculation)

Conclusion

A Tauc plot is typically used for determining the band gap of a sample, but the calculations used are both complex and time consuming. Using this software macro, band gap can easily be calculated by inserting the appropriate low and high energy values for specifying the tangent line.

1) Excel refers to Microsoft Excel, which is a registered trademark or trademark of Microsoft Corporation in the United States and other countries.

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