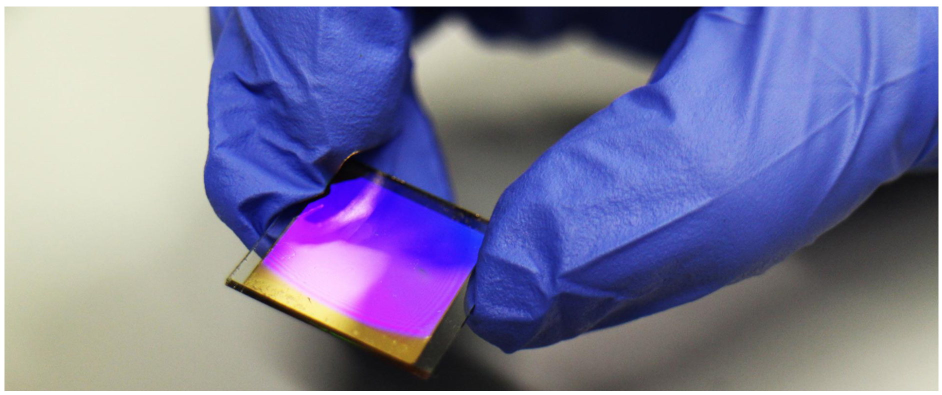
Application Note

Materials Testing & Research

Determination of Band Gap in Metal Oxides Using UV-Vis Spectroscopy



Authors

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Introduction

The band gap of semiconducting materials plays a critical role in shaping their performance across various electronic and optoelectronic applications. UV-Vis spectroscopy stands as an efficient method for evaluating these band gaps, providing insights into the electronic structure of materials. This understanding is pivotal in refining materials used in fields such as photocatalysis and solar energy conversion.[1]

UV-Vis spectroscopy measures the absorbance or reflectance of materials over a range of wavelengths. When the energy of incident photons matches or exceeds the band gap energy, electrons transition from the valence band to the conduction band, leading to distinctive absorption characteristics.

This application note investigates band gap analysis using UV-Vis spectroscopy, and presents a detailed methodology for precise and dependable measurements by leveraging the capabilities of the Agilent Cary 5000 UV-Vis-NIR spectrophotometer and Agilent Cary WinUV software.

Figure 1. Agilent Cary 5000 UV-Vis-NIR spectrophotometer.

Experimental

The Cary 5000 UV-Vis-NIR spectrophotometer was equipped with a Praying Mantis diffuse reflectance accessory (Harrick Scientific Products, Inc.), which is particularly useful for assessing the diffuse reflectance of small volumes of powders and pastes. The accessory uses two large hemispherical mirrors to gather light reflected from crystalline samples. Its small sample volume (as small as 0.03 mL) enables researchers developing new compounds to perform precise analyses. Diffuse reflectance measured using the Praying Mantis is relative to polytetrafluoroethylene reference material.

Additionally, high- and low-temperature reaction chambers can be integrated into the Praying Mantis during diffuse reflectance measurements. This versatility makes it ideal for material science analysis in academic and government research laboratories, as well as in inorganic chemistry and physics laboratories.

Figure 2. The Praying Mantis diffuse reflectance accessory.

The LockDown mechanism of the Cary 5000 UV-Vis-NIR facilitated rapid accessory changes and precise positioning, ensuring reproducible outcomes. Samples were prepared in duplicate, loaded into both the regular powder sample holder and the small cup powder sample holder, and subsequently inserted into the Cary 5000 UV-Vis-NIR for measurement. The samples used in this analysis included germanium dioxide (GeO_2), titanium dioxide (TiO_2), and zinc oxide (ZnO).

A wavelength scan ranging from 2,500 to 200 nm was executed using the Cary WinUV software, which is renowned for its robust analysis capabilities and advanced features for data transfer and report generation. The software's built-in calculator function was employed to derive the first derivative of the wavelength scans, streamlining the band gap analysis process.

Following the derivation of the wavelength scan, the peak of the derivative plot was identified. This peak serves as the determinant for the material's band gap value, which was then cross-referenced against established literature values and Tauc plot calculations to validate the accuracy and reliability of the measurement.

Results and discussion

Figures 3 to 5 present the reflectance spectra of GeO_2, TiO_2, and ZnO measured using large cups, and Figure 6 presents the reflectance spectra for TiO_2 using both small (0.03 mL) and large (0.25 mL) cups. The reflectance (%R) was plotted against the photon energy (eV). All three materials exhibited a significant drop in reflectance, corresponding to their band gaps, with minor differences between small and large cup measurements at the point of inflection.

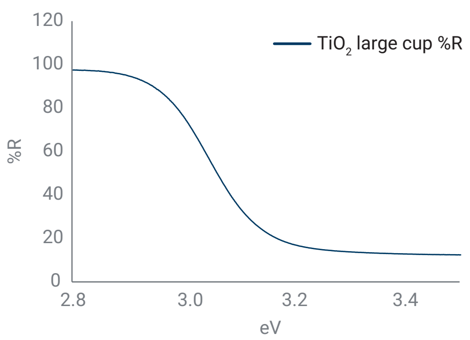

Figure 3. TiO_2 collection spectra.

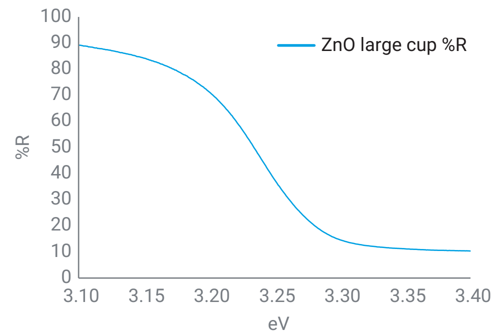

Figure 4. ZnO collection spectra.

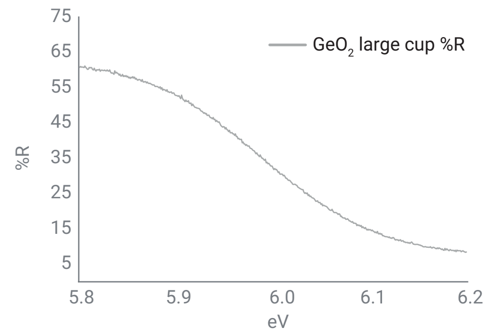

Figure 5. GeO_2 collection spectra.

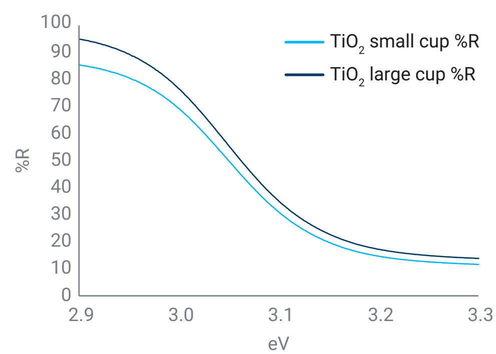

Figure 6. Small versus large cup.

To find the direct band gap of the material from diffuse reflectance spectra:[5]

– Calculate the Kubelka-Munk function, expressed as: $F(R) = (1 - R)^2/2R$, where R is the reflectance of the sample; e.g., 14% R, $F(R) = (1 - 0.14)^2/(2 \times (0.14)) = 2.641$
– Calculate $[F(R) \cdot hv]^2$, where hv is energy in eV; e.g., $[(2.641) \times 3.2]^2 = 71.445$
– Plot $[F(R) \cdot hv]^2$ versus hv
– Extrapolating the linear portion to $[F(R) \cdot hv]^2 = 0$ in that graph to obtain band gap energy

Figure 7 and 8 demonstrate the Tauc plot with manual extrapolation and linear regression methods.[5]

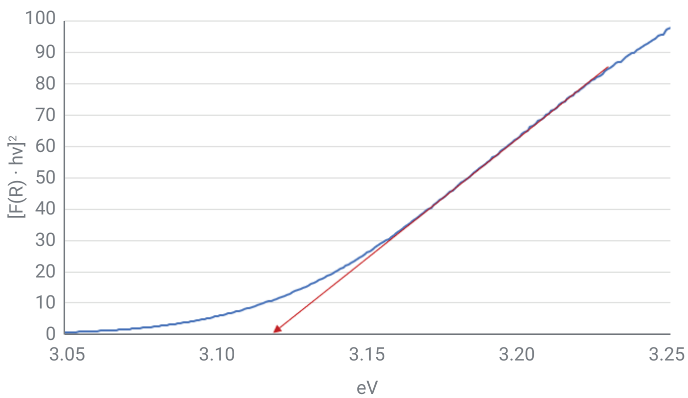

Figure 7. TiO_2 Tauc plot calculation with manual extrapolation.

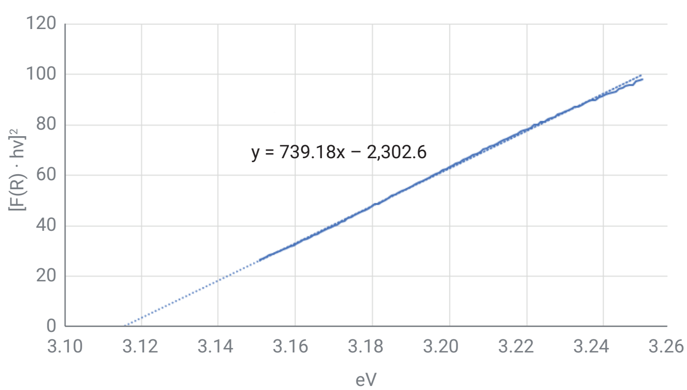

Figure 8. TiO_2 Tauc plot calculation with linear regression.

Using the initial reflection spectrum, the calculator function in the Cary WinUV software was used to obtain the first derivative of the spectrum and identify the value of its peak. This can be done by following these steps:

1. Click the calculator icon.
2. Select the desired trace.
3. Select the derivative option and click **Apply**.
4. Click the peak of the resulting spectra and apply a label.

The labeled peak of the derivative is equivalent to the band gap for the material.[2,5]

The values of the band gaps calculated using Cary WinUV software can be compared with known literature values and values derived from Tauc plot calculations (Table 1).

Table 1. Results comparison.

Sample	Cup Size	Manual Extrapolation (eV)	Linear Regression (eV)	First Derivative (eV)	Literature Values (eV)
GeO_2	Small	6.06	6.07	5.98	5.95[3]
	Large	6.07	6.07	5.99	
TiO_2 (Rutile)	Small	3.12	3.12	3.05	3.00[4]
	Large	3.12	3.11	3.05	
ZnO	Small	3.28	3.27	3.24	3.20[4]
	Large	3.27	3.26	3.24	

The manual extrapolation was a Tauc plot calculation, with the regression line fitted manually and the linear regression fitted using Microsoft Excel. All three calculations are valid methods for determining band gap.

The accuracy and reliability of band gap calculations using the Cary 5000 UV-Vis-NIR spectrophotometer and Cary WinUV software are demonstrated in Table 1. The band gap values calculated using all three methods were remarkably consistent with the literature values, displaying the precision of the instrument.

For GeO_2, the manual extrapolation, linear regression, and first derivative methods produced values of 5.98 to 6.07 eV, which closely match the literature value of 5.95 eV. Similarly, TiO_2 had a calculated band gap of 3.05 to 3.12 eV, and ZnO measured between 3.24 and 3.28 eV, aligning well with their respective literature values of 3.00 and 3.20 eV.

An important feature of the Praying Mantis is the ability to obtain reliable measurements using both small and large sample cups. The small cup measurements yielded band gap values that were almost identical to those obtained with large cups. For instance, the small cup measurement of approximately 2 mL of TiO_2 showed a band gap of 3.05 eV, which was almost identical to the large cup measurement of 3.05 eV. This consistency underscores the instrument's precision and flexibility, allowing users to achieve accurate results while conserving sample material.

Using the small cup not only preserves valuable resources but also reduces costs associated with sample preparation and analysis. This feature is particularly beneficial for laboratories and research institutions that work with materials that are expensive or limited in quantity. The ability to use smaller sample volumes without compromising measurement accuracy translates to significant cost savings and more efficient use of resources.

Conclusion

The findings of this study highlight the efficacy of using the Agilent Cary 5000 UV-Vis-NIR spectrophotometer combined with Agilent Cary WinUV software for accurate and reliable band gap analysis of semiconducting materials. The integration of the Praying Mantis diffuse reflectance accessory ensured reproducible sample positioning and measurements. The use of the first derivative of wavelength scans, facilitated by the software's built-in calculator function, proved to be a streamlined and precise method for determining band gaps. The band gap values obtained were consistent with established literature, confirming the validity of this approach. This methodology offers a robust and efficient tool for researchers working in fields such as photocatalysis and solar energy conversion, enabling precise characterization of electronic structures in various materials.

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Further Information

- Agilent High-Performance UV-Vis, Cary 5000 UV-Vis-NIR spectrophotometer
- Agilent Cary WinUV Software for UV-Vis-NIR Applications
- Agilent Cary UV-Vis Spectrophotometer Accessories
- Agilent Praying Mantis DRA for Cary UV-Vis-NIR Instruments
- UV-Vis Spectroscopy & Spectrophotometer FAQs

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