Studying the Radiative Properties of Ceria

Jingyang Zheng

Purpose and Objective

The purpose of this study was to measure the spectral radiative properties of ceria, estimate the extinction coefficient of the ceria, and calculate the solar weighted properties of the ceria. Through these calculations, the total amount of energy that is transmitted, reflected, and absorbed by the ceria in relation to the amount of solar energy transmitted through the atmosphere is determined. These radiative properties are important for modeling ceria in reactors implementing the ceria redox cycle. Solar weighted values are useful in heat transfer calculations—they provide valuable information for modeling the ceria as a gray or semi gray surface. By taking a total value, the system of equations used for heat transfer models is computationally simplified, allowing for more efficient computing. To calculate these values, the spectral transmittance and reflectance are measured using a spectrophotometer. Spectral and total extinction coefficients for the ceria are determined from the measured transmittance.

Measurement Approach

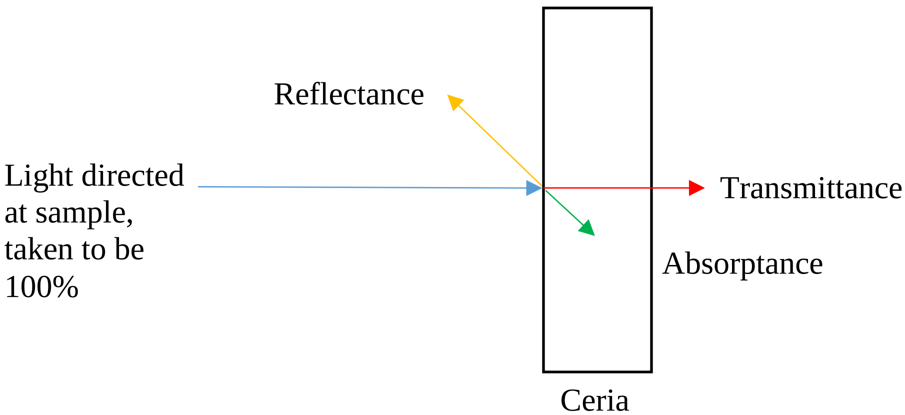

Figure 1. Visual representation of radiative properties.

As depicted in Figure 1, transmittance is the fraction of light passes through the sample, and reflectance is the fraction of light that is reflected by the sample. The spectral transmittance and reflectance of four samples of ceria were measured in the range of 250-2500nm at 5nm increments.

Three reticulated porous ceramic (RPC) ceria samples with a nominal pore density of 30ppi were characterized. The RPC samples had different thicknesses, which allowed an extinction coefficient to be calculated. Details of the samples are shown below, in Table 1.

Table 1. Details of each sample

Sample	Material	Dimensions	Mass	Pore Density	Porosity
1	RPC	$10\ mm \times 25\ mm \times 62.5\ mm$	15.2642 g	30 ppi	0.866
2	RPC	$12.5\ mm \times 25\ mm \times 62.5\ mm$	18.7857 g	30 ppi	0.867
3	RPC	$18.5\ mm \times 25\ mm \times 62.5\ mm$	27.4158 g	30 ppi	0.868
4	Fiber Board	$13\ mm \times 45\ mm \times 71\ mm$	36.1284 g		0.879

Figure 2. Samples 1, 2, and 3, 30ppi RPC ceria

Figure 3. Sample 4, the commercial fiber board

SEM images of the ceria are shown in Figures 4-6. The RPC samples were obtained from SELEE and the fiber board sample from Zircar Zirconia. The three different thicknesses of the 30ppi sample were cut from identical boards. The microstructure of the fiber board is different from that of the RPC. The fiber board consists of fibers averaging 5-8μm in diameter. The RPC has feature sizes on two different scales: small pores on the 10μm scale, and struts with a width on the 100μm scale. The fiber diameters, pore diameters, and strut diameters were determined through analysis of the SEM images using *ImageJ* software.

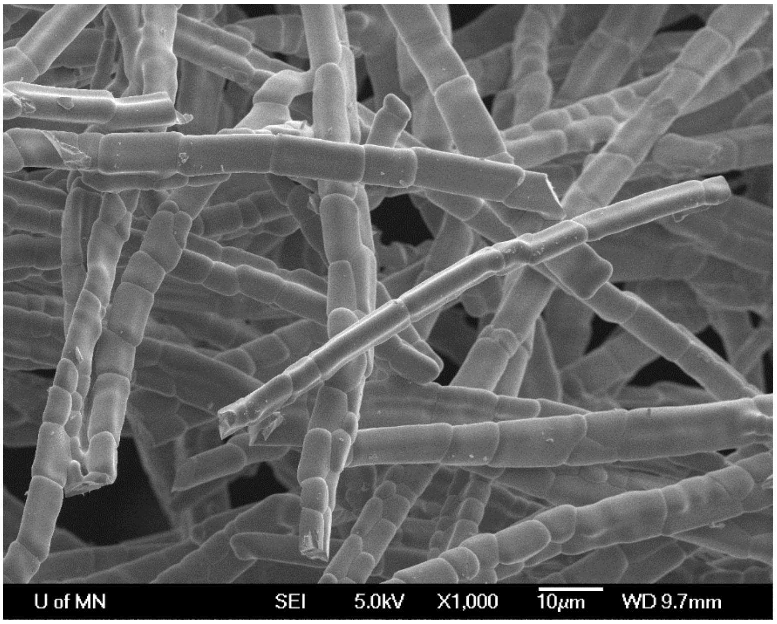

Figure 4. SEM of the fiber board. Width of the fibers ranges between 5-8μm.

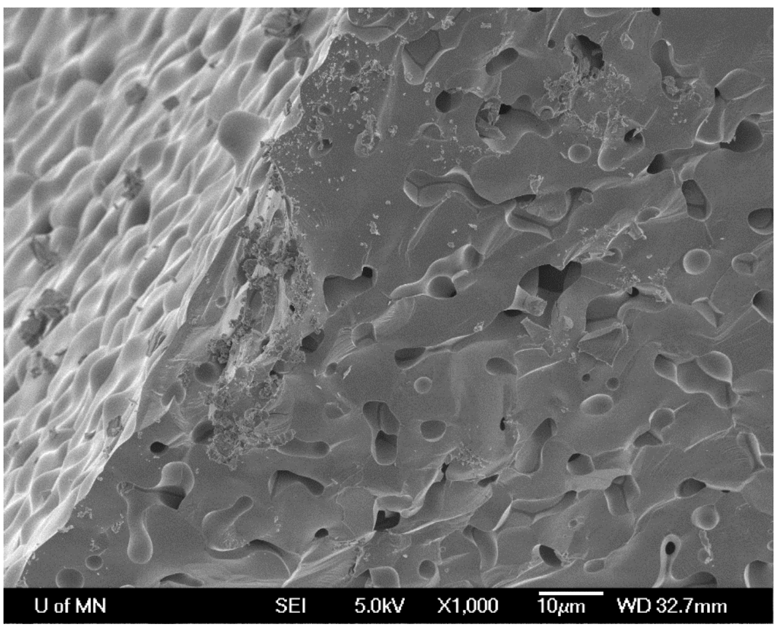

Figure 5. SEM of the RPC

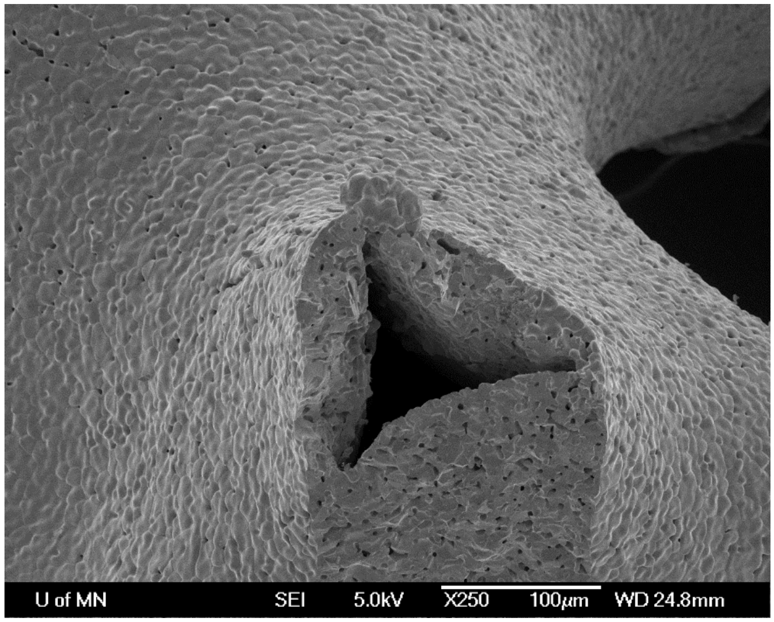

Figure 6. SEM of a strut of the RPC

The porosity of each sample was calculated using the theoretical density of ceria, ρ_{th}=7.22 g cm^{-3} (Mogensen). Using the measured dimensions and the measured mass, the ratio of void volume to total volume was obtained.

$$\phi = 1 - \frac{\frac{m}{lwh}}{\rho_{th}}$$

Measurement Technique

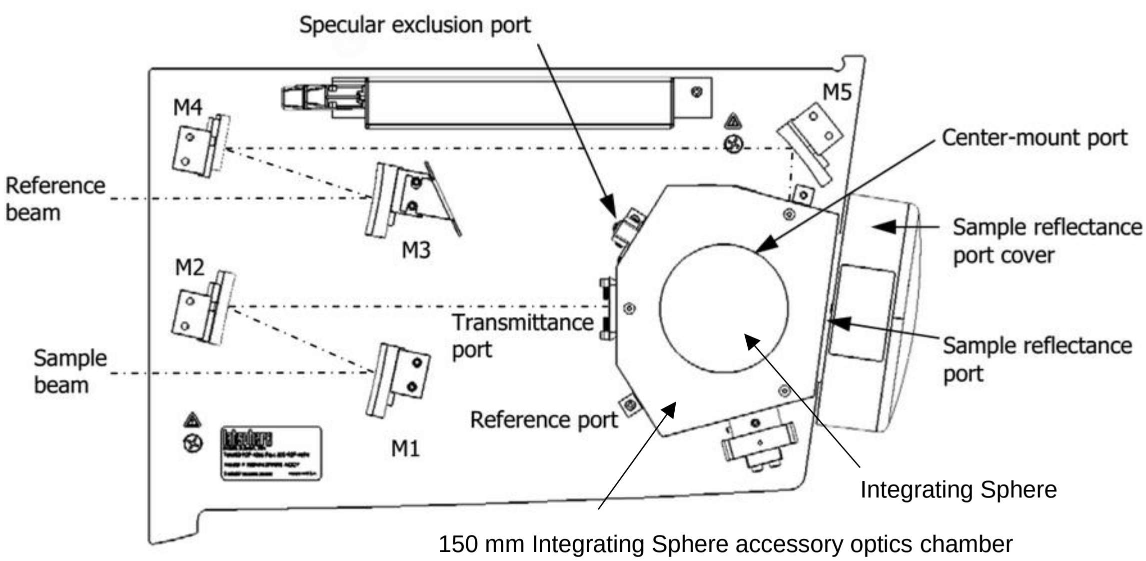

Figure 7. Top view of the spectrophotometer.

Measurements of T_λ and R_λ were taken with the spectrometer, shown schematically in Figure 7. Two ports are used in these measurements: the transmittance port, and the reflectance port. To measure transmittance, the sample is placed in the transmittance port, between the origin of the light beam and the integrating sphere. Any light that is transmitted through the sample enters the integrating sphere and ultimately reaches the detector. For the reflectance measurements, the beam passes through the integrating sphere, reaches the sample, and a portion of the light is reflected back into the integrating sphere, where it is sensed by the detector.

The spectrophotometer was calibrated before each group of transmittance or reflectance samples to be taken. For transmittance, the spectrophotometer first scans over all wavelengths with 100% T and 0% T reference beams, and for reflectance, 100% R and 0% R reference beams. For the 0% R reference beam measurement, the reflectance cover is taken off of the reflectance port, so that none of the light is reflected back to the integrating sphere. The rest of the measurements are taken with the reflectance cover on, and require no other adjustments to the setup.

The measurements were repeated seven times for each sample. In between measurements, the samples were removed and replaced within the spectrophotometer to quantify the uncertainty due to inhomogeneity of the material. Confidence intervals at 95% were calculated. Two scans were taken for each sample at each run through the spectrophotometer, to check for any irregularities in the scanning process. Upon inspection of the data, it could be seen that all of the runs had negligible differences in values between the two scans. The cycles were then averaged to obtain values used in the following calculations.

Absorptance

The average values for T_λ and R_λ that were measured were used to calculate an average absorptance, by Kirchhoff's Law

$$\%A = 100 - (\%T + \%R) \quad (1)$$

All of the light incident on the sample is either transmitted, reflected, or absorbed, so by taking the difference from 100%, the remaining light that is not passed through the material or reflected by it must be absorbed. However, due to the porous nature of the ceria samples used, there is the additional possibility that some of the light was scattered out of the sides of the sample.

Extinction Coefficient

The extinction coefficient β, which describes the relationship between thickness (ℓ) and transmittance within a participating medium, is estimated with the Beer-Lambert Law

$$T = \gamma e^{-\beta\ell} \quad (2)$$

where γ accounts for the possibility of surface reflection before the incident light enters the medium. The MATLAB curvefit tool was used to fit the transmittance measured for the three RPC samples under the assumption that γ=1 and again with γ as a fitting parameter.

Solar Weighting Calculations

The raw data for transmittance and reflectance is used to determine the solar weighted values of the radiative properties.

The values were determined by the following formulae:

$$T_{solar} = \frac{\int_0^\infty T_\lambda \, I_\lambda \, d\lambda}{\int_0^\infty I_\lambda \, d\lambda} \tag{6}$$

$$R_{solar} = \frac{\int_0^\infty R_\lambda \, I_\lambda \, d\lambda}{\int_0^\infty I \, d\lambda} \tag{7}$$

$$A_{solar} = \frac{\int_0^\infty A_\lambda \, I_\lambda \, d\lambda}{\int_0^\infty I_\lambda \, d\lambda} \tag{8}$$

$$\beta_{solar} = \frac{\int_0^\infty \beta_\lambda \, I_\lambda \, d\lambda}{\int_0^\infty I_\lambda \, d\lambda} \tag{9}$$

This gives the total fraction of energy transmitted, reflected, or absorbed by the ceria where the light source is the solar spectrum. The solar weighted properties are convenient because they capture spectral effects but simplify computations in comparison to exact and hand approximation approaches.

The solar weighting uses the data from the National Renewable Energy Laboratory's SMARTS database, of the beam normal circumsolar irradiance—the spectral intensity—to calculate the amount of energy that is transmitted, reflected, or absorbed.

SMARTS stands for Simple Model of the Atmospheric Radiative Transfer of Sunshine, developed by Dr. Christian Gueymard. The organizational data set for extraterrestrial radiation is maintained by NREL, upon which this model is based and computes clear sky spectral irradiances (including direct beam, circumsolar, hemispherical diffuse, and total on a tilted or horizontal receiver plane) for specified atmospheric conditions. The current version of SMARTS being used, SMARTS 2.9.2, is the basis for American Society of Testing and Materials (ASTM) reference spectra (ASTM G-173 and ASTM G-177) used for photovoltaic performance testing and materials degradation studies.

To account for varying angles of incidence, AM 1.5 was used for the standardized solar spectrum. Direct radiation at 90° is accounted for at AM 1. The algorithms used by SMARTS were developed to match the output from the MODTRAN complex band models within 2%. The algorithms are used in conjunction with files for atmospheric absorption of atmospheric components and spectral albedo functions. The spectral resolution is 0.5 nm for 280-400 nm, 1 nm for 400-1,750 nm, and 10 nm for 1,750-4,000 nm.

The spectral intensity, I_λ used in the solar weighting calculations was generated through compiling and running the FORTRAN source code—the algorithm accounts for the amount of irradiance that is removed from the solar spectrum by the various gases and pollution in the atmosphere. The SMARTS database provides many spectra, and the beam normal + circumsolar data was used for these calculations.

Measured Results

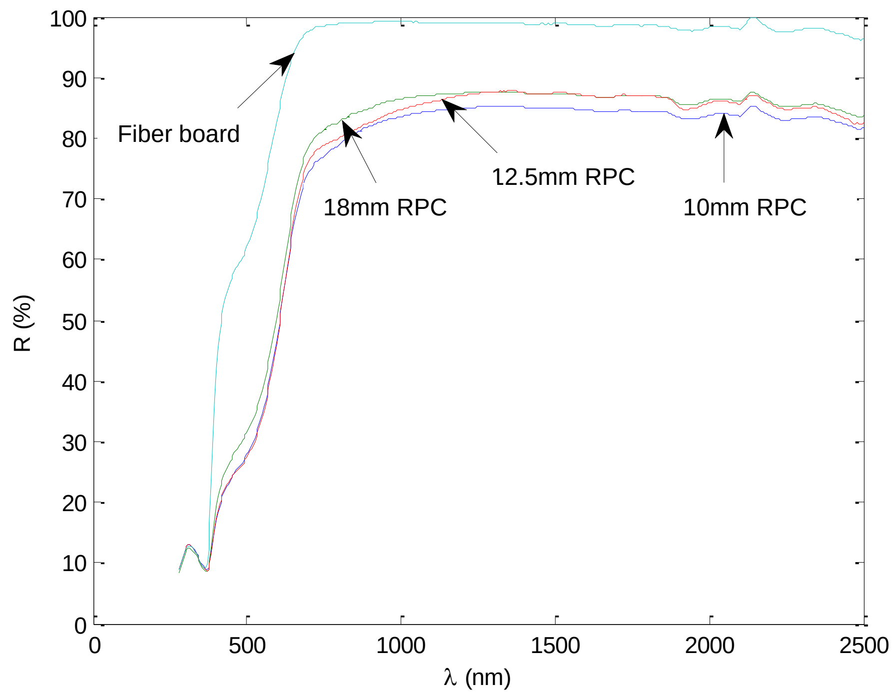

Figure 8. Reflectance as a function of wavelength

Average values of R_λ for each of the samples is shown in Figure 8. The three RPC samples exhibit remarkably similar reflectance, indicating that the reflectance can primarily be attributed to light interactions with ceria in the first 10 mm of the RPC samples. The reflectance of the RPC samples does show a small dependence on sample thickness, increasing slightly with increasing thickness. The fiber board sample (Sample 4) reflects a greater portion of the light because of the higher pore density and smaller feature sizes.

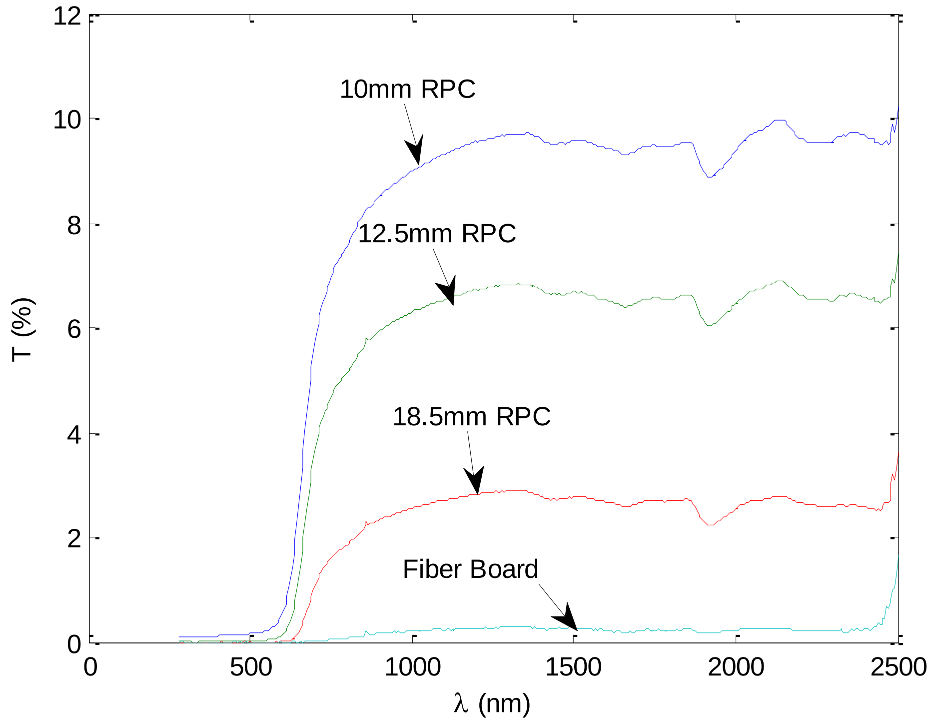

Figure 9. Transmittance as a function of wavelength (note that the scale for Transmittance is between 0% and 12% —this is used for clarity of the graph)

Average values of T_λ for each of the samples is shown in Figure 9. The three RPC samples, which differ only in thickness, have similarly shaped curves. As can be seen from the graph, Sample 1, the thinnest, transmitted the most light, and Sample 3, the thickest, transmitted the least light. This is to be expected, as the light experiences fewer interactions with the ceria, allowing more to be transmitted. The fiber board is less dense, but has much smaller pores and greater pore density, and transmitted a very small amount of light.

The greatest variance between the seven trials were seen in the thinner samples. This is potentially due to the thicker RPC sample and fiber board sample having more interactions with the light before it reaches the integrating sphere, because the sample structure is not perfectly uniform. In the thinner RPC samples, small differences in the number of interactions that the light has with the struts and the pores will have a larger impact on the transmittance and reflectance measured. The light directed at the sample is a beam with a small cross sectional area, and when the sample is taken out and replaced in the spectrophotometer, it is almost certain that the light will be penetrating a different portion of the sample, with potentially a slightly different structure. When the number of interactions that the light has with the ceria is higher, e.g. for the thicker RPC and fiber board samples, the data will be more uniform. The data for the thinner samples are much more susceptible to structure variations in the ceria.

The values given in Table 2 are averages of the seven measurement trials for each of samples 1-3 and three trials for sample 4. The deviation between the measurements of each trial of sample 4 were negligible, and thus more measurements were not taken.

Table 2. Solar Weighted Transmittance, Reflectance, and Absorptance for each sample

Sample	T_{solar}	R_{solar}	A_{solar}
RPC, 10 mm	5.1 ± 0.3%	63.9 ± 0.7%	31.0 ± 0.7%
RPC, 12.5 mm	3.4 ± 0.2%	65.3 ± 0.8%	31.3 ± 0.7%
RPC, 18 mm	1.3 ± 0.1%	64.5 ± 0.1%	33.8 ± 0.1%
Fiber Board	0.1 ± 0.1%	85.6 ± 0.1%	14.3 ± 0.1%

The values given in Table 3 are calculated solar extinction coefficients, averaged over the seven trials conducted for each of the RPC samples. Total extinction coefficients were calculated for the RPC samples. Two models are presented below, based on the volume-independent multiplying factor α.

Table 3. Total extinction coefficients for 30 PPI ceria RPC

	β_{solar}	γ
Model 1	0.049 ± 0.002 mm^{-1}	1
Model 2	0.031 ± 0.001 mm^{-1}	0.271

The results for the extinction coefficient given by the models shown in the above calculations section are graphed in Figures 10 and 11, accounting for the solar spectrum, to give two models of the spectral extinction coefficient.

Comparing the two extinction coefficients derived from the different curvefit models, it can be seen that with the additional multiplying factor, the extinction coefficient drops significantly, from $\beta = 0.2881\ mm^{-1}$ to $\beta = 0.1663\ mm^{-1}$. This suggests that there may be an initial surface interaction between the light and the ceria, and that a certain portion of the light is reflected without regards to the volumetric portion of the extinction coefficient model.

In the initial model, seen below in Figure 10, $\beta = 0.2881\ mm^{-1}$, 95% confidence bounds at $\beta = 0.2801$ and $\beta = 0.2961$, had the R-squared value at 0.8073. Looking at the limits,

$$T = e^{-0.2881\ell} \tag{10}$$

we can see that an infinitesimally small thickness would allow for a transmittance of 100%, which makes logical sense. A thickness that approaches infinity would amount to a transmittance of 0%, also supporting the model's limits when looking at a one-factor extinction coefficient.

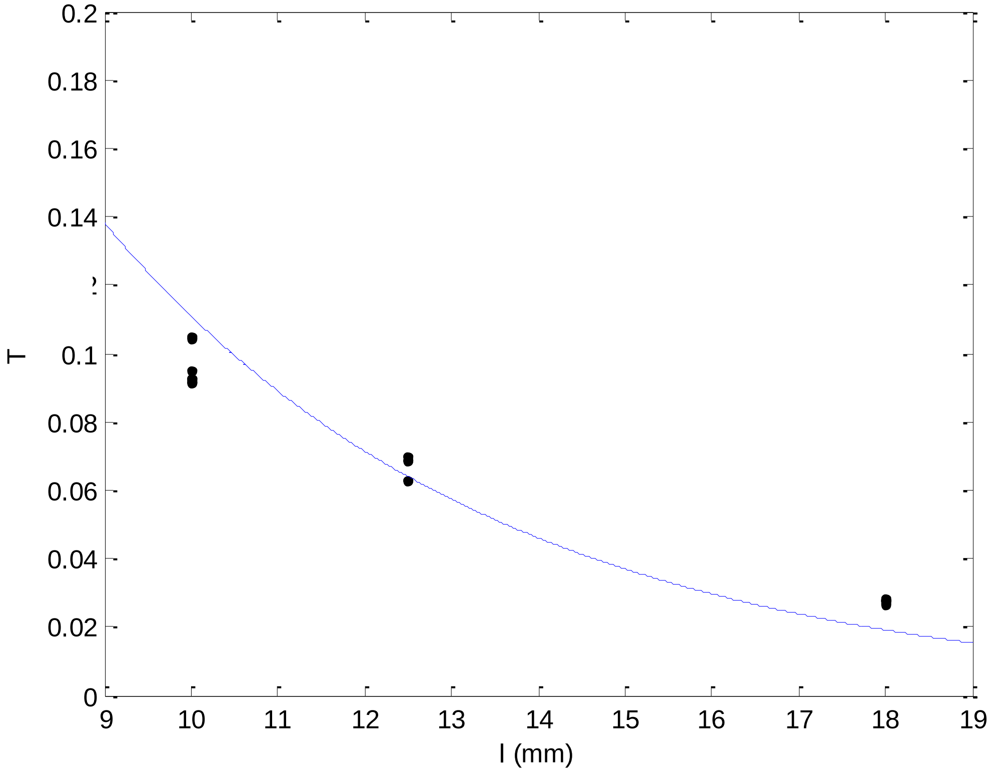

Figure 10. Exponential Fit of Extinction Coefficient

In the second curve fit, $\beta = 0.1663\,mm^{-1}$, with 95% confidence bounds at $\beta = 0.1509\ mm^{-1}$ and $\beta = 0.1816\ mm^{-1}$. $\gamma = 0.2707$, and with 95% confidence bounds of $\gamma = 0.2244$, $\delta = 0.3170$. This fit gives an R-squared value of $R = 0.9799$, which demonstrates that this fit is statistically better adjusted for the data. The plot is shown below, in Figure 11. However, when looking at the secondary model,

$$T = 0.2707e^{-0.1663\ell} \tag{11}$$

and observing the limits, we can see that an infinitesimally small thickness would account for a transmittance of 22.44%, meaning that there is a volume-independent factor that causes the absorptance and reflectance of 77.54%, thus making the maximum transmittance possible 22.44%. At the other limit, an infinitely large thickness would also case a transmittance of 0%. Thus, the two-factor extinction coefficient consists of two interactions—an initial surface interaction, as well as a volumetric interaction of the ceria with light.

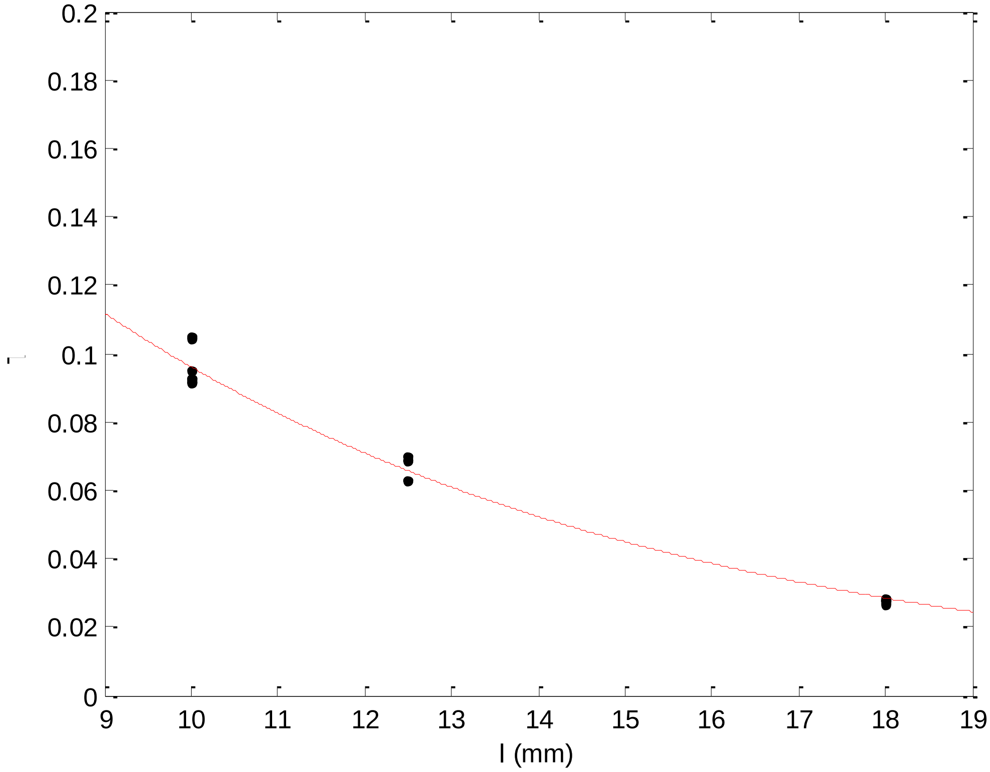

Figure 11. Exponential Fit of Extinction Coefficient with Additional γ Factor

Figure 12 below shows the spectral extinction coefficient as a function of wavelength, calculated from derived volume-independent γ factor. The extinction coefficient for the initial model without the γ factor is higher, because it does not account for any initial surface interactions. The spectral extinction coefficient stays relatively constant at wavelengths above 1000 nm, and experiences some variation at wavelengths below 1000 nm, a result obtained from the solar spectrum.

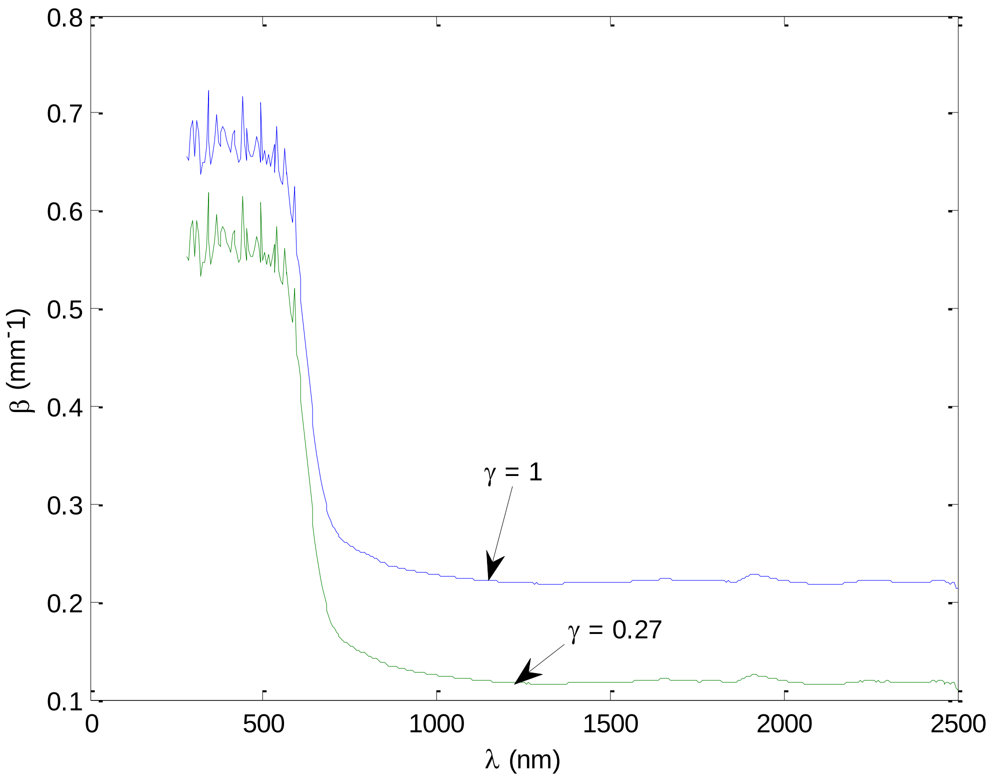

Figure 12. Spectral Extinction Coefficient of the two models

Conclusions

The purpose of these calculations was to determine the solar weighted values of the radiative properties. Measurements taken on the spectrophotometer allowed for the determination of these values. Reflectance and transmittance of four samples of ceria were measured with a spectrophotometer. Using these values, absorptance and the extinction coefficient were calculated. With the use of the SMARTS solar spectrum, total solar radiative properties were also calculated. As can be seen from Table 2, thicker samples have lower values for solar-weighted transmittance and higher values for solar-weighted reflectance than thinner samples. The RPC samples all exhibited similar spectral variations in transmittance and reflectance.

Data from the solar spectrum was used to model the extinction coefficient of the RPC ceria. The extinction coefficient was estimated using two models, one based on Beer-Lambert's Law, and the other containing a pre-exponential volume independent factor. The model was fitted with the extinction coefficient of each of the thicknesses and used in the determination of a spectral extinction coefficient.

Bibliography

Gueymard, C.A. Parameterized Transmittance Model for Direct Beam and Circumsolar Spectral Irradiance. *Solar Energy* **2001**, 325-346.

Gueymard, C.A. SMARTS, A Simple Model of the Atmospheric Radiative Transfer of Sunshine: Algorithms and Performance Assessment. Technical Report No. FSEC-PF-270-95. **1995**, Cocoa, FL: Florida Solar Energy Center.

Gueymard, C.A.; Kambezidis, H.D.; Muneer, T., *Solar Spectral Radiation; Chapter 5. Solar Radiation and Daylight Models*, 3rd ed.; Oxford: Elsevier Butterworth-Heinemann, 2005; pp 221-301.

Mogensen, M.; Sammes, N. M.; Tompsett, G. A. **2000**, *129*, 63–94.