SPECTRAL RADIATIVE PROPERTIES OF THREE-DIMENSIONALLY ORDERED MACROPOROUS CERIA PARTICLES

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ABSTRACT. Radiative properties of spherical heterogeneous particles consisting of three-dimensionally ordered macroporous (3DOM) cerium dioxide (ceria) are numerically predicted in the spectral range 0.3–10 µm. The particles are 1 µm in diameter, with interconnected pores of diameter 330 nm and a face-centered cubic lattice arrangement. Predictions are obtained by solving macroscopic Maxwell’s equations using the discrete dipole approximation and the finite element method as a complementary means of numerical prediction. The scattering and absorption efficiency factors as well as the asymmetry factor are determined as a function of the particle orientation relative to the direction of the incident plane wave. The scattering and absorption efficiency factors show significant dependence on the particle orientation in the spectral range equal to particle diameter to 560 nm. Compared to homogeneous ceria particles, 3DOM particles of identical size tend to cancel the wave extinction for wavelength greater than 560 nm. Approximating the 3DOM particles as a homogeneous sphere with properties calculated from an effective medium theory is also considered. This approach is shown to be valid only for wavelengths much greater than the pore size, demonstrating that a detailed geometrical representation of the internal particle structure is essential to obtain accurate radiative characteristics of nano-structured particles.

NOMENCLATURE

\( a_p \) lattice parameter, m
\( A \) dipole moment coefficient matrix
\( d \) dipole lattice parameter, m
\( D_p \) pore diameter, m
\( \mathbf{E} \) electric field, N C\(^{-1}\)
\( g \) asymmetry factor
\( \mathbf{H} \) magnetic field, A m\(^{-1}\)
\( k \) complex component of refractive index
\( m \) complex refractive index
\( n \) real component of refractive index
\( Q \) efficiency factor
\( p \) porosity
\( \mathbf{P} \) dipole moment vector, A m\(^{-1}\)
\( r_p \) particle radius, m
\( r \) location in space, m
\( \mathbf{S} \) time-averaged Poynting vector, W m\(^{-2}\)
\( V \) integration volume, m\(^3\)

Greek symbols

\( \alpha \) polarizability
\( \Gamma \) integration surface, m\(^2\)
\( \epsilon \) permittivity, F m\(^{-1}\)
\( \eta \) wavenumber, m\(^{-1}\)
\( \theta \) particle orientation angle
\( \lambda \) wavelength, m
\( \sigma \) electrical conductivity, S m\(^{-1}\)
\( \phi \) particle orientation angle
\( \omega \) angular frequency
\( \Omega \) solid angle, sr

Subscripts and superscripts

abs absorption
eff effective
ext extinction
inc incident
rel relative
sca scattering
tot total
0 vacuum

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INTRODUCTION

Cerium dioxide (ceria) has been proposed as a novel reactive material to realize solar-driven thermochemical cycles to split water and carbon dioxide for production of hydrogen and carbon monoxide [1–4]. Ceria forms oxygen vacancies in its lattice structure in response to changes in physical conditions, such as temperature and oxygen partial pressure, making the material suitable for non-stoichiometric redox chemical reactions. Three-dimensionally ordered macroporous (3DOM) ceria structures offer high porosity and specific surface area due to their nano-porous structure. Faster chemical kinetics was observed for packed beds of 3DOM structures in comparison to the kinetics measured for sintered ceria structures [5]. Synthesis techniques have resulted in improved structural stability, as well as retention of the 3DOM structure when the material undergoes thermochemical cycling making the 3DOM structure more desirable than conventional micro-structured porous ceramics [6]. Radiative properties are needed to determine medium temperature and the reaction rates. The characteristics of the reactive medium, which can be tailored by modifying medium morphology and composition, should simultaneously allow for (i) efficient absorption of incident concentrated solar radiation, (ii) rapid heat transfer between the absorption and reaction sites, (iii) confinement of the emitted thermal radiation in the close vicinity of the reaction site, (iv) minimum heat losses from the reacting medium by conduction and convection, and (v) rapid chemical reaction. High specific surface area and porosity as well as varying levels of semi-transparency in the visible and infrared spectral ranges are a desired combination of morphological and optical characteristics to satisfy the above criteria for optimizing reactive media for solar thermochemical applications.

Previous pertinent studies of radiative characteristics of ceria ceramics and packed beds are given in [7–11]. Overall transmittance of ceria with average porosities of 0.08 and 0.72 were experimentally found in [7] for the spectral range 0.3–1.1 μm. Both samples were found to be highly opaque up to 400 nm. Using the same materials for the spectral range 0.9–1.7 μm, it was found in [8] that the mean radiation penetration length is shorter in higher porosity samples suggesting higher scattering. Using the Monte Carlo ray tracing technique along with experimental transmittance data, the transport scattering coefficient of porous ceria was obtained in [11] and found to be in agreement with theoretical estimates based on Mie theory.

Heterogeneous particles as well as their groups were radiatively characterized in the studies [12–16]. Of particular interest to solar thermochemical applications are the effects of internal particle structure on macroscopic radiative characteristics. The effect of porosity on absorption characteristics was previously studied in [12] using the discrete dipole approximation (DDA) for spherical composite particles. It was found that a shift in the inclusion volume fraction corresponded to a shift in the absorption peak of the particle. Results obtained using the DDA for composite particles were in good agreement with observed interstellar extinction efficiency factors [13]. Also using the DDA, Voschinnikov et al. [14] concluded that porosity of particles has only a slight effect on optical properties for porosities less than 0.5. The use of an effective medium theory with exact solutions on approximate geometry, such as the Lorenz–Mie theory, to reproduce scattering characteristics obtained with the DDA as well as the finite element method (FEM) was examined in [15–17]. It was concluded in [15] that effective medium theories agree well with numerical methods directly discretizing the geometry for a wide range of porosities and particle size parameters as long as the effective medium theory assumptions are upheld: statistical uniformity and small inclusions compared to wavelength. Porosities up to 90% were found to be accurately modeled when the inclusions are in the Rayleigh limit [17].

In the present paper, radiative properties of 3DOM ceria particles are studied in the spectral range 0.29–10 μm for particles with a diameter of 1 μm. The DDA is employed to compute
the radiative properties in the entire spectral range for four particle orientations. Orientation-averaged values are computed for 25 particle orientations in the spectral range 0.38–0.8 \( \mu \text{m} \). The FEM is also applied to solve macroscopic Maxwell’s equations to provide a reference numerical solution, particularly where DDA has been shown to be inaccurate. The FEM/DDA results are compared to those obtained using the Lorenz–Mie in conjunction with effective medium theories.

**PROBLEM STATEMENT**

3DOM ceria structure consists of a face-centered cubic (FCC) lattice of overlapping pores in a continuous matrix of cerium dioxide as shown in Figure 1. This geometry can be described by two parameters, the lattice constant \( a_p \) and the pore diameter \( D_p \), as shown in Figure 2. In this study, we consider a 3DOM structure with \( a_p = 440 \text{ nm} \) and \( D_p = 330 \text{ nm} \), for which the width of the interconnecting struts is approximately 90 nm and the porosity is \( p = 0.85 \). We consider an idealization of the non-uniform particle morphology seen in Figure 1b. This study examines a single particle of 3DOM ceria under the following assumptions: (i) the particle is spherical with a diameter of 1 \( \mu \text{m} \) with a uniform pore structure (ii) the pores are vacuous (iii) the electromagnetic behavior is sufficiently described by a continuous complex index of refraction,
Table 1: Particle orientations considered in this study. Cases 1, 3, and 4 represent a plane wave traveling along a major symmetry plane of the lattice resulting in transparent windows in the particle.

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ</td>
<td>0</td>
<td>22.5</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>φ</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>45</td>
</tr>
</tbody>
</table>

$m = n - ik$. Since ceria is non-magnetic and the smallest feature size of the structure is greater than 10 nm, the last assumption should be valid [18].

An interesting aspect of optical characterization of highly-ordered nano-structured materials is the potentially strong dependence of properties on particle orientation due to the anisotropy of the pore arrangement. Such dependence is expected to be most pronounced for orientations corresponding to transparent windows in the direction of electromagnetic wave propagation. The windows exist along the major symmetry planes of the FCC lattice. In this work, the particle orientation with respect to a fixed reference frame is described by two angles $\theta$ and $\phi$ shown in Figure 2. $\theta$ is the angle between the particle main axis $\hat{\zeta}$ and the $x$ axis of the fixed reference. $\phi$ is the rotation angle of the $\hat{\zeta}$ axis around $x$ axis, which is taken equal to the incident wavevector direction. Particle orientations considered for the full 0.29–10 $\mu$m spectral range considered in this study are given in Table 1.

The complex refractive index of ceria at 950°C is taken from Patsalas et al. [19] for the spectral range 0.29–1.5 $\mu$m. It is observed from this data that ceria is non-absorbing in the near to far infrared spectral ranges, and strongly absorbing for wavelengths less than $\lambda \approx 700$ nm. The real part of the complex refractive index is wavelength independent in the near to far infrared range. This is consistent with numerous experimental data reported for ceria such as in [20, 21].

**GOVERNING EQUATIONS**

The electromagnetic theory is applied. Assuming linear constitutive models, and the relative permeability equal to unity, Maxwell’s equations are given as

\[ \nabla \times \nabla \times \mathbf{E} - \eta_0^2 m^2 \mathbf{E} = 0 \]  
\[ \nabla \times \nabla \times \mathbf{H} - \eta_0^2 m^2 \mathbf{H} = 0 \]

where $\mathbf{E}$ and $\mathbf{H}$ are complex-valued electric and magnetic field vectors, respectively, and $\eta_0$ is the vacuum wave number. The complex refractive index is given by $m^2 = (n - ik)^2 = \epsilon_{\text{rel}} - \sigma/\omega \epsilon_0$, where $\epsilon_{\text{rel}}$ is the relative permittivity of the material, $\omega$ is the angular frequency of radiation, $\sigma$ is the electrical conductivity of the material, and $\epsilon_0$ is the vacuum permittivity. We assume a time-harmonic (or quasi-steady) field of constant frequency such that $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) \exp(i \omega t)$. At an interface between two materials, indicated by subscripts 1 and 2, boundary conditions enforce the normal and tangential components of the fields to be equal.

\[ \mathbf{n} \times (\mathbf{E}_1 - \mathbf{E}_2) = 0 \]  
\[ \mathbf{n} \cdot (\mathbf{E}_1 - \mathbf{E}_2) = 0 \]  
\[ \mathbf{n} \times (\mathbf{H}_1 - \mathbf{H}_2) = 0 \]  
\[ \mathbf{n} \cdot (\mathbf{H}_1 - \mathbf{H}_2) = 0 \]

where we have assumed the surface charge density and surface current density are zero. Ra-
The diative properties of the particle will be related to the time-averaged Poynting vector given by

\[ \mathbf{S} = \frac{1}{2} (\mathbf{E} \times \mathbf{H}^*) \]  

(7)

where \( \mathbf{H}^* \) is the complex conjugate of the magnetic field. Equation (7) represents the time-averaged flux of electromagnetic energy in \( \text{W m}^{-2} \). The domain is excited by a plane wave propagating in the \( x \)-direction with the electric field only having a \( z \)-component (perpendicularly polarized) given by

\[ \mathbf{E} = E_z \hat{z} \exp(-\eta_0 i x) \]  

(8)

where \( E_z \) and \( \hat{z} \) are the electric field component and the unit vector in the \( z \)-direction, respectively.

**SOLUTION METHODS**

The DDA and FEM are used to solve Maxwell’s equations, (1)–(2), and accurately account for the complex 3DOM structure of the ceria particle. The DDA is known to produce inaccurate results for scattering targets with large \(|m|\) as shown in the work of Yurkin et. al [22]. Ceria reaches a maximum \(|m| \approx 3.4\) in the spectral range considered in the present study, resulting in an anticipated relative error in \( Q_{\text{ext}} \) as high as 105%. Therefore, We employ the FEM to provide a complementary solution. Given the expense and complexity associated with the DDA and FEM solutions, we also consider the approximation of 3DOM ceria particles as homogeneous spheres, with effective properties given by volume averaging theory, and apply Lorenz–Mie theory as a computationally inexpensive approach to obtaining radiative properties of the 3DOM ceria particle. Details on each numerical method and expressions used to recover spectral radiative properties are given in the following text.

**Discrete dipole approximation** The DDA can be viewed as discrete solution method of the integral form of Maxwell’s equations. More precisely, the DDA subdivides the target into cubic sub-volumes and models each sub-volume as a dipole point. The points acquire dipole moments in response to the local electric field. They interact with each other through the electric fields. As for all discrete approaches of a continuum problem, the accuracy of the DDA depends on the choice of the discretization. The smaller the dipole spacing, the more accurate the results. The DDA is attractive due to its ability to easily handle non-homogeneous and anisotropic targets of arbitrary geometry. The method faces computational limits in the presence of targets with large relative refractive index, size, and/or irregular boundaries.

Several implementations of the DDA exist as reviewed by Penttilä et al. [23]. DDSCAT [24–26] and ADDA [22] are popular open-source programs. In this work, DDSCAT is employed since it has been demonstrated to be more accurate than ADDA even though it is computationally more expensive than the latter [23]. Moreover, DDSCAT is highly portable and modifiable, able to automatically generate a number of standard target shapes, and offers the option of supplying a list of occupied lattice sites to describe any desired target geometry, making it attractive for non-homogeneous targets. The inputs to DDSCAT are the list of dipole locations and the refractive index \( n_j - i k_j \) for each dipole \( j \), \( j = 1 \) to \( N \), as well as the parameters for controlling convergence, the target orientation or the incident wave direction, and the desired output data such as the Mueller scattering matrix components.

A spherical particle consisting of dipoles arranged in a cubic lattice of parameter \( d \) is generated first. Next, a cubic arrangement of spherical pores in the FCC lattice is obtained. The size of the cube is taken larger than the particle diameter to locate one of the pores at the basis of the FCC lattice at the center of the particle to ensure symmetry of the porous structure. The resulting dipole representation of the 3DOM ceria particle can be seen in Figure 3.
The validity condition of the DDA (but not its accuracy) is now established. The discrete dipole spacing should be small as compared to any structural length in the target geometry, and the radiation wavelength $\lambda$ [25]. These criteria are satisfied if

$$|m|\eta d < 0.5$$

where $m$ is the relative complex refractive index of the target material with respect to the host medium. The dipole spacing is then obtained as the minimum in the entire spectral range considered in this study,

$$d < \frac{1}{2 \max(|m|\eta)}$$

For ceria as the target material and air as the host medium, the dipole spacing is selected as $d = 0.008\,\mu m$, resulting in 125 discrete dipoles along the particle diameter.

By substituting the continuum target as a finite array of $N$ dipoles, each one is located at position $\vec{r}_j$ where $j \in \{1, 2, 3, ..., N\}$, the solution to a scattering problem can be found by solving the local electric field $\vec{E}_j$ for each dipole $j$ [24]:

$$\vec{E}_j = \vec{E}_{\text{inc},j} + \sum_{m \neq j} \vec{E}_m$$

where $\vec{E}_{\text{inc},j}$ is the incident electric field vector on the dipole $j$. The quantity $\vec{E}_m = -A_{jm}\vec{P}_m$ is the electric field vector from the dipole $m$, in which $\vec{P}_m$ is the dipole moment vector and $A_{jm}$ is a $3 \times 3$ complex symmetric matrix constituted of the wavenumber $\eta = 2\pi/\lambda$ and the space vector separating the dipoles $j$ and $m$, namely $\vec{r}_{jm} = \vec{r}_j - \vec{r}_m$. It can be shown that the solution to the scattering problem is reduced to solving a system of $3N$ complex linear equations with $3N$ unknown dipole moments [24]:

$$\sum_{m=1}^{N} A_{jm}\vec{P}_m = \vec{E}_{\text{inc},j}$$

Once Eq. (12) is solved, the calculation of complete scattering quantities is straightforward.
Figure 4: FEM geometrical representation of the model 3DOM ceria particle for (a) $\theta = 0$ and $\phi = 0$, (b) $\theta = 22.5$ and $\phi = 0$, (c) $\theta = 45$ and $\phi = 0$, and (d) $\theta = 45$ and $\phi = 45$.

The extinction, absorption and scattering cross sections are obtained from:

$$Q_{\text{ext}} = \frac{4\eta}{E_{\text{inc}}^{2}r_{p}^{2}} \sum_{j=1}^{N} \text{Im}(E_{\text{inc},j}^{*}P_{j})$$  \hspace{1cm} (13)

$$Q_{\text{abs}} = \frac{4\eta}{E_{\text{inc}}^{2}r_{p}^{2}} \sum_{j=1}^{N} \left\{ \text{Im}[P_{j}(\alpha_{j}^{-1})^{*}P_{j}^{*}] - \frac{2}{3}k_{0}P_{j}^{2} \right\}$$  \hspace{1cm} (14)

and

$$Q_{\text{sca}} = \frac{\eta^{4}}{E_{\text{inc}}^{2}r_{p}^{2}} \int_{4\pi} d\Omega \left| \sum_{j} \left[ \hat{P}_{j} - \hat{n}(\hat{n} \cdot \hat{P}_{j}) \right] \exp(-i\eta \hat{n} \cdot \hat{r}_{j}) \right|^{2}$$ \hspace{1cm} (15)

where $E_{\text{inc}}$ is the amplitude of the incident electric field, $\alpha_{j}$ is the polarizability of the dipole $j$, and the integration takes place over the solid angle $d\Omega$ corresponding to the unit vector $\hat{n}$. Finally, the asymmetry parameter can be recovered by

$$g = \frac{\eta^{4}}{E_{\text{inc}}^{2}Q_{\text{sca}}r_{p}^{2}} \int_{4\pi} \hat{n} \cdot \hat{x} \left| \sum_{j} \left[ \hat{P}_{j} - \hat{n}(\hat{n} \cdot \hat{P}_{j}) \right] \exp(-i\eta \hat{n} \cdot \hat{r}_{j}) \right|^{2} d\Omega$$ \hspace{1cm} (16)

where we have $\hat{x}$ since the incident plane wave is in the $x$-direction.

**Finite element method** The FEM is a powerful and general method of solving partial differential equations. Unlike DDA, FEM has no limitation to material parameters. The method is based on the spatial decomposition of the solution domain into small finite elements, allowing for precise geometry representation through computer-aided drafting software. FEM geometrical representations of the model 3DOM ceria particle is shown in Figure 4.

For this study, we have employed a commercially available FEM package, COMSOL 4.3. FEM can be computationally very expensive in the case of optical studies. Around 6 elements per wavelength in each spatial direction is recommended to properly resolve the wave solution [28].

The application of the non-reflecting, absorbing boundary conditions is important to the accuracy of electromagnetic scattering calculations. The perfectly matched layer (PML) approach, developed by Berenger [29], allows for the convenient geometry representation and conservation of matrix sparsity in the finite element paradigm making it the proper choice for the proposed study. The perfectly matched layer introduces a layer of elements around the domain under study. The layer was chosen to be 5–6 elements across as recommended in [30]. In addition to implementing a spherical PML, we have applied a simple first-order absorbing condition [28].
given by
\[ \mathbf{n} \times \left[ \nabla \times \left( \mathbf{E}_{\text{tot}} + \mathbf{E}_{\text{inc}} \right) \right] - i \eta_0 \mathbf{n} \times \left( \mathbf{E}_{\text{tot}} \times \mathbf{n} \right) = 0 \]  
(17)

This condition perfectly absorbs waves at normal incidence making the PML more effective.

In order to introduce an incident plane wave with a desired wavelength into the numerical model with the existence of this artificial layer, the field variables are split into relative and incident fields [28],
\[ \mathbf{E}_{\text{tot}} = \mathbf{E}_{\text{rel}} + \mathbf{E}_{\text{inc}} \]  
(18)

where \( \mathbf{E}_{\text{tot}} \) is the total electric field, \( \mathbf{E}_{\text{inc}} \) is the incident plane wave propagating through a medium without scatterers, and \( \mathbf{E}_{\text{rel}} \) is the electric field resulting from interactions with scatterers. Using the split field formulation, (18), the radiative properties are obtained in terms of the relative and total fields. The absorption efficiency factor is calculated by volume-integrating over a sphere encompassing the 3DOM ceria particle,
\[ Q_{\text{abs}} = \frac{1}{S_{\text{inc}} \pi r_p^2} \int_V \sigma E_{\text{tot}}^2 \, dV \]  
(19)

where \( \sigma \) is the electrical conductivity of ceria and \( S_{\text{inc}} \) is the magnitude of the Poynting vector of the incident radiation given by \( S_{\text{inc}} = \sqrt{\epsilon_0 / \mu_0} E_0 / 2 \).

The scattering efficiency factor is calculated by integrating over the surface of a sphere containing the particle,
\[ Q_{\text{sca}} = \frac{1}{S_{\text{inc}} \pi r_p^2} \int_{\Gamma} \mathbf{S}_{\text{rel}} \cdot \mathbf{n} \, d\Gamma \]  
(20)

Since the PML is known to be a poor absorber of evanescent waves [31], the radius of the integration sphere is chosen to be a wavelength larger than the radius of the model particle. The extinction efficiency factor is then obtained from
\[ Q_{\text{ext}} = Q_{\text{abs}} + Q_{\text{sca}} \]  
(21)

The asymmetry factor is calculated by
\[ g = \frac{\int_{\Gamma} \mathbf{S}_{\text{rel}} \cdot \mathbf{n} (\mathbf{n} \cdot \hat{x}) \, d\Gamma}{\int_{\Gamma} \mathbf{S}_{\text{rel}} \cdot \mathbf{n} \, d\Gamma} \]  
(22)

where the surface integral is now defined to be in the far-field zone of the scatterer.

**Lorenz-Mie theory** Lorenz-Mie theory is an exact analytical solution to Maxwell’s equations for the problem of a homogeneous sphere in a non-absorbing background subject to an impinging plane wave. The solution depends on the particle radius, wavelength of incident radiation, and the complex index of refraction of the particle and background. For the properties under study in this exposition, the expressions are given by [32],
\[ Q_{\text{sca}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \left( |a_n|^2 + |b_n|^2 \right) \]  
(23)

\[ Q_{\text{ext}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \Re(a_n + b_n) \]  
(24)

\[ Q_{\text{abs}} = Q_{\text{ext}} - Q_{\text{sca}} \]  
(25)

\[ g = \frac{4}{x^2 Q_{\text{sca}}} \sum_{n=1}^{\infty} \left\{ \frac{n(n+2)}{n+1} \Re \left( a_n a_{n+1}^* + b_n b_{n+1}^* \right) + \frac{2n+1}{n(n+1)} \Re \left( a_n b_{n+1}^* \right) \right\} \]  
(26)
where

$$a_n = \frac{\Psi'(mx)\Psi(x) - m\Psi(mx)\Psi'(x)}{\Psi'(mx)\zeta(x) - m\Psi(mx)\zeta'(x)}$$

$$b_n = \frac{m\Psi'(mx)\Psi(x) - \Psi(mx)\Psi'(x)}{m\Psi'(mx)\zeta(x) - \Psi(mx)\zeta'(x)}$$

(27) (28)

The functions $\Psi_n$ and $\zeta_n$ are Riccati-Bessel functions, $\mathbb{R}()$ denotes the real part of its arguments, and $x$ is the size parameter defined as $x = 2\pi r / \lambda$.

Studies of the validity of various effective medium theories in the radiative characterizations of particles are widely reported in the literature [12, 16, 17, 33]. Existing results suggest that effective medium theories can be valid for a wide range of porosities and size parameters when the particle inclusions are in the Rayleigh limit. Such a result does not include the entire spectral range under study. As such, we expect that this effective medium approach to give large errors in the optical and even near infrared range. However, we consider this approach for the purpose of exploration of its applicability to highly-ordered porous particles as well as to provide a reference solution to highlight the change in particle radiative behavior due to the existence of the ordered pores. Following the studies analyzing the application of effective medium theories to radiative characterization of ordered porous thin films [34–36], we apply the volume averaging theory (VAT) developed in [37, 38] to Maxwell’s equations, (1)–(2) to obtain the effective complex index of refraction $m_{\text{eff}} = n_{\text{eff}} - k_{\text{eff}}$, $n_{\text{eff}}^2 = \frac{1}{2} \left( A + \sqrt{A^2 + B^2} \right)$

$\quad k_{\text{eff}}^2 = \frac{1}{2} \left( -A + \sqrt{A^2 + B^2} \right)$

(29) (30)

where

$$A = p \left( n_{\text{pore}}^2 - k_{\text{pore}}^2 \right) + (1-p) \left( n_{\text{CeO}_2}^2 - k_{\text{CeO}_2}^2 \right)$$

$$B = 2n_{\text{pore}}k_{\text{pore}}p + 2n_{\text{CeO}_2}k_{\text{CeO}_2}(1-p)$$

(31) (32)

The effective complex index of refraction is used as an input to the Lorenz–Mie calculations to obtain the radiative efficiency factors to be compared to those obtained using the DDA and FEM calculations.

**RESULTS**

Simulations were run using DDA in the spectral range 290–6000 nm at 310 nm increments and 6–10 µm at 1000 nm increments. This corresponds to a range of particle size parameters from 0.314 to 10.833. FEM calculations were carried out at four wavelengths (size parameters) of interest, the endpoints of the DDA study, 290 nm (0.314) and 10,000 nm (10.833) as well as near the peak of the solar spectrum, 510 nm (6.160), and near the peak in the emission spectrum corresponding to an expected typical temperature of a solar thermochemical reactor, 2000 nm (1.571). It is acknowledged that for a result capturing the potentially intricate fluctuating behavior typical for a scattering characteristics analysis, a higher resolution scan of the spectrum is necessary. However, even without a high spectral resolution, noteworthy conclusions are drawn.

**Orientation-averaged results** The 4 particle orientations found in Table 1 where averaged to obtain the radiative properties shown in Figure 5. The 25-direction orientational averaging seen in Figure 5 is performed by considering 5 angular intervals between 0° to 45° for $\theta$ and 5
angular intervals between 0° to 45° for $\phi$. Very small differences in the predicted properties are observed for 4-orientation average and the higher angular resolution. At an example wavelength of 383 nm, averaging with 5 and 9 angular intervals for $\phi$ and $\theta$, respectively, leads to the difference of less than 0.5%.

The scattering and extinction efficiency factors increase monotonically for particle size parameters from 0.5 to 5.5, corresponding to increasing values of the parameter $2x|m - 1|$ from 1.15 to 14. For size parameters from 5.5 to 8.25 corresponding to $2x|m - 1|$ from 14 to 25, the scattering and extinction efficiency factors are maximum with some fluctuations known as the interference structures due to interference between diffracted waves and transmitted waves through the particle. It is interesting to note that the 3DOM ceria particle reduces the range of the interference structure to values of $2x|m - 1|$ between 14 to 25 (here for wavelengths between 375 nm and 550 nm, which are comparable to the pore size). Recall that the location of the interference structure for a homogeneous particle (shown in Figure 5) is generally for $2x|m - 1|$ from 4...
Figure 6: Spectral radiative properties of the 3DOM ceria for various particle orientations: (a) absorption efficiency factor, (b) scattering efficiency factor, (c) extinction efficiency factor, and (d) asymmetry factor.

(at wavelength 1800 nm here) to 24. Above this value, the interference structure disappears because the particle becomes totally absorbing. More precisely, for $2x|m - 1|$ between 4 to 14, the diffracted waves and waves crossing the particles either through pore channels and/or through solid interfere destructively. At the limit of large particle $2x|m - 1| > 30$, typically for wavelengths less than 350 nm, the DDA and FEM results converge to the asymptotic result for a large particle corresponding to the radiative properties: $Q_{ext} = 2$, $Q_{abs} = 1$ and $Q_{sca} = 1$.

Effect of particle orientation The orientational dependence of the optical characteristics is shown to be important in the range of the aforementioned interference structures as shown in Figure 6. This behavior could prove to be important for the particles being incorporated into a reactive flow as in a solar thermochemical reactor since the flow could cause a preferred orientation of the particles. Indeed, it has been shown that for groups non-spherical and non-homogeneous particles, radiative properties can significantly differ from those of a volume equivalent sphere, even if the particles are randomly oriented [39]. For values of $2x|m - 1|$ less than 3.6, the standard deviation between orientational values of all radiative properties considered in this study is less than 0.002.

The FEM predicted properties show satisfactory agreement with those obtained using the
DDA. Asymmetry parameter calculations at short wavelengths demonstrate the computational challenges of the FEM approach as a very high spatial resolution is needed to obtain the properties for even the homogeneous particle. The maximum relative error between DDA and FEM results of about 10% occurs in this spectral range. This error of DDA is expected to originate from the inaccurate modeling of pore edges, which impact the interference pattern, and can be addressed by reducing the dipole spacing.

It is noteworthy that there is no strong distinction between the radiative properties of particles oriented such that the window features of the 3DOM ceria are in line with the incident wave and the properties of particles oriented differently.

**Lorenz-Mie theory** For incident wavelengths much greater than pore diameter, the structure of the 3DOM ceria particle is anticipated to have little effect on the radiative properties obtained using the FEM and DDA approaches. In this case, the properties become consistent with those obtained using VAT with Lorenz-Mie theory. For the absorption efficiency factor and asymmetry parameter, VAT gives accurate predictions up to particle size parameters of 7.8 and 4 (\(\lambda = 400 \text{ nm}\) and \(\lambda = 775 \text{ nm}\)), respectively. This is a much larger range of validity than expected. The extinction and absorption efficiency factors were found to be accurately predicted using VAT with Lorenz-Mie theory for wavelengths greater than 5000 nm. Convergence to the VAT prediction for the extinction efficiency factor is shown in Figure 7 where the results for the extinction efficiency factor at long wavelengths are shown to detail the small size parameter region shown in Figure 5c. The effective medium theory given by VAT, however, does not accurately capture the scattering and absorption efficiency factors of 3DOM ceria particles when the interference structure between diffracted and transmitted waves through the particle is present. This is consistent with previous studies which have confirmed the validity of effective medium approximations only for pore size in the Rayleigh scattering limit. The Effective medium theory does, however, accurately predict the occurrence of the interference. That is to say, Lorenz-Mie theory along with VAT does provide qualitative agreement with orientation-averaged radiative transfer quantities.

**Numerical validation** The DDA and FEM simulations were verified by comparing the scattering and absorption efficiency factors as well as the asymmetry parameter for the case of a homogeneous sphere with those obtained using the exact solution given by Lorenz–Mie theory. A comparison at wavelengths of 300 nm, 500 nm, 1000 nm, and 10000 nm showed that (i) the FEM simulation match accurately the exact results confirming the correctness of its implementation, and (ii) the DDA is satisfactory with a maximum error of approximately 3% at 500 nm. To check for convergence of the FEM simulations, solutions at successive mesh refinements were compared. Relative errors of the predicted radiative properties were found be less than 5%.

![Figure 7: Extinction efficiency factor of 3DOM ceria particles in the near infrared range. It can be seen that the predictions made using VAT with Lorenz-Mie theory converge to the DDA and FEM predictions in this range.](image-url)
The iterative solver was considered converged when the relative tolerance reached $10^{-3}$. For DDA this value was set at $10^{-5}$.

**SUMMARY AND CONCLUSION**

Radiative characteristics of 3DOM cerium dioxide particles have been computed using two numerical approaches, the discrete dipole approximation and the finite element method. The particle characteristics were found to be strongly dependent upon the orientation at small wavelengths comparable to the pore size at which (i) the solar radiation power is maximum and (ii) the role of interference phenomenon seems very important. Scattering efficiency was found to be over 5 times smaller than for the solid ceria particle case. The incorporation of ordered overlapped pores within the 1000 nm ceria particle cancels the incident wave extinction for wavelengths greater than 560 nm. A spherical particle made up of an effective medium based on volume averaging theory was also considered as computationally economical alternative. The scattering problem was then solved using the Lorenz–Mie theory and found to give excellent agreement in the scattering, absorption, and extinction efficiency factors for wavelengths greater than 5000 nm—five times the diameter of the particle. Poor quantitative predictions were found at lower wavelengths but the approximation still exhibited behavior analogous to that calculated from FEM and DDA.

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