A multiphase equation of state for cerium (IV) oxide

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Abstract. I describe the construction of a theoretical equation of state (EOS) for cerium (IV) oxide, CeO$_2$, that includes low- and high-pressure solid phases and the liquid. After a very brief summary of our procedure, I discuss two challenges with this EOS. The first is the presence of high-frequency optical modes in the material's vibrational spectrum, which is difficult to capture with current modeling capabilities. The second is the difficulty of validating a full-density EOS against highly porous Hugoniot data, which requires additional modeling beyond the EOS itself.

1. Introduction
Cerium (IV) oxide, CeO$_2$, is a compound of interest in various technological applications, from catalytic converters to solid fuel cells. Because experimental effort on cerium oxide has been spread across both of its stoichiometric forms, CeO$_2$ and Ce$_2$O$_3$ (cerium (III) oxide), as well as a continuous range of nonstoichiometric forms CeO$_{2-x}$ where $0 \leq x \leq 0.5$, less data is available for CeO$_2$ than one usually has to make EOS for the SESAME database. The nonstoichiometric forms have complex phase diagrams, but available data for CeO$_2$ show only three phases:

(i) A cubic fluorite phase at ambient conditions (1 atm and room temperature).

(ii) A high-pressure solid phase. At room temperature, the solid-solid phase transition occurs at about 31 GPa and exhibits a $7 - 8\%$ volume collapse [1].

(iii) A liquid phase into which the material appears to melt from the cubic fluorite phase at 1 atm and 2750 K [2].

Therefore I have made an explicit three-phase EOS for CeO$_2$: such an EOS is built by creating separate EOS for the ambient solid, high-pressure solid, and liquid phases, determining the phase boundaries by matching Gibbs free energies, and then combining all three EOS into a single SESAME table. (The single table would be used in hydrodynamic simulations that assume the material is in thermodynamic equilibrium at all times; the EOS of the three phases separately can be used with a kinetic model to allow non-equilibrium transitions between phases.) The single table is currently designated SESAME 96171, and it may be further modified before final entry into the official SESAME database. In section 2 I describe the formalism and models used to construct the EOS, and in section 3 I compare it with available data. Comparing with shock data is difficult for this material because the data were collected using very porous powder samples; the reason this is a problem is discussed in section 4.
2. Formalism
The EOS is created by calculating a Helmholtz free energy per unit mass $F(\rho, T)$ for each phase, from which I determine pressure $P$ and internal energy per unit mass $E$ for each phase by

\[ P(\rho, T) = \rho^2 \left( \frac{\partial F}{\partial \rho} \right)_T \quad \text{and} \quad E(\rho, T) = F - T \left( \frac{\partial F}{\partial T} \right)_{\rho}. \]  

(1)

As is standard for EOS for the SESAME database, $F$ is expressed as a sum of three parts,

\[ F(\rho, T) = \phi(\rho) + F_{\text{nuc}}(\rho, T) + F_{\text{elec}}(\rho, T). \]  

(2)

$\phi(\rho)$ is the energy of static nuclei in their reference configuration with electrons in their ground state; this is also called the static structure energy or the cold curve. $F_{\text{nuc}}$ is the free energy of nuclei in a potential given by the electrons’ ground-state energy as a function of nuclear positions. Finally, $F_{\text{elec}}$ is the free energy of the electrons excited thermally while the nuclei are static in their reference configuration. (The free energy is completed by a fourth term, representing simultaneous excitation of the electrons and nuclei, but this is small in most circumstances and is neglected in this treatment.) Each of these three terms is independently calculated for each phase using various models described in two Los Alamos National Laboratory reports [3, 4]. The parameter values were mostly derived from comparison with experimental data; I give more details in the next section.

Given the EOS for the individual phases, I construct a multiphase EOS as described in [5]. At each point on the SESAME table grid we determine mass fractions $\lambda_i(\rho, T)$ and densities $\rho_i$ for each phase that minimize the total Gibbs free energy while keeping the phases in pressure equilibrium. The total Helmholtz free energy is given by

\[ F(\rho, T) = \sum_i \lambda_i(\rho, T) F_i(\rho_i, T), \]  

(3)

with a similar equation for the internal energy; the pressure is simply the equilibrium pressure of the phases.

3. Comparison with data
I used three sets of data while constructing the EOS.

- Data at ambient conditions and the melting point, given in table 1, were used to set the parameters for the low-pressure solid and the liquid.
- Room-temperature diamond anvil cell (DAC) data for pressure as a function of volume from Duclos et al. [1] were used to test the low-pressure solid EOS and set parameters for the high-pressure solid.
- I further tested the low-pressure solid EOS using two curves at $P = 1$ atm: the volume coefficient of thermal expansion $\alpha_P$ versus $T$ from Touloukian et al. [6] and Taylor [7], and the constant-pressure specific heat $C_P$ versus $T$ from Westrum and Beale [8], King and Christensen [9], and Ricken et al. [10].

The phase diagram predicted by the EOS at moderate conditions is shown in figure 1. Each circle is a point in the SESAME table grid that lies in a single-phase region. The open areas also contain grid points at which two or three phases are in equilibrium. The diagram shows the very large density changes as one crosses the phase boundaries, as well as a substantial change in slope of the melt line when one passes through the triple point at about 4000 K. The figure also shows the 1 atm isobar, and melt occurs where the isobar crosses from the low-pressure
Table 1. Experimental data at ambient conditions and melt at 1 atm.

| Quantity | Value          | Reference |
|----------|----------------|-----------|
| $\rho_{\text{ref}}$ | 7.215 g/cm$^3$ | [1]       |
| $\alpha_P$  | $2.92 \times 10^{-5}$ K$^{-1}$ | [6, 7]    |
| $C_P$      | 3.58 MJ/kg/K | [8]       |
| $B_T$      | $236 \pm 4$ GPa | [11]      |
| $B_T'$     | 4.4           | [11]      |
| $T_m$      | 2750 K        | [12]      |

solid to the liquid phase, at approximately 2750 K. Finally, the figure also shows the nonuniform gridding used in the EOS to allow more accurate interpolation in certain regions.

The behavior of the EOS under compression is excellent, as shown by figure 2. The room-temperature isotherm follows the experimental data all the way to the solid-solid phase transition, which I placed at 31 GPa, as suggested by Duclos et al. [1]. The high-pressure phase then accurately reproduces the remaining data. This confirms the accuracy of the bulk modulus at ambient conditions, and it makes the strongest case for constructing an EOS with two solid phases.

Figure 1. The phase diagram and 1 atm isobar calculated from the EOS. The material melts at approximately 2750 K.

Figure 2. Pressure at $T = 298$ K versus relative density calculated from the EOS shown alongside data.

Figure 3 shows the thermal expansion comparison. The two data sets have noticeably different trends at both low and high temperatures, and I attempted to capture both. I overshoot the data in the 300 – 1000 K region and I am beginning to undershoot the Touloukian data at higher temperatures. The general shape of $\alpha_P$ is a little difficult for our models to capture, which is more obvious in the specific heat data. In figure 4, the low-temperature specific heat is very well reproduced, but the EOS lies systematically above the high-temperature data, which is consistent across multiple sources. These data lie in the low-pressure solid phase, in which I omitted the
thermal electronic term; these data support that choice, because an electronic term would add to the specific heat and increase disagreement with data. The remaining discrepancy is thus largely due to the nuclear contribution, which in this case is a Debye model at low temperatures. Now a Debye model can be reliable even if the phonon spectrum is not Debye-like, as long as the temperature is sufficiently high that only the logarithmic moment of the spectrum contributes to the thermodynamics. There is evidence [13, 14] of high-frequency optical modes in the phonon spectrum of CeO$_2$, which suggests that even moderately high temperatures are not high enough to reach the Debye-like regime. To remedy this requires a nuclear model with an independent Einstein-like term, and this new model has not yet been developed.

![Figure 3](image1.png) ![Figure 4](image2.png)

**Figure 3.** $\alpha_P$ versus $T$ at $P = 1$ atm calculated from the EOS shown alongside data.

**Figure 4.** $C_P$ versus $T$ at $P = 1$ atm calculated from the EOS shown alongside data.

4. Porous Hugoniot data

Legacy Hugoniot data taken for this material [15] did not use crystalline samples; instead, the samples were compacted powders whose initial density was only 16% of the nominal crystal density. More recent Hugoniot data [16] used samples with much higher initial densities, but still only 53% of the crystal density at ambient. Comparison of such data to a crystal EOS is problematic, because the effects of porosity on the Hugoniot must be modeled. The simplest model assumes that the shock process completely squeezes out the porosity, so only the initial state lies off the crystal EOS. Then the initial condition in the Rankine-Hugoniot relations is set without reference to the EOS, and the relations are solved using the full EOS only for the final state. When that is done with this EOS, the results disagree wildly with the data. This is not too surprising, because the experiments did not compress the material very much, so the final states are probably still porous.

Another way to include porosity is to invoke a crush-up model such as $P - \alpha$ or $P - \lambda$ and solve the Rankine-Hugoniot relations using the crystal EOS supplemented by this model. This means that the shock data are no longer testing the EOS itself but a combination with other models. Such integrated tests do not provide as much confidence that the EOS is valid, because one cannot rule out the possibility that multiple combinations of EOS parameters and crush model parameters would equally well reproduce the shock data. Nonetheless, such comparisons have been carried out by Fredenburg et al. [17], and they found agreement with the shock data.
Their underlying EOS is not this one, but it was based on the same experimental data. Neither their EOS production codes nor ours can calculate a Hugoniot using both the EOS constructed here and a crush-up model simultaneously. The ability to do so will be important to develop for the future.

5. Conclusions
I have constructed an EOS for cerium (IV) oxide over the full standard SESAME range that includes two solid phases and the liquid. I have described the three-term construction of the EOS for each phase (cold curve, nuclear, and thermal electronic) and the multiphase construction for the final EOS. I also discussed the determination of the EOS parameters by comparison with experimental data at $P = 1$ atm, including the constant-pressure specific heat, coefficient of thermal expansion, and melting point. The comparison with data is good, but the presence of high-frequency optical modes in the phonon spectrum of CeO$_2$ limits the agreement of our models with thermal data. Another remaining issue is comparing the crystal-density EOS with experimental porous Hugoniot data, which may require using more sophisticated models to represent porosity.

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