7-25-2019

A Comprehensive Assessment of the Low-Temperature Thermal Properties and Thermodynamic Functions of CeO₂

Tyler D. Morrison
Texas A&M University

Elizabeth Sooby Wood
University of Texas at San Antonio, elizabeth.soobywood@utsa.edu

Phillippe F. Weck
Sandia National Laboratories

Eunja Kim
University of Nevada, Las Vegas, eunja.kim@unlv.edu

Sung Oh Woo
Texas A&M University

Follow this and additional works at: https://digitalscholarship.unlv.edu/physastr_fac_articles

[next page for additional authors](#)
Part of the [Biological and Chemical Physics Commons](#)

Repository Citation

Morrison, T. D., Wood, E. S., Weck, P. F., Kim, E., Woo, S. O., Nelson, A. T., Naugle, D. G. (2019). A Comprehensive Assessment of the Low-Temperature Thermal Properties and Thermodynamic Functions of CeO₂. *Journal of Chemical Physics*, 151 1-11. AIP Publishing.
<http://dx.doi.org/10.1063/1.5110178>

This Article is protected by copyright and/or related rights. It has been brought to you by Digital Scholarship@UNLV with permission from the rights-holder(s). You are free to use this Article in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/or on the work itself.

This Article has been accepted for inclusion in Physics & Astronomy Faculty Publications by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.

Authors

Tyler D. Morrison, Elizabeth Sooby Wood, Phillippe F. Weck, Eunja Kim, Sung Oh Woo, Andrew T. Nelson, and Donald G. Naugle

A comprehensive assessment of the low-temperature thermal properties and thermodynamic functions of CeO_2

Cite as: J. Chem. Phys. **151**, 044202 (2019); <https://doi.org/10.1063/1.5110178>

Submitted: 14 May 2019 . Accepted: 02 July 2019 . Published Online: 25 July 2019

Tyler D. Morrison , Elizabeth Sooby Wood , Phillippe F. Weck, Eunja Kim , Sung Oh Woo , Andrew T. Nelson , and Donald G. Naugle

View Online

Export Citation

CrossMark

ARTICLES YOU MAY BE INTERESTED IN

Thermodynamics of pure liquid water: Sound speed measurements to 700 MPa down to the freezing point, and an equation of state to 2300 MPa from 240 to 500 K

The Journal of Chemical Physics **151**, 054501 (2019); <https://doi.org/10.1063/1.5097179>

Bond dissociation energies of FeB, CoB, NiB, RuB, RhB, OsB, IrB, and PtB

The Journal of Chemical Physics **151**, 044302 (2019); <https://doi.org/10.1063/1.5113511>

Revisiting the replica theory of the liquid to ideal glass transition

The Journal of Chemical Physics **150**, 154504 (2019); <https://doi.org/10.1063/1.5088811>

The Journal
of Chemical Physics

Submit Today

The Emerging Investigators Special Collection and Awards
Recognizing the excellent work of early career researchers!

A comprehensive assessment of the low-temperature thermal properties and thermodynamic functions of CeO₂

Cite as: J. Chem. Phys. 151, 044202 (2019); doi: 10.1063/1.5110178

Submitted: 14 May 2019 • Accepted: 2 July 2019 •

Published Online: 25 July 2019

Tyler D. Morrison,¹ Elizabeth Sooby Wood,^{2,a),b)} Phillippe F. Weck,³ Eunja Kim,⁴ Sung Oh Woo,¹ Andrew T. Nelson,^{5,b)} and Donald C. Naugle¹

AFFILIATIONS

¹Department of Physics and Astronomy, Texas A&M University, College Station, Texas 77843, USA

²Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, Texas 78249-1644, USA

³Sandia National Laboratories, P.O. Box 5800, Albuquerque, New Mexico 87123, USA

⁴Department of Physics and Astronomy, University of Nevada-Las Vegas, Las Vegas, Nevada 89154, USA

⁵Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

^{a)}Electronic mail: elizabeth.soobywood@utsa.edu

^{b)}Previously at: Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA.

ABSTRACT

Reported is an experimental and computational investigation of the low temperature heat capacity, thermodynamic functions, and thermal conductivity of stoichiometric, polycrystalline CeO₂. The experimentally measured heat capacity at $T < 15$ K provides an important correction to the historically accepted experimental values, and the low temperature thermal conductivity serves as the most comprehensive data set at $T < 400$ K available. Below 10 K, the heat capacity is observed to obey the Debye T^3 law, with a Debye temperature of $\Theta_D = 455$ K. The entropy, enthalpy, and Gibbs free energy functions are obtained from the experimental heat capacity and compared with predictions from Hubbard-corrected density functional perturbation theory calculations using the Perdew, Burke, and Ernzerhof parameterization revised for solids. The thermal conductivity is determined using the Maldonado continuous measurement technique, along with laser flash analysis, and analyzed according to the Klemens-Callaway model.

Published under license by AIP Publishing. <https://doi.org/10.1063/1.5110178>

I. INTRODUCTION

Cerium dioxide (CeO₂) is used in a wide range of technological applications owing to its favorable redox properties, physico-chemical stability, optical transparency, high dielectric constant, and refractive index, and mixed electronic-ionic conduction properties. CeO₂ has attracted considerable attention recently as a catalyst due to its high oxygen mobility and storage capacity.^{1,2} CeO₂ is also suitable for epitaxial growth on Si,³ making it desirable for applications in microelectronics. CeO₂-based materials find applications as automotive and biomedical catalysts,^{4,5} gas sensors,⁶ in high-temperature superconducting tapes,⁷ hydrogen production and fuel cells,^{8–10} and luminescence devices.¹¹ CeO₂ also serves as a surrogate for actinide dioxide nuclear fuels, such as UO₂ and PuO₂,

and other f-electron oxide materials of interest in nuclear waste management.^{12,13}

With the wide applicability of CeO₂ in modern technology, there is great interest and a wealth of information available for this material in the literature. Despite the vast amount of published data, limited thermal data exist in the low-temperature range below ≈ 400 K. As recently discussed in the review by Konings *et al.*,¹⁴ the most extensive set of low-temperature heat capacity data for CeO₂ was collected in 1961 by Westrum and Beale between 5 and 300 K by adiabatic calorimetry.¹⁵ Heat-capacity measurements were also reported by Riess *et al.*¹⁶ (350–900 K) using adiabatic scanning calorimetry, and by Gallagher and Dworzak¹⁷ (418–758 K) and Krishnan and Nagarajan¹⁸ (280–820 K) using differential scanning calorimetry (DSC). High-temperature enthalpy

increment data were reported by Kuznetsov *et al.*¹⁹ (in the range of 608–1172 K, although data down to 298 K were mentioned in other studies¹⁸), by King and Christensen²⁰ (400–1800 K), and by Yashvili *et al.*²¹ (391–1624 K).

Furthermore, limited density functional theory (DFT) studies focused recently on the high-temperature thermodynamic properties of CeO_2 .^{22–24} These computational investigations utilized Hubbard-corrected DFT (DFT+ U) within either the local-density approximation (LDA+ U) or the generalized-gradient approximation (GGA+ U) to correctly describe strong on-site Coulomb repulsion between localized Ce $4f$ electrons. Both GGA+ U studies by Gopal and van de Walle²² and Niu *et al.*²⁴ utilized the standard parameterization of Perdew, Burke, and Ernzerhof²⁵ (PBE) to calculate the thermodynamic properties of CeO_2 . However, a recent GGA+ U study by Weck and Kim²⁶ demonstrated that the more recent Perdew, Burke, and Ernzerhof revised parameterization for solids²⁷ (PBEsol) describes experimental crystalline parameters and properties of CeO_2 and Ce_2O_3 with superior accuracy, compared to other standard GGA functionals such as PBE. Therefore, a reexamination of the thermodynamic properties of CeO_2 using DFT+ U /PBEsol appears timely.

This joint experimental and first-principles investigation of the thermodynamic properties of CeO_2 below ≈ 400 K is motivated by a need to extend the fundamental understanding of the lower temperature behavior of this versatile material and to present a comprehensive and accurate thermodynamic picture of this material in the lower temperature regime.

Specifically, the $T \leq 400$ K heat capacity, thermodynamic functions, and thermal conductivity measurements of stoichiometric, polycrystalline, sintered CeO_2 monolithic samples are reported. The heat capacity is measured using adiabatic calorimetry employing a combination of relaxation and the dual slope techniques. The entropy, enthalpy function, and Gibbs free energy function are obtained from the experimental heat capacity data and compared with predictions from Hubbard-corrected density functional perturbation theory (DFPT) calculations using the PBEsol functional. The thermal conductivity is determined using the Maldonado continuous measurement technique, along with Laser Flash Analysis (LFA), and analyzed according to the Klemens-Callaway model (KCM). The results reported in this study below ≈ 400 K provide accurate thermal data for CeO_2 in a temperature range of high relevance for technological applications.

II. EXPERIMENTAL METHODS

A. CeO_2 preparation

The experimental investigations in this study were performed on rodlike cylinders prepared via conventional powder metallurgical methods. CeO_2 monoliths were prepared using a modified procedure to that reported by Nelson *et al.*¹² CeO_2 powder [Alfa Aesar 99.99% purity rare-earth oxide (REO) basis, Lot C09Y013] was mixed with a binding agent, 0.45% ethylene bis(stearamide) (Sigma Aldrich Lot 1204CD). The binder and powder were homogenized using a high energy ball mill for 30 min in a zirconia jar and with a zirconia ball. The resulting powder was sieved through a -200 mesh sieve to produce a fine power for pressing. The powder was pressed into cylindrical geometries (pellets) with a 4.17 mm diameter and

approximately 6.5 mm tall. The pellets were sintered on a bed of CeO_2 powder at 1873 K for 4 h in an Al_2O_3 crucible. A 1473 K isothermal soak, following the sintering step, was employed to set the $\text{CeO}_{2.0}$ stoichiometry.

Following the sintering profile, each pellet was weighed on a balance calibrated to 1 mg. The height and diameter were measured using calipers. These measurements were used to calculate a geometric density and percent theoretical density (7.21 g/cm^3),²⁸ which was determined to be $97\% \pm 1\%$. The average grain size was measured to be $20.5 \mu\text{m}$ with a $1.9 \mu\text{m}$ standard deviation using the ASTM standard E112-12 Circular Intercept Procedure. A characteristic micrograph of this microstructure is displayed in Fig. 1.

The stoichiometry of the CeO_2 is assumed to be minimally reduced (i.e., $\text{CeO}_{1.995}$). See Nelson *et al.*¹² for more details on the achievable stoichiometries of CeO_2 via powder metallurgical methods.

B. Raman spectroscopy

Raman spectroscopy measurements were performed at room temperature using a Jobin Yvon Horiba LabRAM HR instrument coupled to an Olympus BX41 microscope with a 503 objective using 514.5 nm laser excitation from an Ar-ion laser. A grating (1800 lines/mm) spectrometer equipped with a Peltier-cooled charge-coupled device (CCD) detector (Andor) was used to acquire spectra giving a spectral resolution better than 2 cm^{-1} .

C. Heat capacity

Prior to heat capacity measurements, three flat disks of approximately 1 mm in height were segmented from the pellets using a wire diamond saw. All three heat capacity samples were weighed to within 0.1 mg with an analytical balance. Measurements were

FIG. 1. Micrograph of CeO_2 at $700\times$ magnification using a backscatter detector. Sample was cross-sectioned and thermally etched prior to imaging.

performed in a Quantum Design Physical Properties Measurement System (PPMS) from 2 to 400 K. In all measurements, Apiezon N grease was placed on the sample platform to facilitate thermal conduction between the sample and the platform. The combined addenda heat capacity (C_a) of the platform, temperature sensor, heater, and grease was measured over the desired temperature range before the sample was loaded onto the platform. Addenda measurements were performed before each run. After sample measurements, C_a was subtracted from the total measured heat capacity to obtain the heat capacity of the sample. The standard relaxation technique was adopted for the entire temperature range, but augmented finer spaced data; the dual-slope method²⁹ was employed from 2 to 40 K.

D. Thermal conductivity

Thermal conductivity was measured while cooling from 400 K to 2 K and heating from 2 K to 400 K at a rate of 0.5 K/min. Prior to thermal conductivity measurements, samples were prepared by first cutting the CeO₂ pellet into a small brick of approximately $7 \times 1 \times 1$ mm. These bricks were covered with Kapton tape exposing only the ends and small sections where the leads were to be attached. Approximately 5 nm of gold-palladium was then sputter coated onto the surface with an Anatech Hummer Sputtering System. Leads to the sample were made using high thermal conductivity epoxy (EpoteK EK2000) and 5 mil (0.127 mm) diameter bare copper wire. The bare copper wire was wrapped around the sample and twisted together to make a snug fit on the sputtered gold-palladium surface to provide temperature measurement leads. The epoxy was then used to cement the copper wire leads to the sample. Finally, the Kapton tape was removed and the epoxy cured. In order to attain the highest thermal conductivity, the epoxy was cured at 125 °C for 2 h, followed by 150 °C for 36 min, and finally 200 °C for 15 min according to manufacturer's instructions. All samples were prepared in a 4 probe configuration. Thermal conductivity measurements were performed using the thermal transport option (TTO) of the Quantum Design PPMS. The PPMS was operated in continuous measurement mode, which employs the Maldonado³⁰ technique. This technique utilizes a square wave a.c. drift method for measurements.

E. Thermal diffusivity

Laser flash analysis (LFA) was performed on three CeO₂ samples using a method similar to that described elsewhere.^{12,31} However, the thermal conductivity measurements performed via cryostat were done on small brick samples reduced from the original pellets, LFA measurements were performed on pellets approximately 9.50 mm in diameter and 1.60 mm in height. These samples were coated on both faces using a layer of graphite spray to maximize both deposition of heat and detection of the temperature rise. LFA measurements were performed in a static air atmosphere in a liquid nitrogen furnace capable of cooling the samples from ambient temperatures to below 155 K. Data were collected at 10 K intervals from 155 K to 295 K. Five measurements were performed at each step, once the temperature had reached within 3 K of the target and was stable to better than 0.5 K/min. The standard deviation of the mean thermal diffusivity data at each temperature was below the

standard error associated with the technique (3%) for all temperatures with the exception of the data collected at 155 and 145 K. At these temperatures, the standard deviation in the mean of the five shots was slightly greater than 3%. Room temperature thermal diffusivity measurement was performed prior to initial cooling as well as a final step. Both room temperature measurements agreed within the standard error of the technique (3%) and provide confirmation that stoichiometry was retained.

III. COMPUTATIONAL METHODS

Total-energy calculations were conducted using spin-polarized density functional theory (DFT), as implemented in the Vienna *Ab initio* Simulation Package (VASP).^{32,33} The exchange-correlation energy was calculated using the generalized-gradient approximation³⁴ corrected with an effective Hubbard parameter to describe strong on-site Coulomb repulsion between localized Ce 4*f* electrons. The parameterization of Perdew, Burke, and Ernzerhof revised for solids²⁷ (PBEsol) was utilized, since it accurately reproduces the measured crystal parameters and properties of CeO₂.^{26,35}

Following Dudarev's formalism,³⁶ a penalty functional was added to the standard DFT functional, E_{DFT} , in order to force the on-site occupancy matrix in the direction of idempotency,

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{(\bar{U} - \bar{J})}{2} \sum_{\sigma} [\text{Tr}(\rho^{\sigma}) - \text{Tr}(\rho^{\sigma} \rho^{\sigma})], \quad (1)$$

where $\bar{U}$ and $\bar{J}$ are spherically averaged matrix elements of the screened electron-electron Coulomb and exchange interactions, respectively, and ρ^{σ} is the density matrix of Ce 4*f* electrons, with a given projection of spin σ . The fully localized, limitlike Dudarev's scheme was utilized for the double-counting correction. Using this approach, only $U_{\text{eff}} = \bar{U} - \bar{J}$ is meaningful and $\bar{J}$ was fixed to an arbitrary value of 0.6 eV. A value of $U_{\text{eff}} = 4.5$ eV determined from self-consistent linear-response calculations³⁷ was adopted in this study; this value is in line with typical $+U_{\text{eff}}$ corrections utilized in previous investigations of CeO₂.^{26,38–41} The Projector Augmented Wave (PAW) method^{42,43} was used to describe the interaction between valence electrons and ionic cores. In the Kohn-Sham (KS) equations, Ce(5*s*², 5*p*⁶, 6*s*², 4*f*¹, 5*d*¹) and O(2*s*², 2*p*⁴) electrons were treated explicitly as valence states and the remaining core electrons, together with the nuclei, were represented by PAW pseudopotentials. The plane-wave cutoff energy for the electronic wavefunctions was set to 500 eV, ensuring total-energy convergence to within 1 meV/atom. The conjugate gradient method using Methfessel-Paxton Fermi-level smearing⁴⁴ with a Gaussian width of 0.1 eV was utilized in electronic relaxation calculations. A 12-atom ($Z = 4$) periodic unit cell was used to represent nonmagnetic bulk CeO₂; the cubic fluorite-type CeO₂ structure (space group $Fm\bar{3}m$; IT No. 225) reported by Gerward *et al.*⁴⁵ was used as starting geometry in relaxation calculations. Ionic and cell relaxations were carried out simultaneously without symmetry constraints applied and the Hellmann-Feynman forces acting on atoms were initially calculated with a convergence tolerance set to 0.01 eV/Å. The Brillouin zone (BZ) was sampled using the Monkhorst-Pack *k*-point scheme,⁴⁶ with a *k*-point mesh of $5 \times 5 \times 5$. Using the equilibrium structures obtained from total-energy minimization, successive relaxations with respect to Hellmann-Feynman forces were then carried out with more a

stringent convergence of 0.001 eV/Å and phonon properties were obtained with the linear response method, which utilizes density functional perturbation theory (DFPT) to calculate forces.

IV. RESULTS AND DISCUSSION

A. Structure analysis

The lattice parameter of bulk CeO₂ calculated at $T = 0$ K is 5.435 Å, which is only 0.4%–0.5% larger than the X-ray diffraction (XRD) values of $a_0 = 5.4113(1)$, 5.411(1), and 5.406(10) Å measured by Hisashige *et al.*,⁴⁷ Gerward *et al.*,⁴⁵ and Duclos *et al.*,⁴⁸ respectively.

1. Phonon density of states

At the athermal limit, the present phonon density-of-states (DOS) DFPT results (see Fig. 2) are overall consistent with the PBEsol predictions by Buckeridge and co-workers,³⁵ and with Raman scattering,^{49,50} infrared spectroscopy,⁵¹ reflectivity,⁵² and inelastic neutron scattering measurements⁵³ discussed in great detail in their computational study. In particular, the calculated F_{1u} transverse optical (TO) and F_{2g} phonon modes at the Γ point are at $\omega_{F_{1u}TO} = 293$ cm^{−1} (8.8 THz) and $\omega_{F_{2g}} = 450$ cm^{−1} (13.5 THz), in close agreement with the experimental values of $\omega_{F_{1u}TO} = 283$ cm^{−1} (8.5 THz) by Santha *et al.*⁵⁴ and $\omega_{F_{1u}TO} = 276$ cm^{−1} (8.3 THz) and $\omega_{F_{2g}} = 460$ cm^{−1} (13.8 THz) measured by Clausen *et al.*⁵³ As shown by Buckeridge *et al.*,³⁵ the agreement between calculations and measurements at the Γ point can be slightly improved by using an empirical nonanalytical correction term to the high-frequency dielectric constant ϵ^∞ . However, since no nonanalytical correction term is needed at the nonzero exact wave-vector points, this correction was not utilized in this study.

2. Raman spectroscopy

The experimentally determined Raman spectrum of a typical CeO₂ sample in this study (see Fig. 3) shows the distinct F_{2g} band

FIG. 2. Phonon density of states (DOS) of bulk CeO₂ calculated at the DFPT/PBEsol level of theory.

FIG. 3. Typical Raman shift of CeO₂ samples in this study. The vertical line at 465 cm^{−1} represents the F_{2g} peak and is typical of high quality samples.

at 465 cm^{−1}. This band is consistent with single crystal CeO₂ at 465 cm^{−1}.^{49,50,55} As detailed in previous polycrystalline sample measurements,^{56,57} large grain size samples show Raman spectra consistent with single crystal samples. DFPT calculations predict a value of 458 cm^{−1}. The full width at half maximum is measured to be 7 cm^{−1} using a Lorentzian fit. The lack of any other peaks in the 400–600 cm^{−1} range indicates that the samples are highly stoichiometric with no detectable oxygen vacancies. See Schilling *et al.*⁵⁷ for a thorough discussion of the effect of oxygen vacancies on the F_{2g} band.

B. Thermal properties and thermodynamic function predictions

DFPT calculations were also carried out near equilibrium volume in order to predict the thermal properties of bulk CeO₂ using the quasi-harmonic approximation (QHA). A temperature effect was added to the calculated total energy $U(V)$ of the system through the phonon contribution,

$$F_{\text{phonon}}(T; V) = \frac{1}{2} \sum \hbar \omega + k_B T \sum \ln[1 - e^{-\beta \hbar \omega}], \quad (2)$$

where $\hbar$ is Planck's reduced constant, $\hbar \omega$ is the energy of a single phonon with angular frequency ω , k_B is Boltzmann's constant, T is the temperature of the system, and $\beta = (k_B T)^{-1}$. The variation of $U(V) + F_{\text{phonon}}(T; V)$ as a function of the unit-cell volume in the temperature range of 0–450 K is displayed in Fig. 4.

At constant hydrostatic pressure P , the Gibbs free energy, G , was obtained by the following transformation to introduce a volume dependence:⁵⁸

$$G(T, P) = \min_V [U(V) + F_{\text{phonon}}(T; V) + P(V)V], \quad (3)$$

where $\min_V[\text{function of } V]$ corresponds to a unique minimum of the expression between brackets with respect to the unit-cell volume V . $U(V) + F_{\text{phonon}}(T; V)$ was computed as discussed above,

FIG. 4. Variation of the total energy with phonon contribution, $U(V) + F_{\text{phonon}}(T; V)$, of bulk CeO_2 as a function of the unit-cell volume calculated with PBEsol from $T = 0$ –450 K in steps of 10 K. Red circles indicate the local minima of free energy curves.

and the thermodynamic functions of Eq. (3) were fitted to the universal Vinet equation of state,⁵⁹ i.e.,

$$P(V) = 3K_0 \frac{(1-x)}{x^2} \exp\left[\frac{3}{2}(K'_0 - 1)(1-x)\right], \quad (4)$$

with $x = (V/V_0)^{1/3}$, where V_0 and V are the equilibrium and deformed unit-cell volumes, respectively, and the bulk modulus, K_0 , and its derivative with respect to the pressure, K'_0 , are obtained according to

$$K_0(T) = -V \left(\frac{\partial P}{\partial V} \right)_{P=0} \quad \text{and} \quad K'_0(T) = \left(\frac{\partial K}{\partial P} \right)_{P=0}. \quad (5)$$

The thermal evolution of K_0 and K'_0 is depicted in Fig. 5. The computed bulk modulus and its pressure derivative vary from $K_0 = 194.5$ –179.1 GPa and $K'_0 = 4.5$ –4.9 GPa between 0 and 450 K. The single-crystal athermal value of $K_0 = 194.5$ GPa is consistent with the value of 200.0 GPa previously calculated for polycrystalline CeO_2 with PBEsol+ U ($U_{\text{eff}} = 4.5$ eV) within the Voigt-Reuss-Hill (VRH) approximation.²⁶ This value is also in fair agreement with the experimental VRH value of 204 GPa derived from the measurements of Nakajima *et al.*,⁴⁹ although it remains much below the experimental estimates of 220 GPa and 236 GPa reported by Gerward *et al.*^{45,60} and the early measurement of 230 GPa by Duclos and co-workers.⁴⁸

Using the variation of the unit-cell volume with temperature in Fig. 4, the linear coefficient of thermal expansion (CTE), $\alpha = (3V)^{-1}(\partial V/\partial T)_{P=0}$, was computed assuming isotropic thermal expansion of bulk CeO_2 (see Fig. 6). As shown in Fig. 6, the calculated CTE is in excellent agreement with the measurements of Gupta and Singh⁶¹ in the temperature range of 110–291 K, while slightly underestimating the data of Westrum and Beale¹⁵ below room temperature. A value of $\alpha = 10.06 \times 10^{-6} \text{ K}^{-1}$ is predicted with

FIG. 5. Thermal evolution of (a) the bulk modulus K_0 and (b) its pressure-derivative K'_0 for bulk CeO_2 calculated using the Vinet equation of state with DFPT/PBEsol.

DFPT/PBEsol at $T = 298.15$ K, in the ballpark of data measured near room temperature, i.e., $10.14 \times 10^{-6} \text{ K}^{-1}$ at 291 K by Gupta and Singh,⁶¹ $10.00 \times 10^{-6} \text{ K}^{-1}$ at 298 K by Sameshima *et al.*,⁶² $9.78 \times 10^{-6} \text{ K}^{-1}$ at 300 K by Westrum and Beale,¹⁵ $10.79 \times 10^{-6} \text{ K}^{-1}$ at 304 K Stecura and Campbell,⁶³ and $9.31 \times 10^{-6} \text{ K}^{-1}$ at 292 K by Taylor.⁶⁴ Above room temperature, CTE predictions are in overall agreement with the measurements of Körner *et al.*⁶⁵ while systematically overestimating other data sets.

C. Molar heat capacity

The isobaric molar heat capacity, C_p , was computed as the second derivative of the Gibbs free energy [see Eq. (3)] with respect to

FIG. 6. Variation of linear thermal expansion coefficient of bulk CeO_2 calculated with DFPT/PBEsol. The measurements of Gupta and Singh,⁶¹ Sameshima *et al.*,⁶² Nelson *et al.*,¹² Stecura and Campbell,⁶³ Körner *et al.*,⁶⁵ Westrum and Beale,¹⁵ and Taylor⁶⁴ are represented for comparison.

the temperature,

$$C_p(T, P) = -T \frac{\partial^2 G(T, P)}{\partial T^2} = T \frac{\partial V(T, P)}{\partial T} \frac{\partial S(T, V)}{\partial V} \bigg|_{V=V(T, P)} + C_V[T, V(T, P)], \quad (6)$$

where $V(T, P)$ corresponds to the equilibrium volume at T and P . In Eq. (6), the isochoric molar heat capacity C_V is defined as

$$C_V = k_B \sum (\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{[e^{\beta \hbar \omega} - 1]^2}, \quad (7)$$

and the entropy is computed using the following expression:

$$S = -k_B \sum \ln[1 - e^{-\beta \hbar \omega}] - \frac{1}{T} \sum \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}. \quad (8)$$

Figure 7 displays the computed isochoric molar heat capacity and isobaric molar heat capacity at standard pressure ($P = 1$ bar), and Fig. 8 depicts the entropy for bulk CeO_2 , along with the low-temperature calorimetric measurements of the present study and Westrum and Beale.¹⁵ Figure 7 also shows calorimetric data from Kuznetsov *et al.*,¹⁹ Krishnan and Nagarajan,¹⁸ Gallagher and Dworzak,¹⁷ Riess *et al.*,¹⁶ and King and Christensen.²⁰ The standard values calculated at $T = 298.15$ K in this study are $C_p^0 = 63.4 \text{ J mol}^{-1} \text{ K}^{-1}$ and $S_p^0 = 61.1 \text{ J mol}^{-1} \text{ K}^{-1}$ and are in good agreement with calorimetric data.

1. Discussion on the correction to molar heat capacity

Measured results are in excellent agreement with those of Westrum and Beale throughout most of the temperature range, with an important correction at $T < 15$ K. Estimated error bars are $\pm 5\%$ or smaller as detailed in Lashley *et al.*⁶⁶ Datum presented here is an

FIG. 7. Measured standard-pressure isobaric molar heat capacity (C_p) of CeO_2 and DFPT/PBEsol calculated C_p and isochoric molar heat capacity (C_V). Calorimetric data from previous studies are also displayed: Westrum and Beale,¹⁵ Kuznetsov *et al.*,¹⁹ Krishnan and Nagarajan,¹⁸ Gallagher and Dworzak,¹⁷ Riess *et al.*,¹⁶ and King and Christensen.²⁰ Inset shows experimental data as C_p/T vs T^2 and a fit of the data to the low-temperature T^3 limit of the simple Debye model.

FIG. 8. Calorimetric data and DFPT/PBEsol results for the entropy of CeO_2 . Calorimetric data from Westrum and Beale¹⁵ are also represented.

average of 3 different samples. Each data point was also taken 3 times for each sample and averaged together (2 times for dual slope data).

As shown on the inset C/T vs T^2 plot in Fig. 7, below 15 K ($< 200 = T^2$), there is a significant deviation in the data from the previously published values. The deviation in the current and previously reported data can, in part, be due to improvement in measurement techniques over the last 60 years. However, the difference is hypothesized here to be due to impurities in Westrum and Beale's original samples. This argument is supported by the excellent work of Gruber *et al.*⁶⁷ concerning impurities in Ce_2O_3 samples measured by Westrum and Beale. The deviation of Westrum and Beale's CeO_2 data from that report here at low temperatures shows characteristics similar to that of a Schottky anomaly, which could be due to sample impurities. This is supported by measurement of C_p in nonstoichiometric samples ($\text{CeO}_{2-\delta}$, $\delta = 0-0.032$) yet to be published.

All measurements showed the expected sigmoid behavior typical of crystalline salts. At low temperatures, the well-known Debye model provides a simple yet successful one parameter model to describe the heat capacity.⁶⁸ For the phonon contribution, the low temperature limit of the heat capacity reduces to

$$C = \frac{12}{5} \pi^4 N_A k_B \left(\frac{T}{\Theta_D} \right)^3, \quad (9)$$

where N_A is Avogadro's number, Θ_D is the Debye temperature, k_B and T are the same as defined above, and $C = C_V \approx C_p$. Thus, at sufficiently low T , C varies as T^3 and a plot of C/T against T^2 will be a straight line. It must be stressed that Eq. (9) is valid only for temperatures of the order of $T < \Theta_D/50$.

As shown in the inset of Fig. 7, there is no indication of magnetic or electronic contributions to the heat capacity in this study. To extract Θ_D , a linear least squares regression was performed on C/T vs T^2 data. Since CeO_2 is not a monatomic solid, Eq. (9) must be multiplied by the number of atoms per molecule to properly fit the data. Using the simple Debye model, Θ_D was calculated to be 455 K.

This value lies in between previously reported data, $\Theta_D = 409$ K,⁶⁹ 480 K,⁴⁷ and also within the range of recent theoretical calculations $\Theta_D = 481$ K²⁶ and $\Theta_D = 414.5$ –582.9 K²³ depending on calculated parameters.

D. Thermodynamic functions

In order to derive the enthalpy and entropy functions, the thermal evolution of the isobaric heat capacity calculated from DFPT/PBESol for bulk CeO₂ was fitted using a nonlinear least-squares regression to a Haas-Fisher-type polynomial,

$$C_P = a + bT + cT^{-2} + dT^{-0.5} + eT^2, \quad (10)$$

with the resulting optimized coefficients in the temperature range of 100–450 K, $a = 2.04096 \times 10^2$, $b = -1.370 \times 10^{-1}$, $c = 2.44059095 \times 10^5$, $d = -1.901314 \times 10^3$, and $e = 8.5 \times 10^{-5}$. The sum of squared differences between calculated and fitted C_P data was 7×10^{-3} .

The enthalpy function, $(H_T - H_{298.15}) \cdot T^{-1}$, was calculated by analytical integration of the fit to the isobaric heat capacity using the formula,

$$(H_T - H_{298.15}) \cdot T^{-1} = \int_{298.15}^T C_P(T) dT. \quad (11)$$

The Gibbs energy function, $(G_T - H_{298.15}) \cdot T^{-1}$, was computed using the following expression:

$$(G_T - H_{298.15}) \cdot T^{-1} = (H_T - H_{298.15}) \cdot T^{-1} - S, \quad (12)$$

where S is the entropy calculated from Eq. (8). Results for the experimental and computed enthalpy function and Gibbs energy function for bulk CeO₂ are shown in Figs. 9 and 10, along with previous experimental data from Westrum and Beale,¹⁵ King and Christensen,²⁰ and Yashvili *et al.*²¹

FIG. 9. Experimental data and DFPT/PBESol results for the enthalpy function of CeO₂. Calorimetric data from Westrum and Beale,¹⁵ King and Christensen,²⁰ and Yashvili *et al.*²¹ are also shown.

FIG. 10. Experimental data and DFPT/PBESol results for the Gibbs energy function of CeO₂. Calorimetric data from Westrum and Beale¹⁵ are also displayed.

E. Thermal conductivity

Figure 11 presents the thermal conductivity of bulk CeO₂ pellets from 2 to 400 K using the Maldonado³⁰ technique. Also presented are the results of LFA (this work), along with previously published data by Khafizov *et al.*⁶⁹ Low-temperature thermal conductivity data and LFA data in this study are in excellent agreement. Furthermore, measured values are in good agreement with previously published data. The only low-temperature thermal conductivity data of bulk polycrystalline CeO₂ pellets in the literature to date were performed by Khafizov *et al.*⁶⁹ However, the focus of that study was mainly thin films of CeO₂, not the bulk properties and

FIG. 11. Experimental data and Klemens-Callaway fit for the thermal conductivity of CeO₂. LFA data from this study and MTRM data from Khafizov *et al.*⁶⁹ are also displayed. Error bars in this work are equal to or smaller than the symbol size, i.e., 5% for LFA measurements.

used modulated thermorefectance microscopy (MTRM) from 77 to 1000 K. The room temperature value of the thermal conductivity was found to be $16.7 \text{ W m}^{-1} \text{ K}^{-1}$, also in good agreement with that determined for CeO_2 of similar purity.³¹

In order to determine the thermal conductivity using LFA, the thermal diffusivity was measured on three samples. All three samples provided data in good agreement across the temperature range investigated. The thermal diffusivity is observed to monotonically decrease with temperature, as typical of an oxide ceramic in this temperature range. Thermal conductivity can then be calculated using the product of the thermal diffusivity, specific heat capacity, and density. The heat capacity of CeO_2 measured as described earlier in this work provides this data as a function of temperature over the temperature range where LFA was used to collect thermal diffusivity data. These data are converted from a molar heat capacity to a specific heat capacity by assuming a molar mass of CeO_2 as 172.12 g/mol . Density is assumed constant as 6.85 g/cm^3 . This value corresponds to 95% theoretical density, within 1% of the value measured for all samples measured.

A simple model for thermal conductivity at low temperatures is the Klemens-Callaway model (KCM).⁷⁰ To solve the Boltzmann transport equation, this model assumes a Debye phonon dispersion relation and utilizes a relaxation time approximation. The thermal conductivity as a function of temperature T is then given by

$$\kappa = \frac{k_B}{2\pi v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\Theta_D/T} \tau(x, T) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (13)$$

where v is the mean velocity of sound in the solid, $\tau(x, T)$ is the phonon relaxation time, $x = \hbar\omega/k_B T$ is the reduced phonon frequency, and ω , k_B , $\hbar$, and Θ_D are as defined above. Higher order correction terms are neglected for simplicity. The Debye temperature was taken from the above experimental heat capacity measurements to be $\Theta_D = 455 \text{ K}$. Then, the mean velocity of sound is calculated to be 3610 m/s using the relation $v = k_B \Theta_D / \hbar \sqrt{6\pi^2 N/V_0}$, where N is the number of atoms per unit cell, and $V_0 = a^3/4$ is the volume per unit cell, with a being the lattice constant of $5.411 \text{ \AA}$. In general, the Debye temperature is not constant and at higher temperatures anharmonic, and other effects must be considered.^{71,72} A plot displaying the temperature dependence of Θ_D is located in the [supplementary material](#).

1. Discussion on phonon scattering

The scattering rate $\tau^{-1}(x, T)$ is a combination of the different scattering mechanisms that follow the Matthiessen rule and is given by the following equation:⁷

$$\tau^{-1}(x, T) = v/L + \alpha x^4 T^4 + \beta_U x^2 T^3 e^{-\Theta_D/bT} + \beta_N x^2 T^5. \quad (14)$$

Here, included (in order) are the boundary scattering, point defect (Rayleigh) scattering, 3-phonon Umklapp, and Normal phonon-phonon interactions through the adjustable parameters L , α , β_U , and β_N , respectively. To obtain a best fit to the data, b in the Umklapp expression is left as a further adjustable parameter, though decent fits are obtained by leaving it as a constant, i.e., $b = 3$.

For the boundary scattering term, the parameter L represents the Casimir length,⁷³ an effective phonon mean free path. For single

crystal materials, this is given by sample geometry. However, in the context of a polycrystalline aggregate such as this, it can be thought of as the grain size. This analysis gives a best fit when $L = 15.4 \text{ }\mu\text{m}$ which is in general agreement with the measured averaged grain size of $20.5 \text{ }\mu\text{m}$.

Point defect scattering gives a Rayleigh-like term of $\omega^4 \propto x^4 T^{-4}$. Klemens⁷⁴ then gives the relaxation time in terms of mass defect or isotope scattering. The fitting parameter α is then given by

$$\alpha = \left(\frac{k_B}{\hbar} \right)^4 \frac{V_0}{4\pi v^3} \Gamma, \quad (15)$$

where Γ is the scattering parameter due to mass fluctuations and is given by $\Gamma = \sum_i f_i \left(\frac{\Delta M_i}{M} \right)^2$. Here, f_i is the atomic fraction of the i th isotope whose mass is M_i . M is the average atomic mass and $\Delta M_i = |M - M_i|$. This expression must further be modified to include multiple atoms and can also be shown to include effects of strain field scattering.^{75,76} It is difficult to extract physical insights from this term as the matter is further complicated by the easy reduction of CeO_2 into off stoichiometric phases. In addition, as discussed below, analysis shows a nearly complete domination of the scattering by 3-phonon Umklapp processes. This analysis gives an $\alpha = 40.6 \text{ s}^{-1} \text{ K}^{-4}$. This value is similar to the fitting parameter given by Khafizov⁶⁹ as well as parameters used in analysis of high purity UO_2 and ThO_2 single crystals⁷⁷ indicating that the samples are of reasonably high quality.

Results indicate that the 3-phonon Umklapp process was the dominating factor with a value of $\beta_U = 7.31 \times 10^4 \text{ s}^{-1} \text{ K}^{-3}$. In order to obtain the best fit, b was allowed to vary with the best fit giving $b = 3.2$. Assuming the relation

$$\beta_U = \left(\frac{k_b}{\hbar} \right)^2 \frac{\hbar \gamma^2}{M v^2 \Theta_D}, \quad (16)$$

where γ is the Grüneisen parameter and a value of the average atomic mass $M = \rho V_0/N = 9.53 \times 10^{-23} \text{ g}$. These values suggest a Grüneisen parameter of 4.78 which is well beyond the 2.5 obtained by Khafizov *et al.* and the value of 1.24 for optical phonons. As the system temperature approaches the Debye temperature, the normal process becomes important. In order to bring the fitted function in line with the experimental data, an unphysical value of $-0.184 \text{ s}^{-1} \text{ K}^{-5}$ is obtained for β_N . The results for β_U and β_N clearly show the failure of this simple model in explaining the experimental data. Analyses using more complex models, while motivated by this work, are beyond its scope.

V. CONCLUSION

New experimental measurements of the heat capacity and thermal conductivity below 400 K joined with first principles calculations were performed. Experimentally, Raman spectroscopy was performed and the heat capacity was determined by adiabatic calorimetry, while the thermal conductivity was measured with a combination of square wave a.c. drift method (the Maldonado technique) and laser flash analysis. First principles calculations utilized Hubbard-corrected density functional perturbation theory using the PBESol functional. Furthermore, thermodynamic properties were calculated and reported using both the experimental data and DFPT/PBESol results.

Novel heat capacity data were acquired at low temperatures; the new data show a correction to the existing literature data and were used to calculate improved thermodynamic functions reported here. The standard values calculated at $T = 298.15$ K for heat capacity and entropy in this study were $63.4 \text{ J mol}^{-1} \text{ K}^{-1}$ and $61.1 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The heat capacity was examined in terms of the simple Debye model, yielding a Debye temperature of 455 K. DFPT/PBESol results were in good agreement with measured data and previously published literature. The entropy, enthalpy function, and Gibbs function were also tabulated from experimental data and theoretical predictions.

Thermal conductivity was examined using both laser flash analysis and the Maldonado technique. Room temperature values for the thermal conductivity are similar to those of other high quality CeO_2 samples. Finally, the thermal conductivity was analyzed in terms of the Klemens-Callaway model. The mean velocity of sound was determined to be 3610 m/s. At low temperatures, the thermal conductivity is dominated by 3-phonon Umklapp processes. However, heat conduction of CeO_2 is more complex than simple models that can account for and deserves further study in subsequent work.

This study provides a refreshed, accurate, and comprehensive thermodynamic picture of the bulk properties of CeO_2 in the low-temperature regime. Experimental results show excellent agreement with each other and the DFPT/PBESol calculations, reinforcing the accuracy of PBESol in describing properties of CeO_2 .

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the Debye temperature that was calculated by numerical integration of the Debye function in order to fit the Debye model exactly to the measured heat capacity data, as a function of temperature. No corrections have been made to account for thermal expansion of the lattice. The variation in Debye temperature reported here is similar to that of other ionic salts.^{71,72}

ACKNOWLEDGMENTS

The sample preparation presented here was conducted at the Los Alamos National Laboratory under the National Nuclear Security Administration Contract No. DE-AC52-06NA25396. Sandia National Laboratories is a multimission laboratory managed and operated by the National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-NA0003525. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government. Low-temperature experimental work in this study was supported by The Robert A. Welch Foundation (Grant No. A-0514), Houston, TX and TAMU-NSFC (Project No. 2014-30). S.O.W. and T.D.M. acknowledge support as a Welch Postdoctoral Fellow and a Welch Predoctoral Fellow, respectively, during most of this work. T.D.M. acknowledges support as a Charles F. Squire Graduate Fellow during part of this project. D.G.N. acknowledges long term research support from TRAWF. The authors would like to thank S. Banerjee for use of the Raman Spectrometer, T. E. G. Alivio

and N. A. Fler for their help performing Raman measurements, K. D. D. Rathnayaka for help with low-temperature measurements and useful discussions, and C. C. Hays, J. H. Ross, R. E. Allen, and T. Hughbanks for useful discussions. The authors are further indebted to M. Khafizov for freely sharing the data referenced in this study.

REFERENCES

- 1 C. Walkey, S. Das, S. Seal, J. Erlichman, K. Heckman, L. Ghibelli, E. Traversa, J. F. McGinnis, and W. T. Self, "Catalytic properties and biomedical applications of cerium oxide nanoparticles," *Environ. Sci.: Nano* **2**, 33–53 (2015).
- 2 S. Song, X. Wang, and H. Zhang, " CeO_2 -encapsulated noble metal nanocatalysts: Enhanced activity and stability for catalytic application," *NPG Asia Mater.* **7**, e179 (2015).
- 3 S. Logothetidis, P. Patsalas, E. Evangelou, N. Konofaos, I. Tsiaoussis, and N. Frangis, "Dielectric properties and electronic transitions of porous and nanostructured cerium oxide films," *Mater. Sci. Eng.: B* **109**, 69–73 (2004).
- 4 J. A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, and M. Perez, "Activity of CeO_x and TiO_x nanoparticles grown on Au(111) in the water-gas shift reaction," *Science* **318**, 1757–1760 (2007).
- 5 Q. Fu, H. Saltsburg, and M. Flytzani-Stephanopoulos, "Active nonmetallic Au and Pt species on ceria-based water-gas shift catalysts," *Science* **301**, 935–938 (2003).
- 6 H.-J. Beie and A. Gnörich, "Oxygen gas sensors based on CeO_2 thick and thin films," *Sens. Actuators, B* **4**, 393–399 (1991).
- 7 A. Goyal, M. P. Paranthaman, and U. Schoop, "The RABiTS approach: Using rolling-assisted biaxially textured substrates for high-performance YBCO superconductors," *MRS Bull.* **29**, 552–561 (2004).
- 8 M. S. Dresselhaus and I. L. Thomas, "Alternative energy technologies," *Nature* **414**, 332–337 (2001).
- 9 G. A. Deluga, "Renewable hydrogen from ethanol by autothermal reforming," *Science* **303**, 993–997 (2004).
- 10 S. Park, J. M. Vohs, and R. J. Gorte, "Direct oxidation of hydrocarbons in a solid-oxide fuel cell," *Nature* **404**, 265–267 (2000).
- 11 S. Mochizuki and F. Fujishiro, "The photoluminescence properties and reversible photoinduced spectral change of CeO_2 bulk, film and nanocrystals," *Phys. Status Solidi B* **246**, 2320–2328 (2009).
- 12 A. T. Nelson, D. R. Rittman, J. T. White, J. T. Dunwoody, M. Kato, K. J. McClellan, and A. M. White, "An evaluation of the thermophysical properties of stoichiometric CeO_2 in comparison to UO_2 and PuO_2 ," *J. Am. Ceram. Soc.* **97**, 3652–3659 (2014).
- 13 H. S. Kim, C. Y. Jeong, B. H. Lee, J. Y. Oh, Y. H. Koo, and P. Heimgartner, "Applicability of CeO_2 as a surrogate for PuO_2 in a MOX fuel development," *J. Nucl. Mater.* **378**, 98–104 (2008).
- 14 R. J. M. Konings, O. Benes, A. Kovacs, D. Manara, D. Sedmidubsky, L. Gorokhov, V. S. Iorish, V. Yungman, E. Shenyavskaya, and E. Osina, "The thermodynamic properties of the f-elements and their compounds. Part 2. The lanthanide and actinide oxides," *J. Phys. Chem. Ref. Data* **43**, 013101 (2014).
- 15 E. F. Westrum and A. F. Beale, "Heat capacities and chemical thermodynamics of cerium(III) fluoride and of cerium(IV) oxide from 5 to 300 K," *J. Phys. Chem.* **65**, 353–355 (1961).
- 16 I. Riess, M. Recken, and J. Nolting, "On the specific-heat of nonstoichiometric ceria," *J. Solid State Chem.* **57**, 314–322 (1985).
- 17 S. Gallagher and W. Dworzak, "Thermodynamic properties of cerium oxalate and cerium oxide," *J. Am. Ceram. Soc.* **68**, C206–C207 (1985).
- 18 R. Krishnan and K. Nagarajan, "Heat capacity measurements on uranium-cerium mixed oxides by differential scanning calorimetry," *Thermochim. Acta* **440**, 141–145 (2006).
- 19 F. A. Kuznetsov, T. N. Rezhukhina, and A. N. Golubenko, *Zhur. Fiz. Khim.* **34**, 2129 (1960).
- 20 E. G. King and A. U. Christensen, "High-temperature heat contents and entropies of cerium dioxide and columbium dioxide," Report No. 5789, U.S. Department of the Interior, Bureau of Mines, 1961.

- ²¹T. S. Yashvili, D. S. Tsagareishvili, and G. G. Gvelesiani, *Sov. Phys. Usp.* **10**, 409 (1967).
- ²²C. B. Gopal and A. van de Walle, "Ab initio thermodynamics of intrinsic oxygen vacancies in ceria," *Phys. Rev. B* **86**, 134117 (2012).
- ²³Z.-W. Niu, Y. Cheng, H.-Y. Zhang, and G.-F. Ji, "First-principles investigations on structural, phonon, and thermodynamic properties of cubic CeO₂," *Int. J. Thermophys.* **35**, 1601–1612 (2014).
- ²⁴Z.-W. Niu, Z.-Y. Zeng, C.-E. Hu, L.-C. Cai, and X.-R. Chen, "Study of the thermodynamic properties of CeO₂ from *ab initio* calculations: The effect of phonon-phonon interaction," *J. Chem. Phys.* **142**, 001601 (2015).
- ²⁵J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- ²⁶P. F. Weck and E. Kim, "Assessing Hubbard-corrected AM05+U and PBEsol+U density functionals for strongly correlated oxides CeO₂ and Ce₂O₃," *Phys. Chem. Chem. Phys.* **18**, 26816–26826 (2016).
- ²⁷J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, "Restoring the density-gradient expansion for exchange in solids and surfaces," *Phys. Rev. Lett.* **100**, 136406 (2008).
- ²⁸M. Wołczyr and L. Kepinski, "Rietveld refinement of the structure of CeOCl formed in Pd/CeO₂ catalyst: Notes on the existence of a stabilized tetragonal phase of La₂O₃ in LaPdO system," *J. Solid State Chem.* **99**, 409–413 (1992).
- ²⁹S. Riegel and G. Weber, "A dual-slope method for specific heat measurements," *J. Phys. E* **19**, 790–791 (1986).
- ³⁰O. Maldonado, "Pulse method for simultaneous measurement of electric thermopower and heat conductivity at low temperatures," *Cryogenics* **32**, 908–912 (1992).
- ³¹K. Suzuki, M. Kato, T. Sunaoshi, H. Uno, U. Carvajal-Nunez, A. Nelson, and K. McClellan, "Thermal and mechanical properties of CeO₂," *J. Am. Ceram. Soc.* **102**, 1994–2008 (2018).
- ³²G. Kresse and J. Hafner, "Ab initio molecular dynamics for liquid metals," *Phys. Rev. B* **47**, 558–561 (1993).
- ³³G. Kresse and J. Furthmüller, "Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set," *Phys. Rev. B* **54**, 11169–11186 (1996).
- ³⁴J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," *Phys. Rev. B* **46**, 6671–6687 (1992).
- ³⁵J. Buckeridge, D. O. Scanlon, A. Walsh, C. R. A. Catlow, and A. A. Sokol, "Dynamical response and instability in ceria under lattice expansion," *Phys. Rev. B* **87**, 214304 (2013).
- ³⁶S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, "Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study," *Phys. Rev. B* **57**, 1505–1509 (1998).
- ³⁷M. Cococcioni and S. de Gironcoli, "Linear response approach to the calculation of the effective interaction parameters in the LDA+U method," *Phys. Rev. B* **71**, 035105 (2005).
- ³⁸J. L. F. Da Silva, M. V. Ganduglia-Pirovano, J. Sauer, V. Bayer, and G. Kresse, "Hybrid functionals applied to rare-earth oxides: The example of ceria," *Phys. Rev. B* **75**, 045121 (2007).
- ³⁹S. Fabris, S. de Gironcoli, S. Baroni, G. Vicario, and G. Balducci, "Reply to 'Comment on "Taming multiple valency with density functionals: A case study of defective ceria,"'" *Phys. Rev. B* **72**, 237102 (2005).
- ⁴⁰J. L. F. Da Silva, "Stability of the Ce₂O₃ phases: A DFT+U investigation," *Phys. Rev. B* **76**, 193108 (2007).
- ⁴¹P. F. Weck, P.-A. Juan, R. Dingreville, and E. Kim, "Density functional analysis of fluorite-structured (Ce, Zr)O₂/CeO₂ interfaces," *J. Phys. Chem. C* **121**, 14678–14687 (2017).
- ⁴²P. E. Blöchl, "Projector augmented-wave method," *Phys. Rev. B* **50**, 17953–17979 (1994).
- ⁴³G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," *Phys. Rev. B* **59**, 1758–1775 (1999).
- ⁴⁴M. Methfessel and A. T. Paxton, "High-precision sampling for Brillouin-zone integration in metals," *Phys. Rev. B* **40**, 3616–3621 (1989).
- ⁴⁵L. Gerward, J. S. Olsen, L. Petit, G. Vaitheeswaran, V. Kanchana, and A. Svane, "Bulk modulus of CeO₂ and PrO₂—An experimental and theoretical study," *J. Alloys Compd.* **400**, 56–61 (2005).
- ⁴⁶H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations," *Phys. Rev. B* **13**, 5188–5192 (1976).
- ⁴⁷T. Hisashige, Y. Yamamura, and T. Tsuji, "Thermal expansion and Debye temperature of rare earth-doped ceria," *J. Alloys Compd.* **408–412**, 1153–1156 (2006).
- ⁴⁸S. J. Duclos, Y. K. Vohra, A. L. Ruoff, A. Jayaraman, and G. P. Espinosa, "High-pressure x-ray diffraction study of CeO₂ to 70 GPa and pressure-induced phase transformation from the fluorite structure," *Phys. Rev. B* **38**, 7755–7758 (1988).
- ⁴⁹A. Nakajima, A. Yoshihara, and M. Ishigame, "Defect-induced Raman spectra in doped CeO₂," *Phys. Rev. B* **50**, 13297–13307 (1994).
- ⁵⁰G. A. Kourouklis, A. Jayaraman, and G. P. Espinosa, "High-pressure Raman study of CeO₂ to 35 GPa and pressure-induced phase transformation from the fluorite structure," *Phys. Rev. B* **37**, 4250–4253 (1988).
- ⁵¹H. Ohura, M.Sc. thesis, University of Tohoku, 1977.
- ⁵²F. Marabelli and P. Wachter, "Covalent insulator CeO₂: Optical reflectivity measurements," *Phys. Rev. B* **36**, 1238–1243 (1987).
- ⁵³K. Clausen, W. Hayes, J. E. Macdonald, R. Osborn, P. G. Schnabel, M. T. Hutchings, and A. Magerl, "Inelastic neutron scattering investigation of the lattice dynamics of ThO₂ and CeO₂," *J. Chem. Soc., Faraday Trans. 2* **83**, 1109–1112 (1987).
- ⁵⁴N. L. Santha, M. T. Sebastian, P. Mohanan, N. M. Alford, K. Sarma, R. C. Pullar, S. Kamba, A. Pashkin, P. Samukhina, and J. Petzelt, "Effect of doping on the dielectric properties of cerium oxide in the microwave and far-infrared frequency range," *J. Am. Ceram. Soc.* **87**, 1233–1237 (2004).
- ⁵⁵W. H. Weber, K. C. Hass, and J. R. McBride, "Raman study of CeO₂: Second-order scattering, lattice dynamics, and particle-size effects," *Phys. Rev. B* **48**, 178–185 (1993).
- ⁵⁶A. Filtschew, K. Hofmann, and C. Hess, "Ceria and its defect structure: New insights from a combined spectroscopic approach," *J. Phys. Chem. C* **120**, 6694–6703 (2016).
- ⁵⁷C. Schilling, A. Hofmann, C. Hess, and M. V. Ganduglia-Pirovano, "Raman spectra of polycrystalline CeO₂: A density functional theory study," *J. Phys. Chem. C* **121**, 20834–20849 (2017).
- ⁵⁸A. Togo, F. Oba, and I. Tanaka, "First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures," *Phys. Rev. B* **78**, 134106 (2008).
- ⁵⁹P. Vinet, J. H. Rose, J. Ferrante, and J. R. Smith, "Universal features of the equation of state of solids," *J. Phys.: Condens. Matter* **1**, 1941–1963 (1989).
- ⁶⁰L. Gerward and J. S. Olsen, "Powder diffraction analysis of cerium dioxide at high pressure," *Powder Diffraction* **8**, 127–129 (1993).
- ⁶¹M. L. Gupta and S. Singh, "Thermal expansion of CeO₂, Ho₂O₃, and Lu₂O₃ from 100° to 300°K by an x-ray method," *J. Am. Ceram. Soc.* **53**, 663–665 (1970).
- ⁶²S. Sameshima, M. Kawaminami, and Y. Hirata, "Thermal expansion of rare-earth-doped ceria ceramics," *J. Ceram. Soc. Jpn.* **110**, 597–600 (2002).
- ⁶³S. Stecura and W. Campbell, "Thermal expansion and phase inversion of rare-earth oxides," Report No. 5847, U.S. Department of the Interior, Bureau of Mines, 1960.
- ⁶⁴D. Taylor, "Thermal expansion data: II. Binary oxides with the fluorite and rutile structures, MO₂, and the antifluorite structure, M₂O," *Br. Ceram. Trans. J.* **83**, 32–37 (1984).
- ⁶⁵R. Körner, M. Ricken, J. Nölting, and I. Riess, "Phase transformations in reduced ceria: Determination by thermal expansion measurements," *J. Solid State Chem.* **78**, 136–147 (1989).
- ⁶⁶J. Lashley, M. Hundley, A. Migliori, J. Sarrao, P. Pagliuso, T. Darling, M. Jaime, J. Cooley, W. Hults, L. Morales, D. Thoma, J. Smith, J. Boerio-Goates, B. Woodfield, G. Stewart, R. Fisher, and N. Phillips, "Critical examination of heat capacity measurements made on a quantum design physical property measurement system," *Cryogenics* **43**, 369–378 (2003).
- ⁶⁷J. B. Gruber, B. H. Justice, E. F. Westrum, Jr., and B. Zandi, "Revisiting the thermophysical properties of the A-type hexagonal lanthanide sesquioxides between temperatures of 5 K and 1000 K," *J. Chem. Thermodyn.* **34**, 457–473 (2002).

- ⁶⁸P. Debye, "Zur theorie der spezifischen wärmen," *Ann. Phys.* **344**, 789–839 (1912).
- ⁶⁹M. Khafizov, I.-W. Park, A. Chernatynskiy, L. He, J. Lin, J. J. Moore, D. Swank, T. Lillo, S. R. Phillpot, A. El-Azab, D. H. Hurley, and D. Clarke, "Thermal conductivity in nanocrystalline ceria thin films," *J. Am. Ceram. Soc.* **97**, 562–569 (2013).
- ⁷⁰J. Callaway, "Model for lattice thermal conductivity at low temperatures," *Phys. Rev.* **113**, 1046–1051 (1959).
- ⁷¹T. Barron, W. Berg, and J. Morrison, "The thermal properties of alkali halide crystals II. Analysis of experimental results," *Proc. R. Soc. London, Ser. A* **242**, 478–492 (1957).
- ⁷²M. Blackman, "On the relation of Debye theory and the lattice theory of specific heats," *Proc. R. Soc. London, Ser. A* **181**, 58–67 (1941).
- ⁷³H. Casimir, "Note on the conduction of heat in crystals," *Physica* **5**, 495–500 (1938).
- ⁷⁴P. G. Klemens, "The thermal conductivity of dielectric solids at low temperatures (theoretical)," *Proc. R. Soc. London, Ser. A* **208**, 108–133 (1951).
- ⁷⁵B. Abeles, "Lattice thermal conductivity of disordered semiconductor alloys at high temperatures," *Phys. Rev.* **131**, 1906–1911 (1963).
- ⁷⁶G. S. Nolas, J. L. Cohn, and G. A. Slack, "Effect of partial void filling on the lattice thermal conductivity of skutterudites," *Phys. Rev. B* **58**, 164–170 (1998).
- ⁷⁷K. Gofryk, S. Du, C. R. Stanek, J. C. Lashley, X. Y. Liu, R. K. Schulze, J. L. Smith, D. J. Safarik, D. D. Byler, K. J. McClellan, B. P. Uberuaga, B. L. Scott, and D. A. Andersson, "Anisotropic thermal conductivity in uranium dioxide," *Nat. Commun.* **5**, 4551 (2014).