New Insights into Phase Separation of Cerium Hydrides under Pressure

Xiaoqiu Ye,* Huan Li, and Shichang Li

ABSTRACT: We report theoretical calculations of the static ground-state structures and pressure-induced phase transformations of four cerium hydrides: CeH, CeH₂, CeH₂.₅, and CeH₃. Under pressure, the experimental CaF₂-type structure of CeH₂ is likely to disproportionate to face-centered cubic (fcc) Ce and a cubic Pm₃n (β-UH₄ type) structure of CeH₃ above 6 GPa. At further increasing pressures, fcc Ce will transform to a tetragonal I4/mmm structure above 12 GPa, while CeH₃ moves through the following sequence of phases: Pm₃n (β-UH₄ type) → Pm₃n (A1₅ type) → R3m; the corresponding transition pressures are calculated to be 10 and 70 GPa, respectively. The tetragonal I4/mmm structure of CeH₃ has the similar decomposition as that of CeH₂. Finding this previously unreported pressure-induced decomposition of CeH₂ will pave the way for investigations on the nature of hydrogen–metal interactions.

1. INTRODUCTION

Rare-earth metal hydrides are suitable compounds to study the hydrogen–metal interactions1,2 since they have various electronic and structural transitions depending on hydrogen concentration, such as metal–insulator transition (MIT), lattice contraction from dihydrides to trihydrides of rare-earth metals,3 and pressure-induced disproportionation of dihydrides.4

The formation of NaCl-type monohydride is likely a common behavior for the disproportionation of rare-earth metal dihydrides, as observed for LaH₂, YH₂, and ScH₂.4 We also found that NaCl-type monohydride of plutonium can also be formed by PuH₂ above 62 GPa on the basis of first-principles density functional theory.5 However, up to now, there is no direct study on the pressure-induced disproportionation of CeH₂. In fact, even the stable phases of CeH₂ and CeH₃ under pressure are still not very clear. Theoretically, Priyanga et al.6 predicted a structural phase transition from fcc (Fm̅3m, CaF₂ type) to hexagonal close-packed (hcp) (P6/mmc, AlB₂ type) of CeH₂ at 52 GPa, while for CeH₃, the phase transition pressure is about 4 GPa from fcc (Fm̅3m, BiF₃ type) to hcp (P6₃/mmc, LaF₃ type). Peng et al.7 also think that there is a phase transition from Fm̅3m to P6₃/mmc for CeH₂, but the transition pressure was predicted to be 33 GPa; CeH₃ will transform to the R3m phase from the fcc phase at around 50 GPa. Recently, Salké et al.8 found that pressurization of CeH₂ in the presence of H₂ up to 33 GPa did not result in any changes in the crystal structure. However, microsecond pulsed laser heating of ~2000 K carried out at 33 GPa resulted in the formation of β-UH₄-type Pm₃n CeH₃, which proved to be stable with further compression up to 80 GPa. Xin Li et al.9 think that further hydrogenation of CeH₂ to form CeH₃ can easily occur when H₂ is excessive in the diamond anvil cell (DAC) chamber since CeH₃ has a lower calculated enthalpy value than that of CeH₂. Above 33 GPa, the distorted fcc phase of CeH₃ gradually transfers to another new cubic phase (Pm₃n, A1₅ type), and A1₅ Pm₃n CeH₃ is stable up to 72 GPa in the presence of H₂. Li et al.10 predicted that CeH₃ can be stable until 39 GPa; for CeH₄, the A1₅-type Pm₃n phase transformed into the R3c phase at 53 GPa.

With this under consideration, the present work was devoted to check whether there is a pressure-induced disproportionation of CeH₂ by conducting a theoretical exploration of phase transformations of four cerium hydrides under pressure: CeH, CeH₂, CeH₂.₅, and CeH₃. The results may shed light on the fundamental principles for understanding the nature of hydrogen–metal interactions.

2. RESULTS AND DISCUSSION

2.1. Stabilities for Different Stoichiometries under Pressure. To predict stable phases in the Ce-H system, the enthalpies of candidate structures of CeHₙ (n = 1, 2, 2.₅, 3) found by us are plotted in a typical convex hull diagram, indicating compositions relative to Ce + solid H₂ at selected pressures, in Figure 1; this can be also seen in Figure S1 in the

Received: January 24, 2022
Accepted: March 22, 2022
Published: April 30, 2022
Supporting Information. We plotted previously predicted Ce polyhydrides in the diagram: CeH₄-I₄/mmm, CeH₅-P₆₃/mmc, CeH₆-P₆₃/mmc, CeH₇-P₆₃/mmc, and CeH₁₀-F₃m. It is important to consider the zero-point energies (ZPEs) when determining the energetics of systems containing light atoms, and the enthalpies plotted in Figure 1 also include ZPEs. The detailed enthalpy curves of CeHₙ (n = 1, 2, 2.5, 3) are listed in Figures S2–S5 in the Supporting Information.

As can be seen in Figure 1, CeH, CeH₂, CeH₂.₅, and CeH₃ are very stable with respect to decomposition into the elements. Indeed, CeH₂, CeH₂.₅, and CeH₃ are known experimentally, and as expected, they are all stable at 1 atm. CeH₂ is the global thermodynamic minimum at 1 atm, while CeH₃ achieves a global thermodynamic minimum above 6 GPa. This is consistent with the experimental observation. Similar to the monohydride of La, Y, and Sc being stable at high pressures, CeH is stable but in a very narrow pressure range near 6 GPa.

Interestingly, CeH, CeH₂, and CeH₂.₅ will decompose into Ce and CeH₃ above 6 GPa through disproportionation reactions. Pure Ce can be obtained by squeezing cerium hydrides, which has not been reported before to the best of our knowledge. On the other hand, it also indicates that CeH₂ will decompose before undergoing any crystal structural changes above 10 GPa, not like the previous suggestions that CeH₂ is stable up to 33 GPa. Figure 2 shows, in another way, the range of stabilities of different stoichiometries of cerium hydrides. All the thermodynamically stable phases are also dynamically stable (see Figures S9–S12). Interestingly, we found that Pm₃m CeH₂ is not dynamically stable above 20 GPa (see Figure S10a), which also indicates that CeH₂ may undergo pressure-induced phase transitions or disproportionation reactions.

We will return to the interconversions between the various structures after presenting initial discussion of the calculated structural types.

2.2. Predicted CeHₙ (n = 1, 2, 2.5, 3) Structures. CeHₙ, CeH₂.₅, and CeH₃ are the experimentally known cerium hydrides. The structure search readily reproduced the observed structure of CeH₂ and CeH₂.₅ at 1 atm. At 1 atm, CeH₃ adopts the CaF₂-type crystal structure (Fm₃m, Z = 4, Figure 3a). All hydrogens occupy the tetrahedral holes of the fcc lattice. The calculated Ce–H separations of 2.35 Å match the experimental crystallographic values at P = 1 atm. CeH₂.₅ adopts the tetragonal I₄/m structure (Z = 8, Figure 3b). This structure is similar to an alternative combination of fcc CeH₂ and fcc CeH₃. Hydrogens occupy the tetrahedral (T) and octahedral (O) holes of the lattice with Ce–H separations between 2.32 and 2.71 Å at 1 atm. This is in accordance with the trend that extra H atoms enter into the octahedral interstices during the formation of continuous solid solution CeHₓ (2.0 < x < 3.0).

Interestingly, at 1 atm, we find several new structures that are calculated to be more stable than the suggested Pm₃m CeH₃ (Z = 4, Figure 3c), and Pm₃m CeH₃ is also dynamically unstable under atmospheric pressure (see Figure S12a). The most stable phase we calculate is the cubic Pm₃n (β-UH₃ type) structure (Z = 8, Figure 3d), in which hydrogen atoms are tetrahedrally coordinated by Ce, with Ce–H separations between 2.32 and 2.39 Å at 1 atm. β-UH₃-type CeH₃ was also found recently in the experiment of Salke. However, compared with Pm₃m CeH₃, Pm₃n CeH₃ can be easily synthesized by the reaction of cerium and hydrogen at normal pressure. We doubt that there may be a kinetic barrier to the transition between Pm₃n CeH₃ and Pm₃m CeH₃. This requires further research. As we know, one of the attractive structural properties exists in the Ce–H system is the lattice contraction from CeH₂ to CeH₃. The predicted structures of CeH₂, CeH₂.₅, and CeH₃ reproduce this experimental observation well.

Above 10 GPa, the β-UH₃-type Pm₃n structure transformed to the A15 type Pm₃n structure (Z = 2, Figure 4a), in which hydrogen atoms are also tetrahedrally coordinated by Ce, with...
Ce-H separations of 2.13 Å at 50 GPa. The hexagonal $R\bar{3}m$ structure (Figure 4b) becomes thermodynamically stable relative to the A15-type $Pm\bar{3}m$ structure at 70 GPa, in which hydrogen atoms are tetrahedrally and octahedrally coordinated by Ce, with Ce-H separations between 2.03 and 2.27 Å at 100 GPa. The evolution of H coordination in CeH₃ with increasing pressure, from tetrahedral to octahedral, is consistent with the anticipated generalization that the number of neighbors of a
hydrogen-occupied site is likely to increase with increasing pressure. Note that especially, the hexagonal $R\overline{3}c$ ($Z = 6$, Figure 4c) structure reported by Li et al.\textsuperscript{10} is the metastable phase, and depending on the tolerance used in the automated symmetry assignment (CASTEP with tolerance larger than 0.01), the program assigns the $R\overline{3}c$ structure to the A15-type $Pm\overline{3}n$ symmetry below 80 GPa.

The ground-state static phase transition sequence of CeH\textsubscript{2} during the pressure increase to 100 GPa is $Fm\overline{3}m$ $\rightarrow$ $P4/nmm$ (tetragonal, $Z = 2$, Figure 5a) $\rightarrow$ $C2/m$ (monoclinic, $Z = 4$, Figure 5b) $\rightarrow$ $P6/mmm$ (MgB\textsubscript{2}-type, $Z = 1$, Figure 5c); the corresponding transition pressures are 10, 24, and 95 GPa with ZPEs included, respectively (see Figure S3). These similar high pressure phases of CeH\textsubscript{2} also emerged in ScH\textsubscript{2}.\textsuperscript{13}

As expected, we reproduced the previously suggested rock-salt structure for CeH\textsubscript{2} at 1 atm ($Z = 4$, Figure 6b) with hydrogen atoms octahedrally coordinated by Ce. At 15 GPa, a new static structure emerges. This is a hexagonal $P63/mmc$ structure ($Z = 2$, Figure 6c), in which hydrogen atoms are also octahedrally coordinated by Ce, with Ce-H separations of 2.32 Å at 20 GPa. Above ~50 GPa, the cubic $Pm\overline{3}m$ structure ($Z = 1$, Figure 6d) becomes thermodynamically stable relative to the $P63/mmc$ structure, in which hydrogen atoms are body-centered by Ce, with Ce-H separations of 2.33 Å at 50 GPa.

### 2.3. Disproportions

With the phase transition sequences of CeH, CeH\textsubscript{2}, CeH\textsubscript{2.5}, and CeH\textsubscript{3} in hand (see Figures S2–S5), we can approach the pressure dependence of the CeH\textsubscript{2} disproportionation reaction. Figure 7 compares the enthalpies of the reactions

\[
\text{CeH}_{2} \rightarrow \frac{1}{2}\text{CeH} + \frac{1}{2}\text{CeH}_{3}
\]

\[
\text{CeH}_{2} \rightarrow \frac{1}{3}\text{Ce} + \frac{2}{3}\text{CeH}_{3}
\]

with and without ZPEs. Positive enthalpies mark a region of stability of CeH\textsubscript{3}, and negative ones mark that of CeH + CeH\textsubscript{3} or Ce + CeH\textsubscript{3}.

Figure 7 shows that CeH\textsubscript{2} is enthalpically stable below 5 GPa but becomes unstable compared to Ce, CeH\textsubscript{3}, and CeH\textsubscript{3} at higher pressure. Pure Ce can be formed by the pressure-induced disproportionation of CeH\textsubscript{2} above 6 GPa. This is different from the case of MH\textsubscript{2} (M = Sc, Y, and La),\textsuperscript{4} in which MH\textsubscript{2} decomposed to MH and MH\textsubscript{3} under high pressure; no pure metal was found. Note that especially, Salke et al.\textsuperscript{8} found that pressurization of CeH\textsubscript{2} in a H\textsubscript{2} atmosphere up to 33 GPa did not result in any changes in the crystal structure. This is not in accordance with our results and the phenomenon of disproportionation reactions of MH\textsubscript{2} (M = Sc, Y, and La).\textsuperscript{4} In the case of excessive H\textsubscript{2}, CeH\textsubscript{2} can easily react with H\textsubscript{2} to form CeH\textsubscript{3}, which was also confirmed by the experiment of Li.\textsuperscript{9} Salke\textsuperscript{8} found that the mixture of CeH\textsubscript{2} and H\textsubscript{2} up to 33 GPa did not result in any changes in X-ray diffraction (XRD) spectra, which may be due to the difficulty in distinguishing the XRD peaks between CeH\textsubscript{2} and CeH\textsubscript{3}. In this work, CeH\textsubscript{2} was pressurized alone in the absence of H\textsubscript{2}, and it is found that when the pressure reaches a certain value, CeH\textsubscript{2} will decompose to form Ce and CeH\textsubscript{3}.

Interestingly, CeH\textsubscript{2.5} also has a similar disproportionation trend as that of CeH\textsubscript{2} (see Figure S7). Our results confirmed that the disproportionation reactions of MH\textsubscript{2+\textsuperscript{x}} (M = rare-earth metals, 0 ≤ x < 1) under high pressure are likely common behaviors. However, for CeH\textsubscript{2+\textsuperscript{x}} (0 ≤ x < 1), pure Ce can be formed under high pressure due to the disproportionation reaction. Indeed, CeH\textsubscript{2} is stable but in a very narrow pressure range near 6 GPa (see Figures 2 and S6), which is to say that CeH\textsubscript{2} or CeH\textsubscript{2.5} is likely to disproportionate to CeH and...
CeH₃, and then, CeH continues to disproportionate to Ce and CeH₂ as shown in Figure S6.

To elucidate the mechanisms for the pressure-induced disproportionation of CeH₂, leading to the formation of Ce and CeHₙ, we examined the evolution of the internal energy (U) and the product of pressure and volume (PV), which contribute to the enthalpy (H = U + PV) of the pertinent material systems and phases in response to pressure change. We show in Figure 8 the pressure dependence of ΔU, Δ(PV), and ΔH, defined as the values for the mixture of 1/3 Ce + 2/3 CeH₂ relative to that for CeH₂, which are set to zero. It is seen clearly that the transition from CeH₂ to the 1/3 Ce + 2/3 CeH₂ mixture is caused by the decrease in the internal energy of the latter; meanwhile, the PV term rises with increasing pressure, although its large negative magnitude is still the main contributor to the overall negative relative enthalpy around the phase transition pressure. Between 10 and 30 GPa, both the U and PV terms make similar contributions to lowering the enthalpy. After 35 GPa, the large negative magnitude of U overcompensates for the increasing PV term, resulting in the stabilization of the 1/3 Ce + 2/3 CeH₂ mixture relative to CeH₂.

For Ce–Ce separations, the number of nearest neighbors in Ce (I4/mmm, Z = 2) is larger than that of CeH₂ (C2/m, Z = 4) at 50 GPa, as shown in Figure S13a, while for Ce-H, the number of nearest neighbors in CeH₃ (A15 type Pm3m, Z = 2) is larger than that of CeH₂ (C2/m, Z = 4) at 50 GPa (see Figure S13b). It indicates that compared with CeH₂, the Ce–Ce bonding in the I4/mmm phase of Ce and the Ce–H bonding in the Pm3m phase of CeH₂ may increase as well. We then calculated the projected crystal orbital Hamilton population (pCOHP)¹⁴ between Ce–Ce, Ce–H, and H–H pairs in Ce, CeH₂, and CeH₃ all at 50 GPa, as shown in Figure S14. Compared with CeH₂, the Ce–Ce bonding in the I4/mmm phase of Ce and the increasing Ce–H bonding in the Pm3m phase of CeH₂ may play an important role in the phase transition and stabilization. The calculated electronic structures show that each phase of CeHₙ (n = 1, 2, 2.5, 3) is metallic. Hydrogen in CeH₁ (n = 1, 2, 2.5, 3) has the form of H²− (δ = 0.55−0.72), as can be seen in Table S1. Histograms (Figure S13) also show that the nearest distance of H–H in CeHₙ (n = 1, 2, 2.5, 3) is around 2 Å. Thus, no cage-like structure of hydrogen is formed as reported in cerium polyhydrides.

3. CONCLUSIONS

In summary, we have explored pressure-induced phase transformations of four cerium hydrides: CeH₁, CeH₂, CeH₂.₅, and CeH₃. We find an unusual circumstance; CeH₁, CeH₂, and CeH₂.₅ will decompose into Ce and CeH₂ above 6 GPa through disproportionation reactions. Pure Ce can be obtained by squeezing cerium hydrides, which is different from the case of MH₃ (M = Sc,Y, and La), in which MH₃ decomposed to MH and MH₂ under high pressure; no pure metal was found. Indeed, CeH₂ or CeH₂.₅ is also likely to disproportionate to CeH and CeH₃, and then, CeH continues to disproportionate.
to Ce and CeH₂ since CeH is only stable in a very narrow pressure range near 6 GPa. The increasing Ce—Ce bonding in pure Ce and the increasing Ce—H bonding in CeH₂ may play an important role in the disproportionation reactions of CeHₓ, CeH₂, and CeH₂.₅. The theoretical work indicates that pure metal and its higher hydrides may also be obtained in other metal—hydrogen system.

4. METHODS AND COMPUTATIONAL DETAILS

We searched extensively for CeHₓ (n = 1, 2, 2.5, 3) ground-state structures at 0 K using the particle swarm optimization methodology implemented in the CALYPSO code.¹⁵ This method has been applied successfully to a wide range of crystalline systems ranging from elemental solids to binary and ternary compounds.¹⁵ Our structure searches with system sizes containing up to 6 formula units (fu) per simulation cell were performed at pressures of 0–100 GPa. Each generation contains 30 structures. We usually follow 50 generations to achieve a converged structure.

The underlying structural relaxations were carried out at 0 K using density functional theory using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional¹⁶ as implemented in the VASP code.¹⁷ The projector-augmented wave method¹⁸ was adopted, with 1s¹ (cutoff radius of 1.1a₀) and 5s²5p⁴5d²6s² (cutoff radius of 2.7a₀) treated as valence electrons for H and Ce, respectively. An energy cutoff of 800 eV and dense Monkhorst–Pack¹⁹ k-meshes with a grid spacing of 2a₀×0.03 A⁻¹ gave good convergence of the structural relaxations (see Figure S16). Phonon calculations were carried out using VASP in conjunction with the PHONOPY code.²⁰ Given the light hydrogens in the structure, vibrational properties of cerium and praseodymium hydrogen system REHₓ can be calculated by phonon calculations. Presently, we have investigated a wide range of cerium–hydrogen systems.

Theoretical cerium–hydrogen phase diagram, enthalpy curves, phonon densities of states, electronic properties, structural parameters, and supporting calculation details (PDF)

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00487. Theoretical cerium—hydrogen phase diagram, enthalpy curves, phonon densities of states, electronic properties, structural parameters, and supporting calculation details (PDF)

AUTHOR INFORMATION

Corresponding Author
Xiaoqu Ye — Science and Technology on Surface Physics and Chemistry Laboratory, Mianyang 621908, China; orcid.org/0000-0003-4075-8556; Email: xiaquigood@sina.com

Authors
Huan Li — Science and Technology on Surface Physics and Chemistry Laboratory, Mianyang 621908, China
Shichang Li — School of Science, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00487

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to Roald Hoffmann from Cornell University, Martin Rahm from Chalmers University of Technology, Hui Wang from Jilin University, and Li Huang, Ce Ma, Xiao Tan, Liuhua Xie, and Ruizhi Qiu from Science and Technology on Surface Physics and Chemistry Laboratory for their discussions. We acknowledge the support by the National Natural Science Foundation of China (Grants Nos. 21401173, 21371160, and 11305147).

REFERENCES

(1) Sun, W.; Kuang, X.; Keen, H. D. J.; Lu, C.; Hermann, A. Second group of high-pressure high-temperature lanthanide polyhydride superconductors. Phys. Rev. B 2020, 102, No. 144524.
(2) Chen, W.; Semenok, D. V.; Huang, X.; Shu, H.; Li, X.; Duan, D.; Cui, T.; Ogano, A. R. High-Temperature Superconducting Phases in Cerium Superhydride with a Tc up to 115 K below a Pressure of 1 Megabar. Phys. Rev. Lett. 2021, 127, No. 117001.
(3) Ao, B. Y.; Wang, X. L.; Shi, P.; Chen, P. H.; Ye, X. Q.; Lai, X. C.; Ai, J. J.; Gao, T. Lattice contraction of cerium hydrides from first-principles LDA + U calculations. Int. J. Hydrog. Energy 2012, 37, 5108–5118.
(4) Machida, A.; Honda, M.; Hattori, T.; Sano-Furukawa, A.; Watanuki, T.; Katayama, Y.; Aoki, K.; Komatsu, K.; Arima, H.; Ohshita, H.; et al. Formation of NaCl-Type Monodeuteride LaD by the Disproportionation Reaction of LaD₂. Phys. Rev. Lett. 2012, 108, No. 205501.
(5) Li, S. C.; Ao, B. Y.; Ye, X. Q.; Qiu, R. Z.; Gao, T. New insights into the crystal structures of plutonium hydrides from first-principles calculations. J. Phys. Chem. C 2018, 122, 10103–10112.
(6) Priyanga, G. S.; Rajeswarapalanichamy, R.; Iyakutti, K. First principles study of structural, electronic, elastic and magnetic properties of cerium and praseodymium hydrogen system REHₓ (RE: Ce, Pr and x = 2, 3). J. Rare Earths 2015, 33, 289–303.
(7) Peng, F.; Sun, Y.; Pickard, C. J.; Needs, R. J.; Wu, Q.; Ma, Y. M. Hydrogen Clathrate Structures in Rare Earth Hydrides at High Pressures: Possible Route to Room-Temperature Superconductivity. Phys. Rev. Lett. 2017, 119, No. 107001.
(8) Salke, N. P.; Davari Esfahani, M. M.; Zhang, Y.; Kruglov, I. A.; Zhou, J.; Wang, Y.; Greenberg, E.; Prakapenka, V. B.; Liu, J.; Ogano, A. R.; Lin, J. F. Synthesis of clathrate cerium superhydride CeH₄ at 80-100 GPa with atomic hydrogen sublattice. Nat. Commun. 2019, 10, No. 4453.
(9) Li, X.; Huang, X.; Duan, D.; Pickard, C. J.; Cui, T.; et al. Polyhydride CeH₄ with an atomic-like hydrogen clathrate structure. Nat. Commun. 2019, 10, No. 3461.
(10) Li, B.; Miao, Z. L.; Ti, L.; Liu, S. L.; Chen, J.; Shi, Z. X.; Gregoryanz, E. Predicted high-temperature superconductivity in cerium hydrides at high pressures. J. Appl. Phys. 2019, 126, No. 235901.
(11) Labet, V.; Hoffmann, R.; Ashcroft, N. W. A fresh look at dense hydrogen under pressure. III. Two competing effects and the resulting intra-molecular H-H separation in solid hydrogen under pressure. J. Chem. Phys. 2012, 136, No. 074503.
(12) Manchester, F. D.; Pitre, J. M. The Ce-H (cerium-hydrogen) system. J. Phase Equilib. 1997, 18, No. 63.
(13) Ye, X. Q.; Hoffmann, R.; Ashcroft, N. W. Theoretical Study of Phase Separation of Scandium Hydrides under High Pressure. J. Phys. Chem. C 2015, 119, 5614–5625.
(14) Maintz, S.; Deringer, V. L.; Tchougréeff, A. L.; Dronskowski, R. LOBSTER: A tool to extract chemical bonding from plane-wave based DFT. J. Comput. Chem. 2016, 37, 1030–1035.
(15) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. Crystal structure prediction via particle-swarm optimization. Phys. Rev. B 2010, 82, No. 094116.
(16) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(17) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(18) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(19) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(20) Togo, A.; Oba, F.; Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures. *Phys. Rev. B* **2008**, *78*, No. 134106.