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Novel phase of beryllium fluoride at high pressure

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A previously unknown thermodynamically stable high-pressure phase of BeF2 has been predicted using the evolutionary algorithm USPEX. This phase occurs in the pressure range 18–27 GPa. Its structure has C2/c space group symmetry and contains 18 atoms in the primitive unit cell. Given the analogy between BeF2 and SiO2, silica phases have been investigated as well, but the new phase has not been observed to be thermodynamically stable for this system. However, it is found to be metastable and to have comparable energy to the known metastable phases of SiO2, suggesting a possibility of its synthesis.

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I. INTRODUCTION

Beryllium fluoride has many applications, such as coolant component in molten salt nuclear reactors, production of special glasses, manufacture of pure beryllium, etc. Structurally, BeF2 phases are similar to the phases of SiO2 (Fig. 1): α-quartz phase of BeF2 and SiO2 is stable from 0 to ~2 GPa, and then transforms to coesite phase which persists up to ~8 GPa, and then transforms to stishovite (rutile-type phase) in SiO2. However, the behavior of BeF2 experimentally is not known for pressures above 8 GPa (see Scheme I in Ref.7).

Beryllium compounds are extremely toxic for humans, and this limits experimentation. Computer simulation is a safe and cheap alternative to investigate such structures. In recent ab initio study8 authors explored 13 well-known AB2 structure types for their possible stability for BeF2: α-quartz-type (P3121), β-quartz-type (P6222), α-cristobalite-type (P41212), β-cristobalite-type (Fd-3m), cubic CaF2-type (Fm-3m), α-PbCl2-type (Pnna), Ni2In-type (P63/mmc), coesite-type (C2/c), rutile-type (P4/nmm), baddeleyite-type (P21/c), α-PbO2-type (Pbcn), α-CaCl2-type (Pnnm) and pyrite-type (Pa-3) structures. They found that the sequence of pressure-induced phase transitions of BeF2 up to 50 GPa is as follows: α-quartz-type → 6.47 GPa → coesite-type → rutile-type → 24.94 GPa → α-PbO2-type structures. Although BeF2 under pressure has been theoretically investigated by Yu et al.8, we revisit these results to check for previously unknown structure(s), and we explore the relevance of these findings for SiO2. Moreover, recently there has been a renewed interest on the phase diagram of other related fluoride (CaF2, SrF2, BaF2) and oxide (UO2) materials9,10 at high-P and high-T conditions, and our results may be relevant to the possibility of new superionic phases.

II. COMPUTATIONAL DETAILS

Computer simulations of BeF2 and SiO2 has been performed in two steps: (1) prediction of a new structure of BeF2 using USPEX evolutionary algorithm; (2) calculation of properties of BeF2 and SiO2 in the wide range

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**FIG. 1.** Phase diagrams of SiO2 and BeF2 at low (up to room) temperatures.

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of pressures from 0 to 50 GPa with a 1 GPa step using DFT.

To find stable lowest-energy crystals structures, we performed fixed-composition search of the BeF$_2$ system at different pressures (15, 20 and 25 GPa) using the USPEX code$^{11-13}$, in conjunction with first-principles structure relaxations using density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)$^{14}$, as implemented in the VASP package$^{15}$. We employed projector augmented wave (PAW)$^{16}$ potentials with 2 valence electrons for Be and 7 — for F. The wave functions were expanded in a plane-wave basis set with the kinetic energy cutoff of 600 eV and Γ-centered meshes for Brillouin zone sampling with reciprocal space resolution of $2\pi \times 0.10$ Å$^{-1}$.

We used the VASP package to carefully reoptimize the obtained structures before calculating phonons, elasticity, electronic density of states (DOS), hardness of BeF$_2$ and SiO$_2$. For these relaxations, we also used the plane-wave cutoff of 600 eV and $k$-meshes with resolution of 0.10 Å$^{-1}$. Phonons calculations have been performed using Phonopy$^{17}$ and Quantum Espresso$^{18}$ codes for the relaxed structures at pressures where these structures are found to be thermodynamically stable. Hardness was calculated using 3 methods: Lyakhov-Oganov model$^{19}$ based on the strength of bonds between atoms and bond network topology, Chen-Niu model$^{20}$ which uses elastic constants obtained from DFT calculations and Mukhanov-Kurakevych-Solozhenko thermodynamic model of hardness$^{21}$.

### III. RESULTS AND DISCUSSION

USPEX allowed us to find a new structure of BeF$_2$, stable at 18–27 GPa (Fig. 2). The structure has C2/c space group and contains 12 formula units in the Bravais cell (6 in the primitive cell) with $a=8.742$ Å, $b=8.695$ Å, $c=4.178$ Å and $\beta=66.1^\circ$ (at 20 GPa). Calculated density of this new C2/c phase is 4.2% higher than density of coesite phase, both at 20 GPa. For reference, here are lattice parameters for BeF$_2$-stishovite at 30 GPa: $a=b=3.986$ Å, $c=2.501$ Å and $\alpha=\beta=\gamma=90^\circ$. The value of the bulk modulus $B_0=22.7$ GPa of the C2/c structure of BeF$_2$ with its pressure derivative $B'_0=3.9$ was obtained from a least-squares fit using the Murnaghan equation of state$^{22}$ (Fig. 3). The zero-pressure unit cell volume was taken as $V_0=213.7$ Å$^3$.

#### A. Thermodynamic stability

We have calculated the enthalpies of α-quartz (P3$_2$1), coesite (C2/c), coesite-II (C2/c), stishovite (P4$_2$/mnm), α-PbO$_2$-type (P6cm) structure and our new structure (C2/c) for both BeF$_2$ and SiO$_2$ at different pressures from 0 to 50 GPa with a 1 GPa step. The results are presented in Fig. 4.

#### 1. BeF$_2$ under pressure

For the case of BeF$_2$ α-quartz structure is stable from 0 to 4 GPa, followed by coesite structure stable from 4 to 18 GPa, and the C2/c structure is found to be stable between 18 and 27 GPa, which then gives place to stishovite structure at higher pressures (Fig. 4(a)). We see transition from coesite-type to C2/c, then to rutile-type, but at much higher pressure (27 GPa against 6.47 GPa in Ref.$^8$, where LDA was used). According to Demuth et al.$^{23}$, the LDA approximation used in Ref.$^8$ underestimates phase transition pressures, whereas using the GGA yields more reliable results. The α-PbO$_2$-type structure is not stable at any pressure (in the investigated interval from 0 to 50 GPa) for BeF$_2$ (though it is close to stability at ~27 GPa), while for SiO$_2$ it is indeed stable at pressures above ~80–90 GPa$^{24}$.

#### 2. SiO$_2$ under pressure

From Fig. 4(b) it is clearly seen that in SiO$_2$ the transition from α-quartz to coesite occurs at 5 GPa, followed by transformation to stishovite at ~7 GPa, which continues to be stable up to 50 GPa. This phase transition sequence is in good agreement with experiments$^9$ and
3. Metastable structures of SiO$_2$

It is well known that SiO$_2$ α-quartz is thermodynamically stable at ambient pressure. However, there are numerous known SiO$_2$ polymorphs which are metastable, but exist in nature or can be synthesized. We examined SiO$_2$ feldspar, baddeleyite, melanoplogite and moganite at 0 GPa. El Goresy et al.\textsuperscript{27} claimed a baddeleyite-like post-stishovite phase of silica in the Shergotty meteorite, however later that controversial phase turned out to be α-PbO$_2$-like silica\textsuperscript{28}. Our calculations confirm that the baddeleyite-like form of SiO$_2$ is very unfavorable at 0 GPa and spontaneously (barrierlessly) transforms into the α-PbO$_2$-like structure. We have found that SiO$_2$-feldspar, moganite and melanoplogite are energetically very close to the stable phase (α-quartz) and to the new C2/c structure. Differences in enthalpy between melanoplogite, the new structure and α-quartz are less than 20 meV/f.u. (see Fig. 4(b)). The fact that complex open structure of melanoplogite (138 atoms/cell) has a slightly lower energy than α-quartz, can be explained by errors of the GGA, which were discussed in details by Demuth et al.\textsuperscript{23}. They also found β-cristobalite (Fig. 4(b)) is lower in energy by about 30 meV/SiO$_2$ than α-quartz, confirmed by calculations of Zhang et al.\textsuperscript{29}, showing that the GGA slightly overstabilizes low-density structures.

B. Lattice dynamics

Since the new structure of BeF$_2$ appears to be thermodynamically stable, analysis of dynamical stability (phonon dispersion) has been performed for this structure as well as for all other structures at pressures where they were found to be thermodynamically stable. Our results show that BeF$_2$ α-quartz at 0 GPa, coesite at 5 GPa, new structure at 25 GPa and stishovite at 30 GPa do not have imaginary frequencies. Similar results are observed for SiO$_2$ α-quartz at 0 GPa, coesite at 5 GPa and stishovite at 10 GPa. Fig. 5 shows dynamical stability of the new structure of BeF$_2$ since no imaginary frequencies are observed in the phonon dispersion plot.

C. Electronic properties

According to Fig. 6, all BeF$_2$ phases are insulators, the DFT band gap increases from ~7 to ~10 eV with increasing pressure from 0 to 30 GPa and the value of the gap is in good agreement with data of Yu et al.\textsuperscript{8}.

For SiO$_2$ (Fig. 7) we also observe insulating behavior, and the band gap is about 6 eV and remains almost unchanged with increasing pressure.
FIG. 5. Phonons dispersion curves showing dynamical stability of the C2/c structure of BeF₂ at 25 GPa.

FIG. 6. Density of states of BeF₂ in the α-quartz (at 0 GPa), coesite (at 5 GPa), C2/c structure (at 25 GPa), and stishovite (at 30 GPa) phases.

D. Hardness

Three models have been exploited to calculate hardnesses — the Lyakhov-Oganov\textsuperscript{19}, Chen-Niu\textsuperscript{20} and Mukhanov-Kuravevych-Solozhenko\textsuperscript{21} models. First approach is based on concepts of bond strengths and bond topology to compute hardness. Detailed description of the methodology can be found in Ref.\textsuperscript{19}. This model has been implemented in the USPEX code, and for greater convenience has also been implemented as an online utility available at \url{http://han.ess.sunysb.edu/hardness/}. The second method of hardness calculation is Chen-Niu model, which is based on elastic tensor components and also implemented in the USPEX code. The third one is a thermodynamic model of hardness.

The results can be seen in Table I. Experimental data are provided where available — Vickers hardness of SiO₂-quartz\textsuperscript{20}, SiO₂-coesite\textsuperscript{21} and SiO₂-stishovite\textsuperscript{21}. From Table I it is clearly seen that the calculated hardness of SiO₂ quartz and stishovite is much higher than one of BeF₂ analogs. The hardness of BeF₂ and SiO₂ in the new C2/c structure is comparable with the hardness of α-quartz and coesite.

IV. CONCLUSIONS

We have examined thermodynamic, vibrational, electronic and elastic properties of BeF₂ and SiO₂ phases using DFT calculations. The sequence of pressure-induced phase transitions of BeF₂ up to 50 GPa is as follows: α-quartz-type → C2/c → stishovite (rutile-type) structures. We found a new phase of BeF₂ which is thermodynamically stable at pressures from 18 to 27 GPa. This phase is not observed in SiO₂, but could be synthesized in principle. Electronic properties analysis has shown BeF₂ and SiO₂ remain insulating in a wide range of pressures (from 0 to 50 GPa). Hardness of BeF₂ and SiO₂ in the new structure is comparable with hardness of α-quartz and coesite at 0 GPa. Hardnesses of metastable SiO₂ structures have been examined as well.
TABLE I. Hardness of BeF$_2$ and SiO$_2$ structures at 0 GPa in GPa. For the metastable SiO$_2$ structures we present enthalpies relative to $\alpha$-quartz (in meV per formula unit).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lyakhov-Oganov</th>
<th>Chen-Niu</th>
<th>Mukhanov et al. $^a$</th>
<th>Lyakhov-Oganov</th>
<th>Chen-Niu</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>7.1</td>
<td>7.5</td>
<td>11.0</td>
<td>20.0</td>
<td>12.5</td>
<td>12.0$^b$</td>
</tr>
<tr>
<td>Coesite</td>
<td>8.2</td>
<td>8.3</td>
<td>11.7</td>
<td>22.3</td>
<td>8.4</td>
<td>20.0$^b$</td>
</tr>
<tr>
<td>New structure</td>
<td>7.3</td>
<td>6.8</td>
<td>13.5</td>
<td>19.1</td>
<td>6.7</td>
<td>—</td>
</tr>
<tr>
<td>Stishovite</td>
<td>8.2</td>
<td>12.7</td>
<td>15.1</td>
<td>29.0</td>
<td>28.7</td>
<td>33.0$^b$</td>
</tr>
</tbody>
</table>

Metastable structures (SiO$_2$ only):

<table>
<thead>
<tr>
<th>Structure</th>
<th>Relative enthalpy, meV/f.u.</th>
<th>Hardness, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feldspar</td>
<td>47</td>
<td>6.7</td>
</tr>
<tr>
<td>Baddeleyite</td>
<td>726</td>
<td>29.6</td>
</tr>
<tr>
<td>Melanophlogite</td>
<td>−13</td>
<td>12.5</td>
</tr>
<tr>
<td>Moganite</td>
<td>3</td>
<td>19.5</td>
</tr>
</tbody>
</table>

$^a$ Thermodynamic model of hardness (Ref.21)

$^b$ Vickers hardness

V. AUTHOR CONTRIBUTIONS

M.R., H.N. and M.D. performed the calculations, M.R. and A.R.O. contributed to the analysis and wrote the paper. X.F.Z and G.R.Q. provided technical assistance with calculations. V.L.S. proposed the idea, performed calculations of hardness and participated in the discussion.

VI. ADDITIONAL INFORMATION

Competing financial interests: The authors declare no competing financial interests.

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Appendix A: Densities of BeF$_2$ and SiO$_2$ structures

Table II shows densities of BeF$_2$ structures at 0 and 20 GPa and SiO$_2$ structures at 0 GPa.

Appendix B: CIF file of BeF$_2$ C2/c structure at 20 GPa

# CIF file
# This file was generated by FINDSYM (H.T. Stokes)
117 Be1 Be 0.30175 0.08755 0.27471 1.00000

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_frc_x
_atom_site_frc_y
_atom_site_frc_z
_atom_site_occupancy

Be1 Be 0.30175 0.08755 0.27471 1.00000
Be2 Be 0.00000 0.18404 0.25000 1.00000
F1 F -0.11350 0.09592 0.11433 1.00000
F2 F 0.14707 0.43232 0.42082 1.00000
F3 F -0.11681 0.27080 -0.42582 1.00000

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