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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 BeF<sub>2</sub> 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 BeF<sub>2</sub> and SiO<sub>2</sub>, 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 SiO<sub>2</sub>, 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<sup>1,2</sup>, production of special glasses<sup>3,4</sup>, manufacture of pure beryllium<sup>5</sup>, etc. Structurally, BeF<sub>2</sub> phases are similar to the phases of SiO<sub>2</sub> (Fig. 1):  $\alpha$ -quartz phase of BeF<sub>2</sub> and SiO<sub>2</sub> is stable from 0 to  $\sim$ 2 GPa, and then transforms to coesite phase which persists up to  $\sim$ 8 GPa, and then transforms to stishovite (rutile-type phase) in SiO<sub>2</sub><sup>6</sup>. However, the behavior of BeF<sub>2</sub> experimentally is not known for pressures above 8 GPa (see Scheme 1 in Ref.<sup>7</sup>).

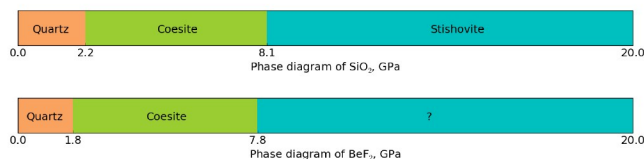


FIG. 1. Phase diagrams of SiO<sub>2</sub><sup>6</sup> and BeF<sub>2</sub><sup>7</sup> at low (up to room) temperatures.

One of our goals in present paper is to reveal which phase transitions can occur at higher pressures in BeF<sub>2</sub>.

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* study<sup>8</sup> authors explored 13 well-known AB<sub>2</sub> structure types for their possible stability for BeF<sub>2</sub>:  $\alpha$ -quartz-type (*P3<sub>1</sub>21*),  $\beta$ -quartz-type (*P6<sub>2</sub>22*),  $\alpha$ -cristobalite-type (*P4<sub>1</sub>2<sub>1</sub>2*),  $\beta$ -cristobalite-type (*Fd-3m*), cubic CaF<sub>2</sub>-type (*Fm-3m*),  $\alpha$ -PbCl<sub>2</sub>-type (*Pnma*), Ni<sub>2</sub>In-type (*P6<sub>3</sub>/mmc*), coesite-type (*C2/c*), rutile-type (*P4<sub>2</sub>/mnm*), baddeleyite-type (*P2<sub>1</sub>/c*),  $\alpha$ -PbO<sub>2</sub>-type (*Pbcn*),  $\alpha$ -CaCl<sub>2</sub>-type (*Pnmm*) and pyrite-type (*Pa-3*) structures. They found that the sequence of pressure-induced phase transitions of BeF<sub>2</sub> up to 50 GPa is as follows:  $\alpha$ -quartz-type  $\xrightarrow{0.59 \text{ GPa}}$  coesite-type  $\xrightarrow{6.47 \text{ GPa}}$  rutile-type  $\xrightarrow{24.94 \text{ GPa}}$   $\alpha$ -PbO<sub>2</sub>-type structures. Although BeF<sub>2</sub> under pressure has been theoretically investigated by Yu *et al.*<sup>8</sup>, we revisit these results to check for previously unknown structure(s), and we explore the relevance of these findings for SiO<sub>2</sub>. Moreover, recently there has been a renewed interest on the phase diagram of other related fluoride (CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>) and oxide (UO<sub>2</sub>) materials<sup>9,10</sup> 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 BeF<sub>2</sub> and SiO<sub>2</sub> has been performed in two steps: (1) prediction of a new structure of BeF<sub>2</sub> using USPEX evolutionary algorithm; (2) calculation of properties of BeF<sub>2</sub> and SiO<sub>2</sub> in the wide range

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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  $\text{BeF}_2$  system at different pressures (15, 20 and 25 GPa) using the USPEX code<sup>11–13</sup>, in conjunction with first-principles structure relaxations using density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)<sup>14</sup>, as implemented in the VASP package<sup>15</sup>. We employed projector augmented wave (PAW)<sup>16</sup> 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  $\Gamma$ -centered meshes for Brillouin zone sampling with reciprocal space resolution of  $2\pi \times 0.10 \text{ \AA}^{-1}$ .

We used the VASP package to carefully reoptimize the obtained structures before calculating phonons, elasticity, electronic density of states (DOS), hardness of  $\text{BeF}_2$  and  $\text{SiO}_2$ . For these relaxations, we also used the plane-wave cutoff of 600 eV and  $k$ -meshes with resolution of  $0.10 \text{ \AA}^{-1}$ . Phonons calculations have been performed using Phonopy<sup>17</sup> and Quantum Espresso<sup>18</sup> 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<sup>19</sup> based on the strength of bonds between atoms and bond network topology, Chen-Niu model<sup>20</sup> which uses elastic constants obtained from DFT calculations and Mukhanov-Kurakevych-Solozhenko thermodynamic model of hardness<sup>21</sup>.

### III. RESULTS AND DISCUSSION

USPEX allowed us to find a new structure of  $\text{BeF}_2$ , 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  $a=8.742 \text{ \AA}$ ,  $b=8.695 \text{ \AA}$ ,  $c=4.178 \text{ \AA}$  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  $\text{BeF}_2$ -stishovite at 30 GPa:  $a=b=3.986 \text{ \AA}$ ,  $c=2.501 \text{ \AA}$  and  $\alpha=\beta=\gamma=90^\circ$ . The value of the bulk modulus  $B_0=22.7 \text{ GPa}$  of the  $C2/c$  structure of  $\text{BeF}_2$  with its pressure derivative  $B'_0=3.9$  was obtained from a least-squares fit using the Murnaghan equation of state<sup>22</sup> (Fig. 3). The zero-pressure unit cell volume was taken as  $V_0=213.7 \text{ \AA}^3$ .

#### A. Thermodynamic stability

We have calculated the enthalpies of  $\alpha$ -quartz ( $P3_221$ ), coesite ( $C2/c$ ), coesite-II ( $C2/c$ ), stishovite ( $P4_2/mnm$ ),  $\alpha$ - $\text{PbO}_2$ -type ( $Pbcn$ ) structure and our new structure ( $C2/c$ ) for both  $\text{BeF}_2$  and  $\text{SiO}_2$  at different pressures from 0 to 50 GPa with a 1 GPa step. The results are presented in Fig. 4.

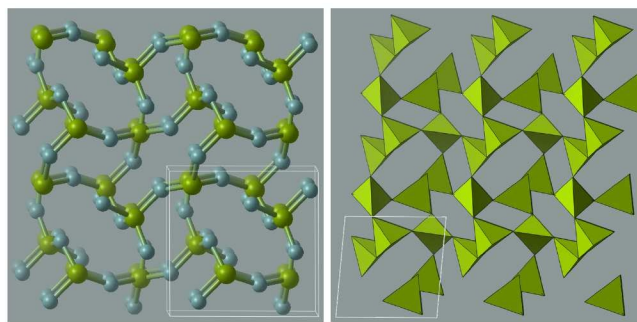


FIG. 2.  $C2/c$  structure of  $\text{BeF}_2$ , stable at 18–27 GPa.

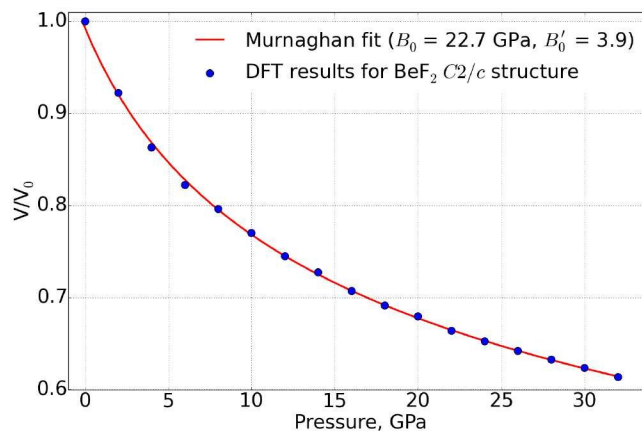


FIG. 3. Equation of state of  $\text{BeF}_2$   $C2/c$  structure.

#### 1. $\text{BeF}_2$ under pressure

For the case of  $\text{BeF}_2$   $\alpha$ -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.<sup>8</sup>, where LDA was used). According to Demuth *et al.*<sup>23</sup>, the LDA approximation used in Ref.<sup>8</sup> underestimates phase transition pressures, whereas using the GGA yields more reliable results. The  $\alpha$ - $\text{PbO}_2$ -type structure is not stable at any pressure (in the investigated interval from 0 to 50 GPa) for  $\text{BeF}_2$  (though it is close to stability at  $\sim 27 \text{ GPa}$ ), while for  $\text{SiO}_2$  it is indeed stable at pressures above  $\sim 80\text{--}90 \text{ GPa}$ <sup>24</sup>.

#### 2. $\text{SiO}_2$ under pressure

From Fig. 4(b) it is clearly seen that in  $\text{SiO}_2$  the transition from  $\alpha$ -quartz to coesite occurs at 5 GPa, followed by transformation to stishovite at  $\sim 7 \text{ GPa}$ , which continues to be stable up to 50 GPa. This phase transition sequence is in good agreement with experiments<sup>6</sup> and



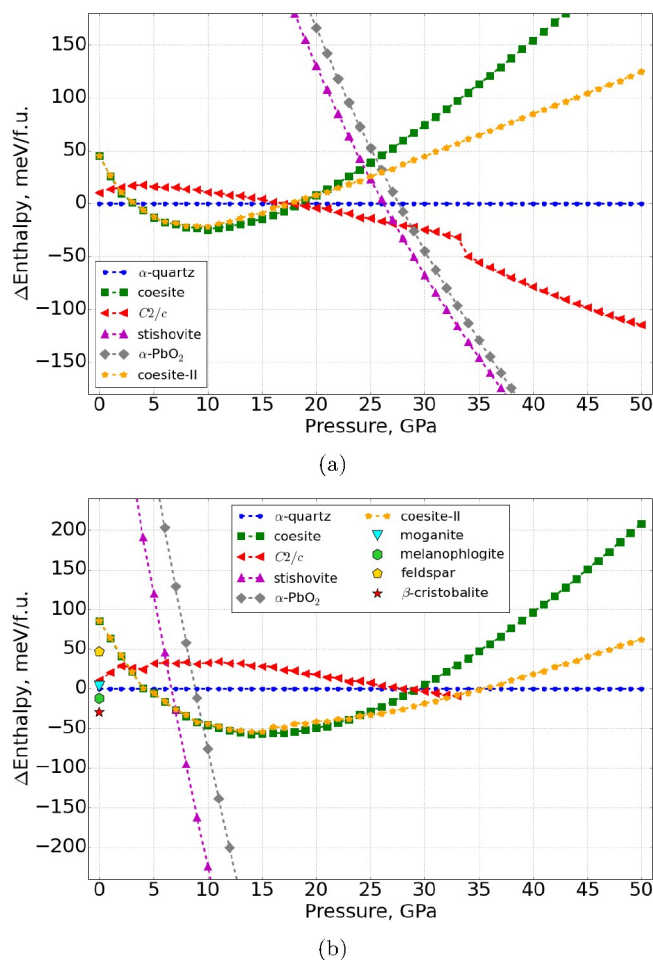


FIG. 4. Enthalpies (relative to  $\alpha$ -quartz) of (a)  $\text{BeF}_2$  and (b)  $\text{SiO}_2$  phases as a function of pressure.

with the GGA results by Demuth *et al.*<sup>23</sup>, Oganov *et al.*<sup>24</sup> and LDA results of Tsuchiya *et al.*<sup>25</sup>; it is known though<sup>23</sup> that the GGA is more accurate than the LDA for phase transition pressures. The new structure is not stable at any pressure for  $\text{SiO}_2$ , but at 0 GPa is only 10 meV/f.u. higher in energy than  $\alpha$ -quartz, and should be synthesizable as a metastable phase. Typically, kinetic barriers in such covalent tetrahedral phases are very high, *i.e.* metastable phases of such type exist in nature for millions of years. However, it is quite hard to estimate the magnitude of the barrier both theoretically and experimentally, and this is out of scope of the present work. Our results of coesite  $\rightarrow$  coesite-II transition are in good agreement with recent study of Černok *et al.*<sup>26</sup>, where they observe coesite at 20.3 GPa, and after an abrupt change in the diffraction pattern between  $\sim 20$  and  $\sim 28$  GPa — coesite-II at 27.5 and 30.9 GPa.

### 3. Metastable structures of $\text{SiO}_2$

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

### B. Lattice dynamics

Since the new structure of  $\text{BeF}_2$  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  $\text{BeF}_2$   $\alpha$ -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  $\text{SiO}_2$   $\alpha$ -quartz at 0 GPa, coesite at 5 GPa and stishovite at 10 GPa. Fig. 5 shows dynamical stability of the new structure of  $\text{BeF}_2$  since no imaginary frequencies are observed in the phonon dispersion plot.

### C. Electronic properties

According to Fig. 6, all  $\text{BeF}_2$  phases are insulators, the DFT band gap increases from  $\sim 7$  to  $\sim 10$  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.*<sup>8</sup>.

For  $\text{SiO}_2$  (Fig. 7) we also observe insulating behavior, and the band gap is about 6 eV and remains almost unchanged with increasing pressure.

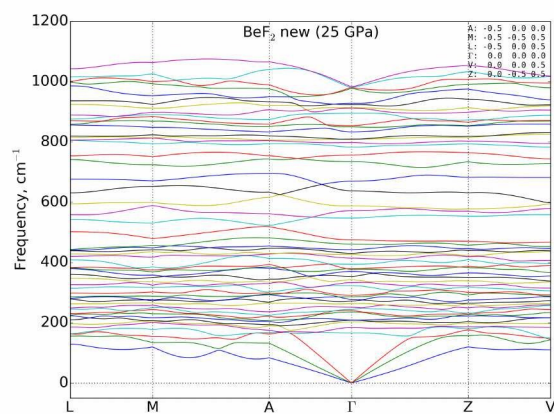


FIG. 5. Phonons dispersion curves showing dynamical stability of the  $C2/c$  structure of  $\text{BeF}_2$  at 25 GPa.

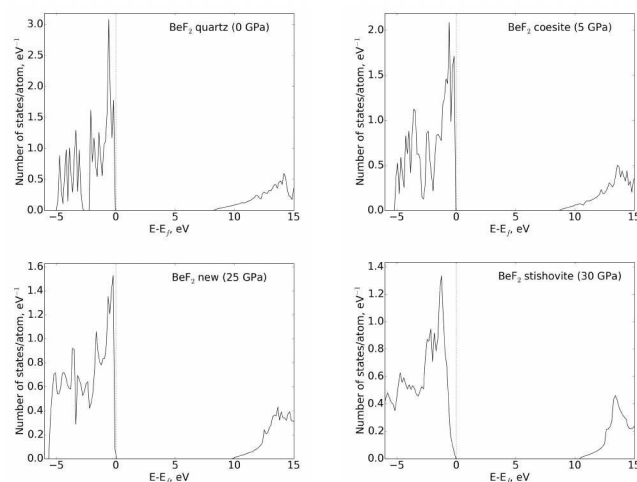
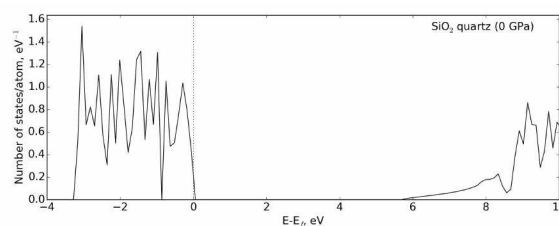


FIG. 6. Density of states of  $\text{BeF}_2$  in the  $\alpha$ -quartz (at 0 GPa), coesite (at 5 GPa),  $C2/c$  structure (at 25 GPa), and stishovite (at 30 GPa) phases.

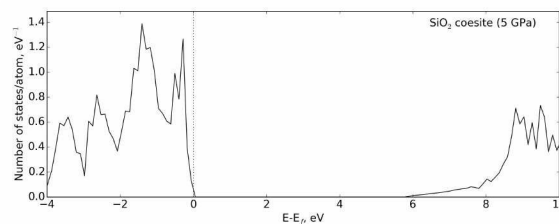
#### D. Hardness

Three models have been exploited to calculate hardnesses — the Lyakhov-Oganov<sup>19</sup>, Chen-Niu<sup>20</sup> and Mukhanov-Kurakevych-Solozhenko<sup>21</sup> 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.<sup>19</sup>. This model has been implemented in the USPEX code, and for greater convenience has also been implemented as an online utility available at <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.

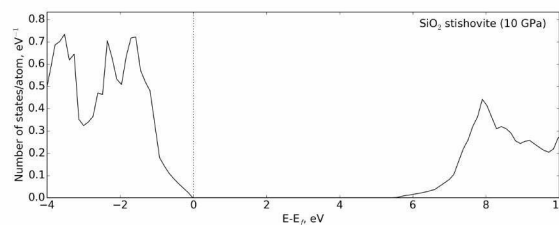
The results can be seen in Table I. Experimental data are provided where available — Vickers hardness of  $\text{SiO}_2$ -quartz<sup>30</sup>,  $\text{SiO}_2$ -coesite<sup>21</sup> and  $\text{SiO}_2$ -stishovite<sup>31</sup>. From Ta-



(a)



(b)



(c)

FIG. 7. Density of states of  $\text{SiO}_2$  in the (a)  $\alpha$ -quartz (at 0 GPa), (b) coesite (at 5 GPa) and (c) stishovite (at 10 GPa) phases.

ble I it is clearly seen that the calculated hardness of  $\text{SiO}_2$  quartz and stishovite is much higher than one of  $\text{BeF}_2$  analogs. The hardness of  $\text{BeF}_2$  and  $\text{SiO}_2$  in the new  $C2/c$  structure is comparable with the hardness of  $\alpha$ -quartz and coesite.

#### IV. CONCLUSIONS

We have examined thermodynamic, vibrational, electronic and elastic properties of  $\text{BeF}_2$  and  $\text{SiO}_2$  phases using DFT calculations. The sequence of pressure-induced phase transitions of  $\text{BeF}_2$  up to 50 GPa is as follows:  $\alpha$ -quartz-type  $\xrightarrow{4 \text{ GPa}}$  coesite-type  $\xrightarrow{18 \text{ GPa}}$   $C2/c$   $\xrightarrow{27 \text{ GPa}}$  stishovite (rutile-type) structures. We found a new phase of  $\text{BeF}_2$  which is thermodynamically stable at pressures from 18 to 27 GPa. This phase is not observed in  $\text{SiO}_2$ , but could be synthesized in principle. Electronic properties analysis has shown  $\text{BeF}_2$  and  $\text{SiO}_2$  remain insulating in a wide range of pressures (from 0 to 50 GPa). Hardness of  $\text{BeF}_2$  and  $\text{SiO}_2$  in the new structure is comparable with hardness of  $\alpha$ -quartz and coesite at 0 GPa. Hardnesses of metastable  $\text{SiO}_2$  structures have been examined as well.

TABLE I. Hardness of BeF<sub>2</sub> and SiO<sub>2</sub> structures at 0 GPa in GPa. For the metastable SiO<sub>2</sub> structures we present enthalpies relative to  $\alpha$ -quartz (in meV per formula unit).

	BeF <sub>2</sub>			SiO <sub>2</sub>		
	Lyakhov-Oganov	Chen-Niu	Mukhanov <i>et al.</i> <sup>a</sup>	Lyakhov-Oganov	Chen-Niu	Experiment
Quartz	7.1	7.5	11.0	20.0	12.5	12.0 <sup>b</sup>
Coesite	8.2	8.3	11.7	22.3	8.4	20.0 <sup>b</sup>
New structure	7.3	6.8	13.5	19.1	6.7	—
Stishovite	8.2	12.7	15.1	29.0	28.7	33.0 <sup>b</sup>

Metastable structures (SiO <sub>2</sub> only):			
	Relative enthalpy, meV/f.u.	Hardness, GPa	
		Lyakhov-Oganov model	Chen-Niu model
Feldspar	47	6.7	11.8
Baddeleyite	726	29.6	28.0
Melanophlogite	-13	12.5	3.3
Moganite	3	19.5	12.8

<sup>a</sup> Thermodynamic model of hardness (Ref.<sup>21</sup>)<sup>b</sup> 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<sub>2</sub> and SiO<sub>2</sub> structures

Table II shows densities of BeF<sub>2</sub> structures at 0 and 20 GPa and SiO<sub>2</sub> structures at 0 GPa.

## Appendix B: CIF file of BeF<sub>2</sub> C2/c structure at 20 GPa

# CIF file  
# This file was generated by FINDSYM (H.T. Stokes)

TABLE II. Densities of BeF<sub>2</sub> and SiO<sub>2</sub> structures.

System	Number of atoms	Volume, Å <sup>3</sup> /cell	Density, g/cm <sup>3</sup>
<b>BeF<sub>2</sub> at 0 GPa:</b>			
$\alpha$ -quartz	9	105.167	2.244
coesite	24	254.636	2.472
coesite-II	96	1021.960	2.464
C2/c	18	213.696	2.209
stishovite	6	47.771	3.294
<b>BeF<sub>2</sub> at 20 GPa:</b>			
$\alpha$ -quartz	9	73.078	3.230
coesite	24	202.001	3.116
C2/c	18	145.159	3.252
stishovite	6	41.492	3.793
<b>SiO<sub>2</sub> at 0 GPa:</b>			
$\alpha$ -quartz	9	116.934	2.580
coesite	24	283.341	2.839
coesite-II	96	1137.296	2.830
C2/c	18	243.569	2.477
stishovite	6	48.185	4.174
$\alpha$ -PbO <sub>2</sub> -type	12	94.623	4.251

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F3 F -0.11681 0.27080 -0.42582 1.00000
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