High-pressure phases of group II difluorides: polymorphism and superionicity

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Abstract—We investigate the high-pressure behaviour of beryllium, magnesium and calcium difluorides using ab initio random structure searching and density functional theory (DFT) calculations, over the pressure range 0–70 GPa. Beryllium fluoride exhibits extensive polymorphism at low pressures, and we find two new phases for this compound – the silica moganite and CaCl2 structures – which are stable over the wide pressure range 12–57 GPa. For magnesium fluoride, our searching results show that the orthorhombic ‘O-I’ TiO2 structure (Pbca, Z = 8) is stable for this compound between 40 and 44 GPa. Our searches find no new phases at the static-lattice level for calcium difluoride between 0 and 70 GPa; however, a phase with P62m symmetry is close to stability over this pressure range, and our calculations predict that this phase is stabilised at high temperature. The P62m structure exhibits an unstable phonon mode at large volumes which may signal a transition to a superionic state at high temperatures. The Group-II difluorides are isoelectronic to a number of other AB2-type compounds such as SiO2 and TiO2, and we discuss our results in light of these similarities.

I. INTRODUCTION

The Group-II difluorides form materials with a wide variety of technological uses. BeF2, and mixtures of it with further fluorides and difluorides, are used to create glasses for use in infrared photonics, which have excellent transmittance in the UV. BeF2 glass itself has a large bandgap of 13.8 eV [1, 2]. BeF2 is chemically stable and is employed as a mixture component in nuclear reactor molten salts, where it is useful as a coolant, and is also capable of dissolving fissile materials [3]. MgF2 is birefringent with a wide wavelength transmission range, and is used in the manufacture of optical components such as polarizers [4]. CaF2 also offers a high transmittance across a wide range of wavelengths and is used in optical systems, as well as an internal pressure standard [5, 6]. MgF2 and CaF2 occur naturally as the minerals sellaite and fluorite, therefore high pressure modifications of these compounds are of interest in geophysics. Group-II difluorides have 16 valence electrons per formula unit, and are isoelectronic to other AB2 compounds of industrial or geophysical significance, such as TiO2 and SiO2. As such, these compounds share many similar crystal structures, albeit stable at different pressures. Because of this structural similarity, Group-II difluorides have been investigated as structural analogues of silica phases [7]. BeF2 is particularly similar to silica at low pressures [8], as in addition to being isoelectronic, the fluoride (F−) and oxide (O2−) ions have similar radii and polarisabilities, and the Be/F and Si/O atomic radii ratios are similar at ≈ 0.3 [9]. MgF2 has also been explored as a model for higher pressure silica phases [10]. We are interested in the structures and phases of Be-, Mg- and CaF2 at ambient and elevated pressures, and the implications of such phases for other AB2 compounds. Our approach to determining stable phases in these compounds uses computational structure searching alongside density functional theory (DFT) calculations, and we elect to explore the pressure range 0–70 GPa.

II. METHODS

The ab initio random structure searching (AIRSS) technique [11] is used to search for Group-II difluoride structures at three pressures: 15, 30 and 60 GPa. AIRSS is a stochastic method which generates structures randomly with a given number of formula units. A minimum atom-atom separation is specified for the generated structures, e.g., we set the Be-Be, Be-F, and F-F minimum separations for the case of BeF2. These separations are chosen based on short AIRSS runs. We can also impose symmetry constraints on our generated structures such that low symmetry structures are not considered. This strategy tends to speed up the searches because such low-symmetry structures are unlikely to have low energies according to Pauling’s principle [12, 13], although we allocate part of our searching time to check low symmetry structures for completeness. AIRSS has a proven track record of predicting structures in a diverse variety of systems that have subsequently been verified by experiment, such as in compressed silane, aluminium hydride, high-pressure hydrogen sulfide and xenon oxides [14–17].

We limit our searches to a maximum of 8 formula units (24 atoms) per cell. In addition to AIRSS, we supplement our searches with a set of 15 known AB2-type structures taken from a variety of compounds; see

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the Appendix for a full list of these structures. Structures generated by AIRSS or taken from known AB$_2$ compounds are relaxed to an enthalpy minimum using a variable-cell geometry optimization calculation. For this, we use density-functional theory (DFT) as implemented in the CASTEP plane-wave pseudopotential code [18], with internally-generated ultrasoft pseudopotentials [19] and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [20]. Our DFT calculations use a 800 eV plane-wave basis set cutoff, and a Brillouin zone sampling density of at least $2\pi \times 0.04 \text{ Å}^{-1}$. Our calculations of phonon frequencies use the quasiharmonic approximation (QHA) [21,22] and a finite-displacement supercell method, as implemented in CASTEP.

As well as searches for new BeF$_2$, MgF$_2$ and CaF$_2$ structures, we have also carried out variable stoichiometry structure searching at 60 GPa, to examine the possibility of other thermodynamically stable compositions. These searches predict that BeF$_2$ and MgF$_2$ are the only stable stoichiometries at 60 GPa, while both CaF$_2$ and CaF$_3$ are stable at that pressure. Our predicted CaF$_3$ structure is cubic with $Pm\overline{3}n$ symmetry, and the same structure has in fact been previously predicted for high-pressure aluminium hydride (AlH$_3$) [23]. We have not examined the properties of high-pressure CaF$_3$ further, and in what follows we focus only on the AB$_2$ difluoride stoichiometry. Convex hulls for our variable stoichiometry searches are given in the Appendix.

Semilocal density functionals such as PBE typically underestimate the calculated band gap in materials. In order to capture the optical properties of the group II difluorides, we perform optical bandgap calculations with the non-local Heyd-Scuseria-Ernzerhof (HSE06) functional [24]. This functional incorporates 25% screened exchange and is expected to generally improve the accuracy of bandgap calculations carried out with DFT, though at a greater computational cost. We adopt the following calculation strategy: structures are first relaxed with the PBE functional, norm-conserving pseudopotentials [25], a basis set cutoff of 1600 eV and a relatively sparse Brillouin zone sampling of $2\pi \times 0.1 \text{ Å}^{-1}$. The HSE06 functional is then used with PBE-relaxed geometries for a self-consistent calculation of the electronic bands of the structure. Our stress calculations indicate that the use of the HSE06 functional with PBE geometries gives rise to small forces of $\lesssim 0.1 \text{ eV/Å}$ on each atom. Electronic density of states calculations are then performed using the OPTADOS code [26-28]. Additional information on the electronic structure calculations in this study can be found in the Appendix.

III. BERYLLIUM DIFLUORIDE

A. Low-pressure results

Beryllium fluoride has several thermodynamically accessible phases which have been obtained in experimental studies. At temperatures below its melting point (820 K) and pressures at or below atmospheric pressure, the α-quartz, β-quartz, α-cristobalite, β-cristobalite and glass phases of BeF$_2$ have been prepared under various conditions [29,30].

Our results from structure searching calculations at low pressures (0−8 GPa) are summarised in Fig. 1(a), which shows the static-lattice enthalpies of several BeF$_2$ structures as a function of pressure. Beryllium fluoride shows extensive polymorphism at low pressures; we find at least 10 structures for BeF$_2$ (all those shown in Fig. 1(a), except Coesite-I and Coesite-II) lying within about 20 meV/f.u. of one another at 0 GPa. The α- and β-quartz, and α- and β-cristobalite structures are part of this set of 10 structures. Within our current calculational framework (DFT−PBE), the α-cristobalite structure is lowest in enthalpy at 0 GPa, lying 8.9 meV/f.u. below α-quartz, but other low enthalpy structures are also of interest as they can be stabilised by temperature. There is some experimental evidence for as-yet-unknown high-temperature low-pressure BeF$_2$ phases [31], and metastable structures produced in our searches provide useful reference crystal structures that could be matched to available experimental data at elevated temperatures. We remark here that the PBE functional may not provide a completely accurate energy ordering for these structures at low pressure. For example in silica, DFT−PBE also predicts that the α-cristobalite structure has a lower enthalpy than the α-quartz structure at 0 GPa. However, high pressure phase transition pressures in silica calculated with PBE are in excellent agreement with accurate Quantum Monte−Carlo calculations [32].

A recent study by Rakitin et al. found a C2/c structure for BeF$_2$ which is close in enthalpy to α-quartz at 0 GPa [33]. Results using AIRSS produce five further polymorphs for BeF$_2$, labelled ‘Moganite’, $P2_12_12_1$, $P2_12_12_2$, C2/c, and $P2_1/c$ in Fig. 1(a), which have static-lattice enthalpies of +0.9, +0.4, −8.9, −4.9 and −0.3 meV/f.u. relative to the α-quartz phase at 0 GPa. We discuss each of these in more detail below.

Moganite. The ‘Moganite’ polymorph, which turned up in our searches (and was also included in our set of 15 AB$_2$ structures – see the Appendix), is BeF$_2$ in the silica moganite structure with Si→Be and O→F. This has space group C2/c and 6 formula units of BeF$_2$ in the primitive cell.

$P2_12_12_1$. At the pressures shown in Fig. 1(a), the $P2_12_12_1$ polymorph has space group symmetry $P4_212_1$ (#96), and is actually an enantiomer of α-cristobalite. A mirror-image transformation $(x,y,z) \rightarrow (−y,−x,z)$, i.e. a reflection of atomic positions in the (110) plane, relates the two structures. This situation is entirely analogous to SiO$_2$, where rigid-unit phonon modes (RUMs) distort the β-cristobalite structure to one of either $P4_212_1$ symmetry (our α-cristobalite or to $P4_212_1$ symmetry (our $P2_12_12_1$-II). Coh et al. [34] employ the notation $\tilde{\alpha}_1$ and $\tilde{\alpha}_1'$ respectively for these two cristobalite structures. Enthalpy-pressure curves for the α-cristobalite
FIG. 1. Static lattice enthalpies for BeF$_2$ calculated with the PBE functional over the pressure ranges (a) 0–8 GPa, (b) 5–35 GPa and (c) 25–70 GPa. In (a) and (b), enthalpies are shown relative to the α-quartz phase, while in (c) they are shown relative to the rutile phase.

![BeF$_2$ structures](image)

FIG. 2. (a) BeF$_2$ in the C2/c morganite phase at 20 GPa with four-fold coordinated Be atoms, viewed down the b (and in this case, monoclinic) axis. The lattice a and c axes point horizontal and almost vertical in the page, respectively. (b) BeF$_2$ in the Pnnm CaCl$_2$ phase at 50 GPa, with six-fold coordinated Be atoms. Beryllium atoms in yellow, fluorine atoms in green. Lattice parameters and atomic positions for these structures are given in the Appendix.

and P2$_1$2$_1$2$_1$-II structures lie on top of one another in Fig. 1(a), and our calculations give the overall change in enthalpy going from β-cristobalite to α$_1$ or α$_1'$ as and −21.2 meV/BeF$_2$; the equivalent quantity is −34.4 meV/SiO$_2$ in silica. Above 11 GPa, the P2$_1$2$_1$2$_1$-II structure distorts to the lower space group symmetry P2$_1$2$_1$2$_1$ (#19), and the enthalpy curves for it and the α-cristobalite structure start to diverge (Fig. 1(b)).

Open framework structures. The P2$_1$2$_1$2$_1$, C2/c–4×2 and P2$_1$/c structures in Fig. 1(a) are low-density polymorphs which are previously unreported in BeF$_2$. The notation ‘C2/c–4x2’ refers to the fact that this structure is a low-pressure variant of the P2$_1$/c (Z=8), 4×2-type structure shown in Fig. 1(c). Our DFT-PBE calculations show that these polymorphs are energetically relevant in silica, where they lie 5.9, 15.7 and 5.9 meV/SiO$_2$ in energy below α-quartz at 0 GPa, which suggests them as likely silica polymorphs as well. The monoclinic angle in the P2$_1$/c structure is close to 90°, hence we also investigate a higher symmetry version of this structure with Pnma symmetry, whose enthalpy is found to be 2.2 meV/SiO$_2$ below α-quartz (this structure is not shown in Fig. 1(a)). Calculated lattice parameters and atomic positions for these structures are provided in the Appendix.

We query the ICSD [35] and International Zeolite Association (IZA) [36] databases to check if these four structures are already known in SiO$_2$. Our C2/c–4×2 structure matches #75654 in the ICSD, which is ‘Structure 8’ in the simulated annealing structure prediction work of Boisen et al. [37], after the latter is relaxed using DFT. However, we find no matching SiO$_2$ structures in these databases for our P2$_1$2$_1$2$_1$-I, P2$_1$/c and Pnma structures. Analysis of these three structures using the TOPOS code [38] shows that they are all of the same topological type as the ABW zeolite. They have framework densities of 18.9, 18.6 and 18.5 Si/1000Å$^3$ (cf. α-quartz, with 24.9 Si/1000Å$^3$), while the ABW silica
structure itself is slightly less dense at 17.6 Si/1000Å³, with an enthalpy 3.9 meV/SiO₂ above α-quartz. While BeF₂ and SiO₂ share many chemical similarities (as mentioned in Sec. 1), the Be–F bond is much weaker than the Si–O bond, resulting in a lower melting point and hardness for BeF₂ [29]. Nevertheless, our results show that BeF₂ also supports open framework zeolite-like structures, and highlights the utility of searching for potential zeolite structures in model systems such as BeF₂. The large number of polymorphs we encounter lying close to one another in energy suggest BeF₂ as a potential tetrahedral framework material.

B. High–pressure results

Our structure searching calculations show that the application of pressure (0.4 GPa) favours the α-quartz phase, as seen in Fig. 1(a). Between 3.1 and 3.3 GPa, the silica ‘coesite-I’ or ‘coesite-II’ structure [39] with Z=8 or 32 then becomes the lowest-enthalpy structure for BeF₂. We find that over the pressure range 0-18 GPa, the coesite-I and II structures are nearly identical. The coesite-II structure is close to a supercell of coesite-I, but the atomic positions in coesite-II deviate slightly from those expected for a perfect supercell, and the coesite-II structure lies consistently about 1 meV/BeF₂ below coesite-I over this pressure range. The coesite-I phase has been found in experimental studies on BeF₂, at 3 GPa and ≈1100 K [31]. Previous work [33] reported that a new structure of C2/c symmetry then becomes stable between 18 and 27 GPa; our calculations instead show that BeF₂ is most stable in the silica moganite structure, which also has C2/c symmetry, between 11.6 and 30.1 GPa (see Fig. 1(b)). Above 30.1 GPa, we find that the orthorhombic CaCl₂ structure with space group Pnnm becomes stable (Fig. 1(b)), eventually giving way to the denser α-PbO₂ structure above 57.5 GPa (Fig. 1(c)). The moganite and CaCl₂ structures are depicted in Fig. 2.

The enthalpy–pressure curve for the CaCl₂ structure emerges smoothly from that for the rutile structure (space group P4₁2₁2), which is also the case in silica, where a ferroelastic phase transition occurs between these two structures near 50 GPa [40]. For BeF₂ at the static lattice level, our calculations exclude the stability of the rutile structure over the pressure range 0–70 GPa, though we note that this phase lies only a fraction of a meV per BeF₂ higher in enthalpy than the CaCl₂ phase at 30.1 GPa, as seen in Fig. 1(b). Earlier studies [33, 41] have already examined a number of the structures discussed here; however, the stability of BeF₂ in the moganite and CaCl₂ structures is new, and according to our calculations dominates the high-pressure phases of BeF₂ over the pressure range 11.6–57.5 GPa.

Fig. 1(c) shows a band of three enthalpy–pressure curves, labelled Pbcn (Z=8), P2₁/c (Z=6) and P2₁/c (Z=8), whose energy lies in close proximity to the α-PbO₂ curve. These three structures emerged from our searches and have a similar, but slightly lower density than the α-PbO₂ phase for BeF₂. They are close to stability at 60 GPa, but are not predicted to be stable over the pressure range 0–70 GPa. We identify these phases as members of the class of silica polymorphs introduced by Teter et al. [42], which are a set of structures described as intermediaries to the CaCl₂ and α-PbO₂ silica phases. Our Pbcn (Z=8) and P2₁/c (Z=6) structures correspond to the ‘3 × 3’ and ‘3 × 2’ structures types, while our P2₁/c (Z=8) structure is not explicitly discussed in Ref. [42] and would be referred to as ‘4 × 2’ type. We will encounter these phases again in our results for MgF₂.

Summary. To briefly summarise our search results for BeF₂, we predict the following series of pressure-induced phase transitions at the static-lattice level:

\[
\begin{align*}
\alpha\text{-cristobalite} (P4₁2₁2) & \xrightarrow{0.4 \text{ GPa}} \alpha\text{-quartz (P3}₃\text{21)} \xrightarrow{3.1/3.3 \text{ GPa}} \text{coesite-I/II (C}2/c\text{)} \xrightarrow{11.6 \text{ GPa}} \text{Moganite (C}2/c\text{)} \xrightarrow{30.1 \text{ GPa}} \text{CaCl₂ (Pnnm)} \xrightarrow{57.5 \text{ GPa}} \alpha\text{-PbO₂ (Pbcn)},
\end{align*}
\]

with the labelled arrows showing the calculated transition pressures. Our searches also demonstrate numerous metastable polymorphs for BeF₂.

C. Optical bandgaps in BeF₂

As mentioned in Sec. 1, BeF₂ has a large bandgap at ambient pressure and is used in a number of optical applications. We examine the optical bandgap in BeF₂ as a function of pressure, with the results shown in Fig. 3. The optical gap is found to be tunable, increasing by around 0.06 eV/GPa over the pressure range 0–70 GPa. We expect BeF₂ to therefore maintain its high UV transmittance with increasing pressure, with potentially useful high pressure applications. The electronic density-of-states (DOS) of the moganite and CaCl₂ phases are also given in the Appendix.

IV. MAGNESIUM DIFLUORIDE

MgF₂ adopts the rutile P4₁2₁2/mnm structure at room temperature and pressure. X-ray diffraction experiments indicate a transformation to the CaCl₂ structure at 9.1 GPa, then to a pyrite structure with space group Pn3 and Z=4 near 14 GPa, and have also recovered a mixture of α-PbO₂ and rutile MgF₂ upon decompression [10]. DFT calculations, including those of the present study, actually show that the CaCl₂ structure is never stable for MgF₂ and instead predict the α-PbO₂ structure to have a window of stability between 10 and 15 GPa, with the CaCl₂ structure slightly higher in enthalpy.
The results from our structure searches are given in Fig. 4. Based on our static-lattice results, we predict the following sequence of stable structures and phase transitions with rising pressure:

\[
\begin{align*}
\text{Rutile} \ (P4_2/mnm) & \quad 9.4 \ \text{GPa} \rightarrow \ \alpha\text{-PbO}_2 \ (Pbcn) \\
15.4 \ \text{GPa} & \rightarrow \ \text{Pyrite} \ (P3) \quad 39.6 \ \text{GPa} \rightarrow \ \text{O-I} \ (Pbca) \\
44.1 \ \text{GPa} & \rightarrow \ \text{Cotunnite} \ (Pnma).
\end{align*}
\]

Previous theoretical studies \cite{43, 44} have already considered the rutile, \(\alpha\)-PbO\(_2\), pyrite and cotunnite phases of MgF\(_2\). In the present work, we find that the \(Pbca\) O-I ‘orthorhombic-I’ structure, which has been reported experimentally for TiO\(_2\) near 30 GPa \cite{45}, is also stable for MgF\(_2\) between 39.6 and 44.1 GPa. This structure is depicted in Fig. 5. Experimental studies on MgF\(_2\) have indeed reported an unidentified ‘Phase X’ stable in the pressure range 49–53 GPa and at 1500–2500 K between the pyrite and cotunnite phases \cite{46}. Our enthalpy calculations identify the O-I structure as the thermodynamically most likely candidate for Phase X, though the authors of Ref. \cite{46} note some difficulty in indexing x-ray diffraction data on Phase X to an orthorhombic structure, possibly due to a mixture of phases being present. We do not find any other energetically competitive structures near 50 GPa.

Silica and its stable polymorphs are of paramount importance in geophysics and planetary sciences. As well as a mineral in its own right, it is expected to be formed from the breakdown of post-perovskite MgSiO\(_3\) at terapascal pressures. SiO\(_2\) follows a very similar set of phase transitions to MgF\(_2\) with increasing pressure \cite{47}, with the Si coordination number rising from 6 in rutile at ambient pressures to a predicted 10 in an \(I4/mmm\) structure near 10 TPa \cite{48}. As pointed out by pre-
vious authors, several features of high pressure silica can readily be modelled in MgF$_2$, but at much lower pressures [10, 46]. For example, the $\alpha$-PbO$_2 \rightarrow$ pyrite transition in SiO$_2$, which our calculations find occurs at 217 GPa, takes place at a much lower pressure of 15.4 GPa in MgF$_2$. Near 690 GPa and for $T \gtrsim 1000$ K, a pyrite $\rightarrow$ cotunnite transition is also predicted for SiO$_2$ [49]; the analogous transition occurs at 44.1 GPa in MgF$_2$.

As mentioned in Sec. III B, Teter et al. [42] have introduced a class of SiO$_2$ polymorphs intermediate to CaCl$_2$ and $\alpha$-PbO$_2$. At least one member of this class of polymorphs has been synthesised in SiO$_2$, the ‘$3 \times 2$’ type $P2_1/c$ structure [50]. The $P2_1/c$ ($Z=6$), $P2_1/c$ ($Z=8$) and $Pbcn$ ($Z=8$) structures of BeF$_2$ depicted in Fig. 1(c) are members of this class, and also turn up in our MgF$_2$ searches (Fig. 4 and its inset). Our calculations show that these polymorphs are closest to stability near 10 GPa in MgF$_2$, compared to $\approx$100 GPa in SiO$_2$ suggesting that, as with other features of silica, they could be studied experimentally at much lower pressures in MgF$_2$.

Fig. 3 shows the optical bandgap in MgF$_2$ as a function of pressure. Like BeF$_2$, the optical gap is tunable with pressure, rising by about 0.04 eV/GPa over 0–70 GPa. We also provide the electronic DOS of the O-I structure in the Appendix.

V. CALCIUM DIFLUORIDE

CaF$_2$ crystallizes in the cubic $Fm\overline{3}m$ ‘fluorite’ structure ($Z=4$, $\alpha$-CaF$_2$) under ambient conditions. The compound has a high-temperature phase above about 1400 K, known as $\beta$-CaF$_2$, and melts near 1700 K at low pressures [51]. A high-pressure modification above 8–10 GPa ($\gamma$-CaF$_2$) is also known, with CaF$_2$ taking on the orthorhombic $Pnma$ cotunnite structure ($Z=4$) [52].

The $\beta$ phase has attracted considerable interest because it exhibits superionicity, with F$^-$ ions as the diffusing species [53]. A number of other compounds in the same fluorite (or ‘anti-fluorite’) variants of this structure, such as Li$_2$O, are also superionic conductors [54]. Such materials are of great technological interest, with applications in solid-state battery design. A recent study has shown that the superionic transition temperature in CaF$_2$ can be decreased through applied stress [55].

A. Results from structure searching

Our results from structure searching in CaF$_2$ are shown in Fig. 6. Unlike BeF$_2$ and MgF$_2$, we find that the potential energy surface for CaF$_2$ is relatively simple, with very few polymorphs for this compound over the pressure range 0–70 GPa. At the static lattice level of theory, we identify only the sequence of stable phases and transitions:

Fluorite ($Fm\overline{3}m$) $\xrightarrow{7.9\text{GPa}}$ Cotunnite ($Pnma$).
The calculated fluorite $\rightarrow$ cotunnite transition pressure here is in agreement with experimental results [52]. Experimental studies have also shown a transition from $\gamma$-CaF$_2$ to an Ni$_2$In-type structure in the pressure range 63–79 GPa with laser heating [56], consistent with the convergence of the red and black-dashed curves in Fig. 6.

Our results in Fig. 6 reveal a hexagonal phase for CaF$_2$ with $P62m$ symmetry which is close to stability, lying only 6 meV/CaF$_2$ higher in enthalpy than the $\gamma$ phase near 36 GPa. The enthalpy curves for the $P62m$ and $\gamma$ phases in Fig. 6 indicate that these two structures have very similar densities, with $P62m$ slightly denser at pressures below 36 GPa and becoming less dense than $\gamma$-CaF$_2$ at higher pressures. The $P62m$ phase has the Fe$_2$P structure, which has also been predicted for SiO$_2$ at very high pressures (>0.69 TPa) and low temperatures [49]. We show the $\gamma$ and $P62m$ structures in Fig. 7.

### B. Pressure-temperature phase diagram for CaF$_2$

The effects of nuclear zero-point motion and temperature are often important and affect the relative stability of crystal phases, particularly in cases where there are two or more structures lying very close in energy [57, 58]. Given the small enthalpy difference between the $P62m$ and $\gamma$ CaF$_2$ phases, we calculate the Gibbs free energy of these structures in the QHA as a function of pressure, as well as that of $Fm\bar{3}m$-CaF$_2$. Selecting the lowest Gibbs free energy structure at each temperature and pressure gives the phase diagram shown in Fig. 8. The solid-liquid phase boundary (dotted black line) in Fig. 8 is taken from the work of Cazorla et al [59]. From this, we do indeed predict that the $P62m$-CaF$_2$ structure is stabilised by temperature, in the region $P \gtrsim 10$ GPa and $T \gtrsim 1500$ K. We remark here that the exact phase boundaries in Fig. 8 are subject to some uncertainty depending on the choice of equation of state used for the Gibbs free energy calculation. This uncertainty is particularly noticeable along the $Pnma (\gamma) - P62m$ phase boundary.

Both the $Fm\bar{3}m$ and $P62m$ structures develop unstable phonon modes at sufficiently large volumes. For $Fm\bar{3}m$-CaF$_2$, these first occur at a static-lattice pressure between $\sim 7$ and $\sim 6$ GPa; for $P62m$ they first occur between 0 and 1 GPa. Cazorla et al also report unstable phonon modes for $Fm\bar{3}m$-CaF$_2$ above 4.5 GPa [59], however we do not encounter any such instabilities in our calculations. We find no unstable phonon modes in $\gamma$-CaF$_2$. In Fig. 8, black dashed lines are used to divide the regions of stability for the $Fm\bar{3}m$ and $P62m$ in two. At temperatures below the lines, these phases have volumes corresponding to stable phonons, while above the lines they exhibit unstable phonon modes, and their Gibbs free energies are extrapolations of quasiharmonic results. Dotted lines separate regions where one or both phases have unstable phonon modes, with the exception of the solid-liquid boundary.

The calculated volume coefficient of thermal expansion, $\alpha(P, T)$, can be used to assess the validity of the QHA. Applying the criteria of Karki et al [60] and Wentzcovitch et al [61], we expect the quasiharmonic approximation to be accurate for $T(\text{K}) \leq 28P (\text{GPa}) + 453$, with an uncertainty of about 100 K. The lower half of the $\alpha$-$\gamma$ phase boundary, and the $\gamma$-$P62m$ phase boundary near 40 GPa, are therefore expected to be accurate within the QHA. At higher temperatures, the QHA is expected to be less applicable as anharmonic effects become increasingly important. Further information on the calculation of $\alpha(P, T)$ and the validity of the QHA can be found in the Appendix.

### C. Superionicity in CaF$_2$

The onset of superionicity in $\beta$-CaF$_2$ has been discussed in connection with the formation of unstable phonon modes in the fluorite CaF$_2$ structure [62]. Indeed, this is the criterion we have used in Fig. 8, where we label the region where $Fm\bar{3}m$-CaF$_2$ has unstable phonons as superionic (‘S/I’), or $\beta$. By this criterion, the $\alpha$-$\beta$ transition is calculated to occur at $\approx 1000$ K at 0 GPa, which is actually in rough agreement with the experimentally observed transition temperature of 1400 K, considering that the QHA should be inaccurate near unstable phonon modes. Fig. 9(a) shows the phonon dispersion...
FIG. 9. Softening of phonon modes in the fluorite \( Fm\bar{3}m \)-\( \text{CaF}_2 \) structure. (a) Phonon dispersion curves of this structure at a static-lattice pressure of 0 GPa (cell volume 41.79 Å\(^3\)/f.u.). (b) The blue-coloured mode in (a) as a function of decreasing static pressure, from 0 to \(-10\) GPa. The mode softens and first develops imaginary phonon frequencies at \( X \) (shown as negative frequencies).

FIG. 10. Phonon dispersion curves for the proposed \( P\bar{6}2m \)-\( \text{CaF}_2 \) structure. This phase has stable phonons at a static pressure of 10 GPa (cell volume 34.45 Å\(^3\)/f.u.). The mode coloured blue softens and becomes unstable at the Brillouin zone \( K \) point with decreasing pressure, as shown by the blue dashed curve. Only the portion from \( \Gamma \) to \( A \) is shown at 0 GPa.

relations in \( Fm\bar{3}m \)-\( \text{CaF}_2 \) at a static-lattice pressure of 0 GPa, while Fig. 9(b) shows how unstable modes develop in this structure with increasing volume (decreasing static-lattice pressure). Unstable phonon modes are first encountered at the Brillouin zone \( X \) point. The corresponding atomic displacements in this unstable mode leave \( \text{Ca}^{2+} \) ions fixed, while \( \text{F}^- \) ions are displaced along the [100], [010] or [001] directions (referred to a conventional cubic cell for \( Fm\bar{3}m \)-\( \text{CaF}_2 \)). The connection to superionicity is that these directions also correspond to easy directions for \( \text{F}^- \) ion diffusion in the fluorite structure, and are almost barrierless at volumes corresponding to unstable \( X \) phonons [63].

Fig. 9(b) also shows that at even larger volumes, unstable phonon modes develop at the Brillouin zone \( W \) point and that the entire \( W - X \) branch becomes soft. As is the case at \( X \), the corresponding phonon modes involve only \( \text{F}^- \) ion displacements, though in different directions: at \( W \), \( \text{F}^- \) ions displace along the [011] and [0-11] directions. This may explain the observed gradual onset of superionicity in the fluorite structure [64]: as volume increases, further low-energy diffusion pathways corresponding to unstable phonon modes are opened up in the lattice.

Fig. 10 shows the phonon dispersion relations in \( P\bar{6}2m \). With increasing volume, this structure first develops unstable phonon modes at the Brillouin zone \( K \) point, and the atomic displacements of \( \text{Ca}^{2+} \) and \( \text{F}^- \) ions in the corresponding mode are depicted in Fig. 11. This mode is similar to the unstable mode found in fluorite \( \text{CaF}_2 \) at \( X \), in the sense that it involves displacements of \( \text{F}^- \) ions and a sublattice of \( \text{Ca}^{2+} \) ions which remain fixed. \( \text{F}^- \) ions move along the [120], [210] or [1-10] directions, and all displacements are confined to the \( ab \)-plane only. The \( P\bar{6}2m \) structure can be visualised as layer-like: in Fig. 11, all atoms that are linked by bonds belong to the same layer, and all ‘isolated’ atoms belong to a different layer. We find that \( \text{Ca}^{2+} \) ions in alternating layers remain fixed in the unstable phonon mode. By analogy with fluorite \( \text{CaF}_2 \), we propose that \( P\bar{6}2m \)-\( \text{CaF}_2 \) also undergoes a superionic phase transition accompanying this phonon mode, and we label the region where \( P\bar{6}2m \) has unstable phonon modes in Fig. 8 as superionic (‘S/I’). As is the case for the fluorite structure, it is possible that other compounds in the \( P\bar{6}2m \) structure could also exhibit superionicity.

The pressure-temperature phase diagram of \( \text{CaF}_2 \) has recently been examined by Cazorla et al. [59, 65]. In addition to the known \( \alpha \), \( \beta \) and \( \gamma \) phases, the authors propose a high-temperature phase transition from \( \gamma \) to a new \( \delta \) phase, which in turn is predicted to undergo a superionic transition at even higher temperatures, to a phase labelled \( \epsilon \)-\( \text{CaF}_2 \). A \( P2_1/c \) symmetry structure was proposed for the \( \delta \)-phase [59], however we find that this structure is close to \( Pnma \) symmetry, and relaxing it using DFT gives the \( \gamma \)-\( \text{CaF}_2 \) structure. The phase diagram of Fig. 8 is in qualitative agreement with these results, where we identify the \( \delta \) phase with our predicted \( P\bar{6}2m \) structure, and the \( \epsilon \) superionic phase with the re-
to 70 GPa through DFT calculations and computational
−
above 70 GPa [66]. The optical bandgap for
γ
properties up until high pressures.
−
to at least 70 GPa, and likely retains its superior optical
bandgap shows that it remains a wide-gap insulator up
ternal pressure standard [52]. Our calculations of the
γ
above 50 GPa. Semilocal DFT calculations using GGA
−
ments. We also give the electronic DOS of the
5
−
Calcium atoms are in red, fluorine atoms in green.
cation where P62m has unstable phonon modes.

D. Optical bandgaps in CaF₂

Our calculations show that optical bandgaps in CaF₂
initially increase but then remain relatively constant over
the pressure range 0–70 GPa (Fig. 3). We also show,
using a dashed line Fig. 3, the calculated bandgap for the
P62m-CaF₂ phase, which begins to slowly decrease
above 50 GPa. Semilocal DFT calculations using GGA
functionals have also shown that this occurs for γ-CaF₂
above 70 GPa [66]. The optical bandgap for γ-CaF₂
lies 0.9–1.2 eV above that of P62m-CaF₂ in the pres-
ure range 10–70 GPa, suggesting that the formation
of P62m-CaF₂ might be detectable in optical
−
asure range 10
−
m-CaF₂ structure develops unstable phonon modes at high temperatures, which we propose
is associated with a superionic transition in this struc-
ture. P62m-CaF₂ and its region of phonon instability
are consistent with the recently proposed δ and ε CaF₂
phases.

Be-, Mg- and CaF₂ are wide-gap insulators. Calcula-
tions using the HSE06 functional show that the bandgaps
in BeF₂ and MgF₂ are tunable with pressure, rising by
0.06 eV/GPa and 0.04 GPa over the pressure range 0–70
GPa. The optical bandgaps in CaF₂ are instead rela-
tively constant over this pressure range.

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[1] W. H. Dumbaugh and D. W. Morgan. Preliminary ultra-
violet transmission data for beryllium fluoride glasses. J.
Non-Crystal. Solids 38, 211-216 (1980).
Appendix for:
“High-pressure phases of group II difluorides: polymorphism and superionicity”

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I. ELECTRONIC STRUCTURE CALCULATIONS

All calculations are carried out with version 8.0 of the CASTEP plane−wave pseudopotential DFT code.

Our calculations of the enthalpy vs. pressure curves in the main paper and in this appendix, lattice parameters, and supercell phonon calculations all use default ultrasoft pseudopotentials for Be, Mg, Ca, F, Si and O as generated internally by the CASTEP code and the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional. A plane−wave cutoff of 800 eV, Brillouin zone sampling density of at least $2\pi \times 0.04 \, \text{Å}^{-1}$, grid scale of 2 (for representing the density) and fine grid scale of 2.5 (grid for ultrasoft core or augmentation charges) are used in these calculations. Calculations of phonon frequencies use the finite−displacement supercell method in CASTEP, and the cumulant force constant matrix cutoff scheme [1, 2]. Details of the supercell sizes used in finite−displacement phonon calculations are given in subsequent sections.

Bandgap calculations (Fig. 3 of the main paper) are instead carried out with norm−conserving pseudopotentials, which are required in order to use hybrid density functionals in CASTEP. Generation strings for these potentials are taken from the version 16.0 CASTEP Norm-Conserving Pseudopotential (‘NCP’) library, and used in version 8.0 of the code. Our bandgap calculations use the ‘HSE06’ variant of the Heyd-Scuseria-Ernzerhof hybrid functional, a plane−wave cutoff of 1600 eV, a Brillouin zone sampling density of at least $2\pi \times 0.1 \, \text{Å}^{-1}$, and grid and fine grid scales of 2 and 2.5 respectively. The structures for bandgap calculations were obtained by geometry optimisation using the same plane−wave cutoff, Brillouin zone sampling and grid scales, but with the PBE functional instead of HSE06.

Optical bandgaps for BeF$_2$ are calculated for the α-quartz, coesite-I, moganite, CaCl$_2$ and α-PbO$_2$ structures and shown in Fig. 3 of the main paper, over the pressure ranges for which these structures are calculated to be stable at the static-lattice level. We therefore exclude the small stability range of α-cristobalite BeF$_2$ (0–0.4 GPa), and use the coesite-I structure instead of coesite-II on the grounds that these two structures are almost identical at low pressures. Optical bandgaps for MgF$_2$ are calculated for the rutile, α-PbO$_2$, pyrite, O-I and cotunnite structures and likewise shown in Fig. 3 of the main paper. Finally for CaF$_2$, we show optical bandgaps for the fluorite, cotunnite and $P6_2m$ structures.
II. STRUCTURE DATA

A. Beryllium fluoride structure data

Moganite, space group \( C2/c \) (\#15)
The table below gives the DFT-relaxed \( \text{BeF}_2 \) moganite structure at 20 GPa. A conventional cell (36 atoms) with full Hermann-Mauguin (HM) symbol \( C12/c1 \) (standard setting for this space group) is given; the primitive cell has 18 atoms.

Fig. 2(a) of the main paper illustrates this structure, but uses different lattice vectors, obtained from those below through the relations \( \mathbf{a}' = \mathbf{a} + \mathbf{c} \), \( \mathbf{b}' = -\mathbf{b} \), \( \mathbf{c}' = -\mathbf{c} \). This has full HM symbol \( I12/c1 \) and a smaller monoclinic angle \( (\beta = 90.446^\circ) \).

| Lattice parameters (Å, deg.) | Atomic coordinates | Wyckoff site |
|-------------------------------|--------------------|--------------|
| \( a = 12.008 \) | Be 0.0000 0.9572 0.2500 | 4e |
| \( b = 4.191 \) | Be 0.1658 0.3268 0.1989 | 8f |
| \( c = 7.103 \) | F 0.2909 0.1705 0.2289 | 8f |
| \( \alpha = 90.000 \) | F 0.1237 0.1811 0.3455 | 8f |
| \( \beta = 125.818 \) | F 0.0421 0.2694 0.9492 | 8f |
| \( \gamma = 90.000 \) | |

CaCl\(_2\) structure, space group \( Pnnm \) (\#58)
The unit cell is primitive and has \( Z = 2 \) (6 atoms). The positions below correspond to 50 GPa, and the structure is depicted in Fig. 2(b) of the main paper.

| Lattice parameters (Å, deg.) | Atomic coordinates | Wyckoff site |
|-------------------------------|--------------------|--------------|
| \( a = 3.796 \) | Be 0.0000 0.0000 0.0000 | 2a |
| \( b = 3.959 \) | Mg 0.9586 0.2259 0.8870 | 8c |
| \( c = 2.445 \) | Be 0.1099 0.1721 0.4653 | 4g |
| \( \alpha = 90.000 \) | F 0.2339 0.9977 0.4653 | 8c |
| \( \beta = 90.000 \) | |
| \( \gamma = 90.000 \) | |

B. Magnesium fluoride structure data

Orthorhombic-I structure, space group \( Pbcn \) (\#61)
The unit cell is primitive and has \( Z = 8 \) (24 atoms). The positions below correspond to 42 GPa, and the structure is depicted in Fig. 5 of the main paper.

| Lattice parameters (Å, deg.) | Atomic coordinates | Wyckoff site |
|-------------------------------|--------------------|--------------|
| \( a = 4.782 \) | Mg 0.9586 0.2259 0.8870 | 8c |
| \( b = 4.556 \) | Be 0.1099 0.1721 0.2008 | 8c |
| \( c = 8.863 \) | F 0.2339 0.9977 0.4653 | 8c |
| \( \alpha = 90.000 \) | |
| \( \beta = 90.000 \) | |
| \( \gamma = 90.000 \) | |

C. Calcium fluoride structure data

Fe\(_2\)P-type structure, space group \( P\bar{6}2m \) (\#189)
The unit cell is primitive and has \( Z = 3 \) (9 atoms). The positions below correspond to 30 GPa, and the structure is depicted in Fig. 7(a) of the main paper.

| Lattice parameters (Å, deg.) | Atomic coordinates | Wyckoff site |
|-------------------------------|--------------------|--------------|
| \( a = 5.697 \) | Ca 0.0000 0.0000 0.5000 | 1b |
| \( b = 5.697 \) | Ca 0.3333 0.6666 0.0000 | 2c |
| \( c = 3.255 \) | F 0.7433 0.0000 0.0000 | 3f |
| \( \alpha = 90.000 \) | F 0.4126 0.0000 0.5000 | 3g |
| \( \beta = 90.000 \) | |
| \( \gamma = 120.000 \) | |
D. Low-pressure SiO\(_2\) polymorphs

Three low-enthalpy structures for BeF\(_2\), labelled \(P2_1 2_1 2_1\)-I, \(C2/c - 4 \times 2\), and \(P2_1/c\) in Fig. 1(a) of the main paper, are examined as possible low-enthalpy polymorphs for SiO\(_2\). The monoclinic angle in \(P2_1/c\) is close to 90\(^\circ\) (=89.958\(^\circ\)), and so we also examine a higher symmetry version of this with \(\alpha=\beta=\gamma=90^\circ\), with the space group \(Pnma\). Structure data for these polymorphs are shown below, alongside their enthalpies relative to the \(\alpha\)-quartz phase. All data is given at 0 GPa.

\(C2/c - 4 \times 2\) structure, space group \#15 (-15.7 meV/f.u.)
A conventional unit cell has \(Z=8\) (24 atoms), and is given below. This has full HM symbol \(C12/c1\).

| Lattice parameters (Å, deg.) | Atomic coordinates | Wyckoff site |
|-----------------------------|---------------------|--------------|
| \(a=8.940\) \(b=5.031\) \(c=8.977\) | Si 0.1877 0.1694 0.3129 | 8f           |
| \(\alpha=90.000\) \(\beta=111.563\) \(\gamma=90.000\) | O 0.2055 0.5806 0.7058 | 8f           |
|                             | O 0.0000 0.0798 0.2500 | 4e           |
|                             | O 0.2500 0.2500 0.5000 | 4d           |

\(P2_1/c\) structure, space group \#14 (-5.9 meV/f.u.)
The unit cell is primitive and has \(Z=8\) (24 atoms). The cell given below has full HM symbol \(P12_1/n1\) (ITA unique axis \(b\), cell choice 2).

| Lattice parameters (Å, deg.) | Atomic coordinates | Wyckoff site |
|-----------------------------|---------------------|--------------|
| \(a=8.583\) \(b=9.626\) \(c=5.207\) | Si 0.0618 0.1781 0.2632 | 4e           |
| \(\alpha=90.000\) \(\beta=89.958\) \(\gamma=90.000\) | Si 0.3654 0.3576 0.2649 | 4e           |
|                             | O 0.1448 0.0263 0.2455 | 4e           |
|                             | O 0.1914 0.2978 0.2191 | 4e           |
|                             | O 0.4278 0.3066 0.5443 | 4e           |
|                             | O 0.4830 0.3001 0.0441 | 4e           |

\(P2_1 2_1 2_1\)-I structure, space group \#19 (-5.5 meV/f.u.)
The unit cell is primitive and has \(Z=8\) (24 atoms).

| Lattice parameters (Å, deg.) | Atomic coordinates | Wyckoff site |
|-----------------------------|---------------------|--------------|
| \(a=5.195\) \(b=8.519\) \(c=9.560\) | Si 0.2933 0.6088 0.8607 | 4a           |
| \(\alpha=90.000\) \(\beta=90.000\) \(\gamma=90.000\) | Si 0.7068 0.1942 0.3192 | 4a           |
|                             | O 0.7237 0.1042 0.6363 | 4a           |
|                             | O 0.9249 0.3308 0.3101 | 4a           |
|                             | O 0.5746 0.7739 0.2020 | 4a           |
|                             | O 0.2499 0.5688 0.3056 | 4a           |

\(Pnma\) structure, space group \#62 (-2.2 meV/f.u.)
The unit cell is primitive and has \(Z=8\) (24 atoms).

| Lattice parameters (Å, deg.) | Atomic coordinates | Wyckoff site |
|-----------------------------|---------------------|--------------|
| \(a=9.415\) \(b=5.285\) \(c=8.683\) | Si 0.6850 0.2500 0.5529 | 4c           |
| \(\alpha=90.000\) \(\beta=90.000\) \(\gamma=90.000\) | Si 0.3577 0.2500 0.6389 | 4c           |
|                             | O 0.5303 0.2500 0.6363 | 4c           |
|                             | O 0.3087 0.2500 0.8176 | 4c           |
|                             | O 0.2041 0.4997 0.0538 | 8d           |
III. CONVEX HULLS FOR BE, MG AND CA–F AT 60 GPa

In addition to our BeF$_2$, MgF$_2$ and CaF$_2$ searches, we carry out variable stoichiometry structure searches for the Be-F, Mg-F and Ca-F systems at 60 GPa. Convex hulls depicting the results of these searches are shown below.

![Diagram showing convex hulls for Be-F, Mg-F, and Ca-F systems at 60 GPa.](image)

FIG. 12. Convex hulls showing the results of structure searching at the static-lattice level of theory at 60 GPa in the Be-F (left), Mg-F (middle) and Ca-F (right) systems.

In each case, we search over 29 stoichiometries, including the elements (Be or Mg or Ca, and F). The convex hulls depict the lowest enthalpy structure at each stoichiometry, relaxed to the same standard as the results in the main paper (800 eV basis set cutoff, Brillouin zone sampling of $2\pi \times 0.04$ Å$^{-1}$, PBE exchange).

At 60 GPa, beryllium has the $\alpha$-Be hexagonal closed-packed (hcp) structure, space group $P6_3/mmc$ [3], which we also verify directly through structure searches. We find a molecular crystal comprised of F$_2$ molecules with space group $Cmce$ to be the lowest enthalpy fluorine structure at 60 GPa; this also applies to the Mg-F and Ca-F systems. Of the stoichiometries searched, only BeF$_2$ is stable at this pressure in the Be-F system.

Magnesium undergoes a phase transition from hcp to bcc between about 45 and 60 GPa; within this pressure range, the coexistence of the hcp and bcc phases is observed at low temperatures [4]. Our PBE–DFT calculations find that the hcp–Mg phase is very slightly lower in enthalpy than bcc–Mg at 60 GPa, so we use the hcp–Mg phase in our hulls above. As is the case for BeF$_2$, we find that MgF$_2$ is the only stable stoichiometry in the Mg-F system at 60 GPa.

DFT and structure searching calculations predict that the $\beta$-tin $I4_1/amd$-symmetry structure is the lowest enthalpy phase for calcium at 60 GPa [5], and we also confirm this in the present study. The $\beta$-tin phase is well known to be slightly at odds with experimental results, which instead observe simple cubic calcium (or distorted versions of it) at 60 GPa [6], although the $\beta$-tin phase has been synthesised near 35 GPa. We carry out our calculations with the lowest enthalpy DFT phase for calcium ($\beta$-tin) in the Ca–F hulls above. Our searches find that both CaF$_2$ and CaF$_3$ are stable stoichiometries at 60 GPa.
IV. ELECTRONIC AND PHONON DOS OF SELECTED STRUCTURES

In this section we show the electronic and phonon density−of−states (DOS) for some of the newly predicted structures discussed in the main paper. Specifically, these are the moganite−BeF$_2$ and CaCl$_2$−BeF$_2$ structures, stable in the pressure ranges 11.6−30.1 GPa and 30.1−57.5 GPa respectively (Fig. 13), and the O-I−MgF$_2$ and $P6_2m$-CaF$_2$ structures (Fig. 14). The O-I−MgF$_2$ structure is predicted to be stable in the pressure range 39.6−44.1 GPa, while the $P6_2m$-CaF$_2$ phase is calculated to become stable at high temperature.

The electronic DOS ((a) in the figures below) is calculated with the Optados code using the same DFT parameters as our bandgap calculations (see Sec. I above) and a Gaussian smearing of 0.25 eV. The valence band maximum (VBM) is set to 0 eV. The majority contributor (species and orbital) to each feature in the DOS is labelled in Figs. 13 and 14 below. In all cases, we find that the valence bands consist of fluorine 2p orbitals, while the conduction bands come from unoccupied $p$ or $d$ orbitals in beryllium, magnesium or calcium.

The dynamic stability of the predicted structures is indicated by the phonon DOS ((b) in the figures below) for these structures having no protrusion into negative (imaginary) frequencies (shown as grey regions).

![Electronic and phonon DOS for moganite−BeF$_2$ phase at 20 GPa (left panel), and for the CaCl$_2$−BeF$_2$ phase at 50 GPa (right panel). A 4×4×3 (864 atom) and 4×4×6 (576 atom) supercell is used for the moganite and CaCl$_2$ phonon calculations, respectively.](image1)

![Electronic and phonon DOS for O-I−MgF$_2$ phase at 42 GPa (left panel), and for the $P6_2m$-CaF$_2$ phase at 30 GPa (right panel). A 4×3×2 (576 atom) and 3×3×6 (486 atom) supercell is used for the O-I and $P6_2m$ phonon calculations, respectively.](image2)
V. KNOWN AB$_2$ STRUCTURES USED

A list of AB$_2$-type structures that were considered in addition to our AIRSS searches is given below. The atoms are substituted appropriately, for example Si→Be, O→F, and the structure relaxed. Structures are taken from the Inorganic Crystal Structure Database (ICSD) [7] or from literature. We give the 5-digit ICSD reference number for the former.

In the table below, Z is the number of formula units in the primitive unit cell, and so 3Z is the total number of atoms in the primitive cell. Our AIRSS searches were restricted to Z ≤ 8.

| Compound | SG (HM) | SG (#) | Lattice | Z | Name(s)      | Reference |
|----------|---------|--------|---------|---|--------------|-----------|
| HfO$_2$  | $P2_1/c$| 14     | monoclinic | 4 | Baddeleyite  | 60903     |
| SiO$_2$  | $P2_1/c$| 14     | monoclinic | 32| Coesite-II   | [8]       |
| SiO$_2$  | $C2/c$  | 15     | monoclinic | 8 | Coesite-I    | [8]       |
| SiO$_2$  | $C2/c$  | 15     | monoclinic | 6 | Moganite     | 67669     |
| BeF$_2$  | $C2/c$  | 15     | monoclinic | 6 | –            | [9]       |
| SiO$_2$  | $Pnmn$  | 58     | orthorhombic | 2 | CaCl$_2$-type | 26158     |
| SiO$_2$  | $Pbca$  | 61     | orthorhombic | 8 | Orthorhombic-I, OI | [10]       |
| ZrO$_2$  | $Pnma$  | 62     | orthorhombic | 4 | Cotunnite, Ortho-II (PbCl$_2$) | [12]       |
| SiO$_2$  | $P4_12_1$ | 92    | tetragonal | 4 | α-cristobalite | 75300     |
| SiO$_2$  | $P4_2/mnm$ | 136  | tetragonal | 2 | Rutile, β-PbO$_2$, Plattnerite | 9160       |
| SiO$_2$  | $P3_11$ | 152    | trigonal   | 3 | α-quartz     | 27745     |
| SiO$_2$  | $P6_22$ | 180    | hexagonal  | 3 | β-quartz     | 31088     |
| SiO$_2$  | $Pm3m$  | 221    | cubic      | 46| Melanophlogite | 159046$^{(b)}$ |
| SiO$_2$  | $Fd3m$  | 227    | cubic      | 2 | β-cristobalite | 77458     |

$^{(a)}$ Has a number of aliases: Seifertite (SiO$_2$), Scrutinyite (α-PbO$_2$), Columbite (TiO$_2$)

$^{(b)}$ Interstitial carbon atoms (representing methane) were removed from this structure before relaxing

For the orthorhombic space groups, a number of different settings are possible with different HM symbols. We list some of the orthorhombic ones below [13]:

| SG (#) | Standard setting | Alternative settings          |
|--------|------------------|-------------------------------|
| 58     | $Pnnm$           | $Pmnn$, $Pnam$                |
| 60     | $Pbcn$           | $Pcna$, $Pnab$, $Pbnm$, $Pcmb$|
| 61     | $Pbaa$           | $Pcab$                        |
| 62     | $Pnma$           | $Pnnb$, $Pbnm$, $Pcmm$, $Pbcn$, $Pnam$ |
VI. QUASIHARMONIC PHASE DIAGRAM FOR CaF$_2$

A. Computational details

To construct the phase diagram shown in Fig. 8 of the main paper, we perform finite-displacement phonon calculations at several different volumes for the $Fm\bar{3}m$, $P\bar{6}2m$ and $Pnma$ CaF$_2$ structures. We use $5\times5\times5$ (375 atom), $3\times3\times6$ (486 atom), and $5\times3\times3$ (540 atom) supercells for the $Fm\bar{3}m$, $P\bar{6}2m$ and $Pnma$ structures, respectively. Volumes corresponding to the following static-lattice pressures are used for these calculations:

$Fm\bar{3}m$: $-6, -4, -2, 0, 4, 8, 12, 16, 20$ GPa
$P\bar{6}2m$: $10, 20, 30, 40, 50, 60, 70$ GPa
$Pnma$: $0, 2, 6, 10, 20, 30, 40, 50, 60, 70$ GPa

This gives us the phonon free energies $F(V,T)$ at each volume for these structures. We fit the resulting energies with a polynomial in $V$. For the $Fm\bar{3}m$ and $P\bar{6}2m$ structures, the calculated $F(V,T)$ values vary reasonably slowly with volume and are well reproduced by a quadratic in $V$. For the $Pnma$ structure, we find that the calculated $F(V)$ values tend to initially increase rapidly with decreasing volume, but then increase less rapidly at lower volumes (see Fig. 15). A cubic polynomial in $V$ is therefore used to capture this trend. Some insight into this behaviour can be found by looking at the dependence of the lattice parameters of these structures on $V$; for $Fm\bar{3}m$ and $P\bar{6}2m$, the lattice parameters steadily decrease on compression. The $Pnma$ structure, however, shows slightly unusual behaviour on compression in that lattice parameter $a$ initially decreases, but then starts increasing for static-lattice pressures above 56 GPa, while lattice parameter $c$ decreases more rapidly at that pressure as well (Fig. 16).

Static-lattice calculations provide relaxed geometries for our calculations, and give us sets of enthalpies $H$, volumes $V$ and static-lattice pressures (or electron pressures) $P_{el}$. Within the QHA, at a given volume $V$, the corresponding Gibbs free energy is the sum of the electronic enthalpy and phonon free energy: $G(V,T) = H(V) + F(V,T)$. The pressure $P$ at that volume is $P = P_{el} + P_{ph}$, where $P_{ph} \equiv -\partial F(V,T)/\partial V$ is the phonon pressure.

![FIG. 15. Phonon free energies $F(V)$ for the $Fm\bar{3}m$ (left), $P\bar{6}2m$ (middle) and $Pnma$ (right) structures of CaF$_2$, as a function of volume and of temperature. The ‘+’ marks indicate values from supercell calculations, while the solid curves show the resulting polynomial fits to $F(V)$.

B. Validity of the QHA

Here we calculate the volume coefficient of thermal expansion:

$$\alpha(P,T) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

at a variety of pressures for the $Fm\bar{3}m$, $P\bar{6}2m$ and $Pnma$ calcium fluoride structures. The results are shown in Fig. 17.
FIG. 16. Lattice parameters of the \( \text{Fm}\overline{3}m \) (left), \( \text{P62m} \) (middle) and \( \text{Pnma} \) (right) structures of \( \text{CaF}_2 \) as a function of volume, calculated at the static lattice level. The lattice parameter for \( \text{Fm}\overline{3}m \) is given for the primitive cell (\( Z=1, a=b=c, \alpha = \beta = \gamma = 60^\circ \)); the lattice parameter for the corresponding conventional cell (\( Z=4 \)) is \( \sqrt{2} \) times larger. Our simulation cell for the \( \text{Pnma} \) structure has \( a < c < b \), and is actually set in the alternative \( \text{Pmcn} \) setting for that space group (#62).

The calculated thermal expansion coefficient can be used to assess the validity of the QHA [14, 15]. We can consider the QHA valid at temperatures lower than the higher temperature inflection point in \( \alpha(P,T) \), i.e. where

\[
\left[ \frac{\partial^2 \alpha(P,T)}{\partial T^2} \right]_p
\]

changes sign. Beyond this point, we generally find that \( \left[ \frac{\partial^2 \alpha(P,T)}{\partial T^2} \right]_p \geq 0 \) and the QHA is expected to be less applicable with further increases in temperature, as anharmonic effects become more important.

For the \( \text{Fm}\overline{3}m \) and \( \text{P62m} \) structures, Fig. 17 shows this inflection point in \( \alpha(P,T) \) using open circles at each pressure. Fitting the resulting \((P,T)\) coordinates of these inflection points gives us the validity rule \( T \leq 28P \) (GPa) + 453 given in the main paper. We note that locating the inflection point is subject to some numerical uncertainty, because \( \alpha(P,T) \) changes quite slowly in the vicinity of this point (Fig. 17). An uncertainty of about 100 K is therefore quoted in the main paper.

This inflection point is harder to locate in the \( \alpha(P,T) \) curves for the \( \text{Pnma} \) structure. The thermal expansion coefficients are slightly unusual in that they initially increase, but then decline at higher temperatures. This is partly due to the fact that the phonon pressure in \( \text{Pnma} \) declines at higher volumes, as can be seen in the slope of the \( F(V,T) \) curves for \( \text{Pnma} \) in the right-hand panel of Fig. 15.

FIG. 17. Calculated volume thermal expansion coefficients \( \alpha(P,T) \) at a variety of pressures as a function of temperature for the \( \text{Fm}\overline{3}m \) (left), \( \text{P62m} \) (middle) and \( \text{Pnma} \) (right) \( \text{CaF}_2 \) structures. The open circles in the left and middle panels show inflection points, where \( \frac{d^2 \alpha}{dT^2} \) changes sign.
VII. UNSTABLE MODES IN $Fm\bar{3}m$ AND $P\bar{6}2m$ $CaF_2$

In Figs. 9 and 10 of the main paper, the $Fm\bar{3}m$ and $P\bar{6}2m$ structures develop unstable phonon frequencies with decreasing pressure / increasing volume. For the $Fm\bar{3}m$ structure, imaginary (‘negative’) phonon frequencies first develop at the Brillouin zone $X$ point, and then at larger volumes at the $W$ point. Fig. 18 shows the smallest mode frequency at $X$ and $W$ as a function of volume for this structure. The solid blue points in Fig. 18 were obtained using a $2\times4\times4$ supercell (96 atoms) for $Fm\bar{3}m$, as the $X$ and $W$ points are both commensurate with a supercell of this size. For comparison, red crosses in Fig. 18 show the results obtained using a $5\times5\times5$ supercell (375 atoms), the size used in our phase diagram calculations. The $X$ and $W$ points are not commensurate with this supercell, so the frequencies shown with red crosses have been obtained by interpolation. These results differ from the exactly commensurate $2\times4\times4$ supercell results by $<4$ cm$^{-1}$. The thin solid and dotted black lines connecting the blue points are shape–preserving interpolants fitted to the data and are intended to guide the eye.

![Graph](image1)

For the $P\bar{6}2m$ structure, imaginary phonons develop at the Brillouin zone $K$ point, and the right–hand panel of Fig. 18 also shows the lowest mode frequency at this point as a function of volume. The solid blue points are obtained using a $3\times3\times1$ supercell (81 atoms) commensurate with $K$, while the red crosses show results using a $3\times3\times6$ supercell (486 atoms), as used in phase diagram calculations. As with the $Fm\bar{3}m$ structure, the red crosses are interpolations; however, we note that $K$ is also commensurate with this larger supercell, and the interpolated results are almost identical to the exactly commensurate ones in this case. The thin solid and dotted black lines are again guides to the eye.

The volume at which these structures first develop imaginary phonon frequencies directly affects the phase diagram of Fig. 8 of the main paper. In particular, this volume determines the location of the dashed lines between the red/light—red and blue/light—blue regions of the phase diagram. We have taken this volume to be simply halfway between the first blue point in Fig. 18 with a frequency >0 cm$^{-1}$, and the first ‘negative-frequency’ blue point. For $Fm\bar{3}m$, this corresponds to $V = 46.47$ Å$^3$/f.u., and is at a static–lattice pressure between −7 and −6 GPa. For $P\bar{6}2m$, we have $V = 37.70$ Å$^3$/f.u., occurring between 0 and 1 GPa.
[1] K. Parlinski, Z. Q. Li, and Y. Kawazoe. First-Principles Determination of the Soft Mode in Cubic ZrO$_2$. Phys. Rev. Lett. 78, 4063 (1997).

[2] Lin-Hui Ye, Bang-Gui Liu, Ding-Sheng Wang, and Rushan Han. Ab initio phonon dispersions of single-wall carbon nanotubes. Phys. Rev. B 69, 235409 (2004).

[3] A. Lazicki, A. Dewaele, P. Loubeyre, and M. Mezouar. High-pressure-temperature phase diagram and the equation of state of beryllium. Phys. Rev. B 86, 174118 (2012).

[4] G. W. Stinton, S. G. MacLeod, H. Cynn, D. Errandonea, W. J. Evans, J. E. Proctor, Y. Meng, and M. I. McMahon. Equation of state and high-pressure/high-temperature phase diagram of magnesium. Phys. Rev. B 90, 134105 (2014).

[5] A. R. Oganov, Y. Ma, Y. Xu, I. Errea, A. Bergara, and A. O. Lyakhov. Exotic behavior and crystal structures of calcium under pressure. PNAS 107, 7646-7651 (2010).

[6] B. Li, Y. Ding, W. Yang, L. Wang, B. Zou, J. Shu, S. Sinogeikin, C. Park, G. Zou, and H.-K. Mao. Calcium with the $\beta$-tin structure at high pressure and low temperature. PNAS 109, 16459-16462 (2012).

[7] Crystallographic databases, ed. F. H. Allen, G. Bergerhoff and R. Sievers, Chester, England: International Union of Crystallography, 1987. Database available online at http://iccd.cds.rsc.org/.

[8] A. Černok, E. Bykova, T. Boffa Ballaran, H.-P. Liermann, M. Hanfland, and L. Dubrovinsky. High-pressure crystal chemistry of coesite-I and its transition to coesite-II. Zeit. für Krist. 229, 761-773 (2014).

[9] M. S. Rakitin, A. R. Oganov, H. Niu, M. M. D. Esfahani, X.-F. Zhou, G.-R. Qian, and V. L. Solozhenko. A novel phase of beryllium fluoride at high pressure. Phys. Chem. Chem. Phys. 17, 26283-26288 (2015).

[10] A. El Goresy, P. Dera, T. G. Sharp, C. T. Prewitt, M. Chen, L. Dubrovinsky, B. Wopenka, N. Z. Doctor and R. J. Hemley. Seifertite, a dense orthorhombic polymorph of silica from the Martian meteorites Shergotty and Zagami. Eur. J. Mineral. 20, 523-528 (2008).

[11] N. A. Dubrovinskaia, L. S. Dubrovinsky, R. Ahuja, V. B. Prokopenko, V. Dmitriev, H.-P. Weber, J. M. Osorio-Guillen, and B. Johansson. Experimental and Theoretical Identification of a New High-Pressure TiO$_2$ Polymorph. Phys. Rev. Lett. 87, 275501 (2001).

[12] J. E. Lowther, J. K. Dewhurst, J. M. Leger, and J. Haines. Relative stability of ZrO$_2$ and HfO$_2$ structural phases. Phys. Rev. B 60, 14485 (1999).

[13] M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga, A. Kirov, and H. Wondratschek. Bilbao Crystallographic Server I: Databases and crystallographic computing programs. Zeit. für Krist. 221, 1, 15-27 (2006).

[14] B. B. Karki, R. M. Wentzcovitch, S. de Gironcoli and S. Baroni. First principles thermoelasticity of MgSiO$_3$-perovskite: consequences for the inferred properties of the lower mantle. Geophys. Research. Lett. 28, 2699-2702 (2001)

[15] R. M. Wentzcovitch, B. B. Karki, M. Cococcioni, and S. de Gironcoli. Thermoelastic Properties of MgSiO$_3$-Perovskite: Insights on the Nature of the Earth’s Lower Mantle. Phys. Rev. Lett. 92, 018501 (2004).