Phase transitions and equations of state of alkaline earth fluorides CaF$_2$, SrF$_2$, and BaF$_2$ to Mbar pressures

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Phase transitions and equations of state of the alkaline earth fluorides CaF$_2$, SrF$_2$, and BaF$_2$ were examined by static compression to pressures as high as 146 GPa. Angle-dispersive x-ray diffraction experiments were performed on polycrystalline samples in the laser-heated diamond-anvil cell. We confirmed that at pressures less than 10 GPa all three materials undergo a phase transition from the cubic ($Fm\overline{3}m$) fluorite structure to the orthorhombic ($Pn\bar{a}m$) cotunnite-type structure. This work has characterized an additional phase transition in CaF$_2$ and SrF$_2$: these materials were observed to transform to a hexagonal ($P6_3/mmc$) Ni$_2$In-type structure between 63–79 GPa and 28–29 GPa, respectively, upon laser heating. For SrF$_2$, the Ni$_2$In-type phase was confirmed by Rietveld refinement. Volumes were determined as a function of pressure for all high-pressure phases and fit to the third-order Birch-Murnaghan equation of state. For CaF$_2$ and SrF$_2$, the fluorite-cotunnite transition results in a volume decrease of 8–10 %, while the bulk modulus of the cotunnite-type phase is the same or less than that of the fluorite phase within uncertainty. For all three fluorides, the volume reduction associated with the further transition to the Ni$_3$In-type phase is ~5%. The percentage increase in the bulk modulus ($\Delta K$) across the transition is greater when the cation is smaller. While for BaF$_2$, $\Delta K$ is 10–30 %, $\Delta K$ values for SrF$_2$ and CaF$_2$ are 45–65 % and 20–40 %. Although shock data for CaF$_2$ have been interpreted to show a transition to a highly incompressible phase above 100 GPa, this is not consistent with our static equation of state data.

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I. INTRODUCTION

The $AX_2$ family includes a variety of compounds of interest in geosciences, materials science, and condensed-matter physics that exhibit extensive polymorphism dependent on ionic size, electronic properties, and pressure. One common highly coordinated polymorph is the fluorite structure, which is the stable polymorph at ambient conditions for the alkaline earth fluorides CaF$_2$, SrF$_2$, and BaF$_2$. Fluorides are widely used as windows and lenses, optical coatings, scintillators, and luminescent materials. At high pressures, CaF$_2$ has been proposed as a pressure calibration standard. The high coordination of the alkaline earth fluorides at ambient conditions can be analogous to the structure of lower coordination $AX_2$ compounds at high pressure, including oxides relevant to geoscience and planetary science. High-pressure studies on CaF$_2$, SrF$_2$, and BaF$_2$ have addressed band structure, electronic properties, melting behavior, shear strength, phase transitions, and elastic properties. The relative simplicity of the AF$_2$ system makes it well suited for evaluating differences between theoretical and experimental studies of these properties.

The alkaline earth fluorides undergo a series of pressure-induced phase transitions to highly coordinated $AX_2$ structures. At ambient conditions, CaF$_2$, SrF$_2$, and BaF$_2$ all crystallize in the cubic fluorite structure ($Fm\overline{3}m$, $Z=4$), which consists of a cubic close-packed array of cations with anions occupying tetrahedral sites. Experiments have shown that these materials transform to the orthorhombic cotunnite-type structure ($Pn\bar{a}m$, $Z=4$) at 9 GPa, 5 GPa, and 3 GPa, respectively.24–27 The cotunnite structure is characterized by anions in a distorted hexagonal-close-packed (hcp) lattice. The cations are situated within tricapped trigonal prisms with the three outer anions in the plane of the cation. An additional phase transition from the cotunnite phase to a hexagonal anti-Ni$_2$In-type phase ($P6_3/mmc$, $Z=2$) has been found experimentally in BaF$_2$ at 12 GPa by Leger et al.16 The anti-Ni$_2$In-type structure is a subgroup of the cotunnite structure with an ideal hcp anion lattice. The higher-symmetry lattice incorporates two more anions in the plane of the cations, forming pentacapped prisms. The transition sequence from fluorite to cotunnite-type to Ni$_3$In-type thus involves an increase in the coordination number from 8 to 9 to 11. These structures are also common in oxides at higher pressures. Cotunnite-type phases have been synthesized for TiO$_2$,28,29 SnO$_2$,30 PbO$_2$,31 ZrO$_2$,32,33 HfO$_2$,32,34 and CeO$_2$,35 and ab initio theory predicts SiO$_2$ will transform to the cotunnite structure above 750 GPa.36 Such high pressures are difficult to access experimentally, so information about the properties of high coordination phases of silica and other oxides must be derived either by theoretical methods or by experiments on analogs, such as fluorides.

As a model ionic system with useful physical properties, the alkaline earth fluorides have been extensively studied by ab initio and atomistic theoretical methods. Theoretical studies have provided predictions of the phase transitions and equations of state for CaF$_2$, SrF$_2$, and BaF$_2$. Although the transition to the cotunnite-type phase at high pressure is well known in CaF$_2$ and SrF$_2$, the
compressibility of these materials is poorly constrained. For CaF$_2$, theoretical predictions of the zero-pressure bulk modulus of the cotunnite phase span a wide range from 66 to 154 GPa, and thus it is not clear whether the transition from fluorite ($K_0=82$ GPa) to cotunnite involves a modest decrease or a large increase in the bulk modulus. Available experimental data\textsuperscript{15} suggest a relatively high bulk modulus ($K_0=170$ GPa) for the cotunnite-type phase of CaF$_2$. The situation is similar for SrF$_2$, where theoretical predictions of $K_0$ for the cotunnite phase span a wide range, but in this case there is no experimental data for comparison.

At higher pressures, the transition to the Ni$_2$In-type phase previously found in BaF$_2$ (Ref. 16) has been predicted in CaF$_2$ and SrF$_2$. Theoretical studies\textsuperscript{6,10,11} of CaF$_2$ predict transition pressures to the Ni$_2$In phase that vary between 68 and 278 GPa. For SrF$_2$, the transformation has recently been predicted to occur at about 46 GPa.\textsuperscript{6} No experimental studies yet exist to compare with these theoretical findings. Existing theoretical studies\textsuperscript{5,6,10,11} predict values of the zero-pressure bulk modulus for 11-coordinated Ni$_2$In-type SrF$_2$ and CaF$_2$ that are comparable or even lower than values for the eight-coordinated fluorite phase. Experimental data\textsuperscript{12} on BaF$_2$ in a quasihydrostatic (He) pressure medium also yield a low bulk modulus for the Ni$_2$In phase in this composition, in contrast to earlier nonhydrostatic results.\textsuperscript{16} Thus, these compounds appear to exhibit surprisingly high compressibilities for dense, highly coordinated high-pressure phases. These results stand in contrast to shock compression studies that suggest fluorides such as CaF$_2$ transform to remarkably incompressible phases above 100 GPa.\textsuperscript{37,38}

In other systems such as dioxides, diborides, and dinitrides, highly coordinated $AX_2$ compounds have been synthesized at high pressure and are associated with low compressibilities. High-pressure phases of TiO$_2$,\textsuperscript{28,29} ReB$_2$,\textsuperscript{39} and IrN$_2$\textsuperscript{40} have been examined as potential ultrahard or ultra-incompressible materials. The cotunnite phase of TiO$_2$ has been reported to be both highly incompressible and hard with a zero-pressure bulk modulus of 294–431 GPa (Refs. 41–43) and a measured Vickers microhardness of 38 GPa.\textsuperscript{41} The compressibility of corresponding fluoride phases is not yet well known.

In this work, we use x-ray diffraction in the laser-heated diamond-anvil cell (DAC) to investigate the equation of state and phase stability in CaF$_2$, SrF$_2$, and BaF$_2$ to Mbar pressures to provide new experimental constraints on the properties of high-pressure phases in this system. The results are used to explore the systematic high-pressure behavior of $AX_2$ fluorides and compare with theoretical predictions.

**II. METHOD**

Powder samples of CaF$_2$ (99.985% purity) and SrF$_2$ (99.99%) were obtained from Alfa Aesar and BaF$_2$ (99.99%) from Sigma-Aldrich. X-ray diffraction confirmed that each material was in the fluorite-type structure and no impurities or other phases were detectable. Zero-pressure volumes were measured to be 163.6(2) Å$^3$, 195.7(2) Å$^3$, and 238.3(2) Å$^3$ for CaF$_2$, SrF$_2$, and BaF$_2$, respectively.

High-pressure experiments were performed using synchrotron x-ray diffraction in a DAC. The samples were ground to a few micron grain size and mixed with 10–15 wt % platinum (99.99% purity, 0.5–1.2 μm particle size, Aldrich) as a laser absorber and pressure calibrant. A foil of the fluoride mixture was loaded into a symmetric DAC, sandwiched between two NaCl foils to provide a quasihydrostatic pressure medium and thermal insulation during laser heating.\textsuperscript{44} For one CaF$_2$ sample, we used a pressurized gas loading system\textsuperscript{45} to load a Ne medium, with a NaCl foil supporting the sample on one side.

For experiments at pressures up to about 65 GPa, we used diamond anvils with 300 μm culets, with the sample placed in a 150 μm hole in a stainless steel gasket. In high-pressure experimental runs, we used 200 μm flat culet or 300/100 μm or 300/75 μm beveled culet diamond anvils. In these runs, we used rhenium gaskets with a 90 μm, 50 μm, or 25 μm sample chamber, respectively. Gaskets were preindenteted to 25 μm thickness before sample loading. Anvils were supported by either tungsten carbide seats with 50° conical holes or x-ray transparent cubic boron nitride seats with 33° conical holes.

Angle-dispersive x-ray diffraction with laser heating was performed at beamlines X17B3 of the National Synchrotron Light Source (NSLS) and 13-ID-D of the GSECARS sector and 16-ID-B of the HPCAT sector of the Advanced Photon Source (APS). At all facilities the x-ray beam was focused with a Kirkpatrick-Baez double mirror system. At X17B3, the x-ray beam size was approximately 20×10 μm, while at GSECARS, the beam size was 5×6 μm and at HPCAT, 5×10 μm. The detector at X17B3 was either an offline Fuj BasS2500 image plate or an online Mar345 image plate. At GSECARS and HPCAT we used a MarCCD charge-coupled device detector. The distance and orientation of the detector was calibrated using a CeO$_2$ standard; at X17B3, an Au standard was also used for confirmation and simultaneous wavelength calibration.

Table I lists all experimental runs reported in this study. We conducted both compression and decompression experiments. Laser annealing was required for equation of state measurements since the NaCl medium is not sufficient by itself to provide quasihydrostatic conditions. All samples were heated from both sides at high pressures with a Nd:YLF (neodymium:yttrium lithium fluoride) or Nd:YAG (neodymium:yttrium aluminum garnet) laser.\textsuperscript{46,47} Temperatures were measured by spectroradiometry.\textsuperscript{38} Heating was carried out to temperatures ranging from 1500 to 3000 K for typical durations of 20 min. For one CaF$_2$ run, we heated the sample with a Nd:YLF laser at the MIT Mineral Physics Laboratory, and then decompressed without additional heating at X17B3. After heating, Debye rings from fluoride samples were smooth, indicating little preferred orientation. Diffraction peak widths sharpened significantly due to heating: an unheated sample at 82 GPa showed a reduction in peak full width at half maximum of over 50% after heating.

Two-dimensional diffraction images were radially integrated using FIT2D software\textsuperscript{49} to produce one-dimensional diffraction patterns. To obtain peak positions, widths, and intensities, patterns were fit with background-subtracted Voigt line shapes. Lattice parameters were refined for all data using UNITCELL.\textsuperscript{50} Rietveld refinement of selected patterns was conducted using GSAS and EXPGUI software.\textsuperscript{51,52}
Pressure was determined from the equation of state of platinum. Measured lattice strains in Pt were also used to evaluate differential stress, \( t \), following the theory by Singh. In the presence of differential stress, the elastic anisotropy \( S \) of Pt results in systematic variations in diffraction lines as a function of lattice plane, \( hkl \). For a pair of reflections at similar diffraction angle, \( 2\theta \), Singh’s equations for lattice strain in a cubic crystal in an axial, angle-dispersive geometry can be approximated as

\[
\frac{\Delta a_{hkl} - \Delta a_{hkl}^*}{a_0} = -S[1 - 3 \cos^2(90^\circ - \theta_{hkl})][\Gamma(hkl) - \Gamma(hk\ell^*)],
\]

where \( a \) is the lattice parameter for a given \( hkl \), \( a_0 \) is the lattice parameter at ambient pressure, and \( \Gamma \) is \((h^2 + k^2 + l^2)/(h^2 + k^2 + l^2)^2\). The angular proximity and strong intensity of the Pt 111 and 200 peaks make them ideal for this analysis. The elastic anisotropy of Pt as a function of pressure was taken from ab initio calculations, which we fit to an exponential relation:

\[
S = \text{constant} \times \exp(-P/P_0),
\]

where \( P \) is in gigapascal and \( S \) is in inverse gigapascal. This analysis showed that laser annealing reduced differential stress to less than 1 GPa in Pt. Only annealed data were used in equation of state fits.

### III. RESULTS

#### A. Phase identification

Representative high-pressure diffraction patterns for CaF\(_2\), SrF\(_2\), and BaF\(_2\) are shown in Figs. 1–3. All patterns can be indexed to the cubic fluorite phase, the orthorhombic cotunnite-type phase, or the hexagonal Ni\(_2\)In-type phase. Representative comparisons of measured and fit \( d \) spacings for the cotunnite and Ni\(_2\)In phases of CaF\(_2\) are shown in Tables II and III. No other phases were observed up to 146 GPa in CaF\(_2\), 89 GPa in SrF\(_2\), and 133 GPa in BaF\(_2\), either at 300 K or during laser heating at 1500–2500 K. For BaF\(_2\), a sample heated to 3000 K at 111 GPa showed additional weak peaks that were preserved up to 133 GPa with further heating and may be due to a reaction between the sample and the surrounding materials.

For all samples, the fluorite-cotunnite phase transition was observed to occur without heating. The observed transition pressure for our room-temperature compression of CaF\(_2\) and SrF\(_2\) is higher than that in other studies; this reflects variations in metastable behavior under different degrees of differential stress. During initial pressurization of the DAC, BaF\(_2\) was compressed to 3.8 GPa, and the transition from fluorite to cotunnite-type was already completed at this pressure.

Our study has experimentally identified the Ni\(_2\)In-type phase in SrF\(_2\) and CaF\(_2\). In SrF\(_2\), the orthorhombic cotunnite-type phase transformed to the hexagonal Ni\(_2\)In-type phase upon compression at 36 GPa with heating to about 1500 K. The new phase was maintained upon decompression with heating down to 29 GPa. At 28 GPa, diffraction patterns measured during heating to 1500–2000 K exhibited the Ni\(_2\)In-type phase, but upon quench the SrF\(_2\) sample had turned to the cotunnite structure. This is evidence that the cotunnite to Ni\(_2\)In-type transition has a negative Clapeyron slope but uncertainty in temperature measurement makes the slope difficult to quantify. Another SrF\(_2\) sample compressed directly to 58 GPa without heating displayed broad diffraction peaks consistent with the Ni\(_2\)In-type phase that sharpened with subsequent heating. CaF\(_2\) transformed from the cotunnite-type phase to the Ni\(_2\)In-type phase at 79 GPa with...
heating to about 2000 K. Upon decompression without heating, diffraction peaks remained sharp to 72 GPa but broadened significantly at lower pressures and the sample appeared to become partially amorphous. Laser heating at 63 GPa produced the cotunnite phase. For all compositions, the Ni$_2$In-type phase could not be recovered to ambient pressure. Based on our temperature-quenched diffraction patterns, these experiments constrain the cotunnite-Ni$_2$In-type transition pressure at 300 K to 28–29 GPa for SrF$_2$ and 63–79 GPa for CaF$_2$.

The transition from the cotunnite-type to Ni$_2$In-type phase in CaF$_2$ and SrF$_2$ has also been investigated at 0 K by theoretical studies using density-functional theory. For CaF$_2$, our results are more consistent with the predicted transition pressure found by Wu et al. (68–72 GPa) than by Shi et al. (105 GPa) or Cui et al. (278 GPa). For SrF$_2$, the transition occurred at pressures lower than predicted (45.6 GPa). Some of the differences in phase-transition pressures between experiment and theory may reflect thermal effects. While the negative Clapeyron slope observed does support higher transition pressures at 0 K than at 300 K, this is unlikely to account for more than a few gigapascals difference. More critical to the accuracy of these predicted transition pressures is the similarity between the cotunnite and Ni$_2$In-type phases and their calculated enthalpies. A small enthalpy difference between these structures over a wide pressure range as observed in these calculations makes the transition pressure particularly sensitive to error in computational parameters. Such a small enthalpy difference would also increase the dependence of experimental results on temperature, differential stress, and kinetics.

The Ni$_2$In-type structure of SrF$_2$ at 58.4 GPa was confirmed by full profile refinement (Fig. 4). Except for a broad unknown peak with a 2θ value of approximately 8°, all peaks could be indexed as NaCl B2 phase, Pt, or SrF$_2$ in the Ni$_2$In structure. Lattice parameters, phase fractions, peak shape parameters, and spherical harmonic terms were refined for all phases. As all atoms are in special positions, no refinement of atomic positions was necessary. The texture index was 1 for NaCl, 1.11 for Pt, and 3.47 for SrF$_2$ indicating substantial preferred orientation, with the (001) plane aligned normal to the compression direction. The refinement yielded lattice parameters $a=3.8130(2)$ Å and $c=4.7788(21)$ Å, and a volume of 60.171(26) Å$^3$, consistent with values obtained by individual peak fitting to within 0.1%.

**B. Equation of state**

Unit-cell volumes for CaF$_2$, SrF$_2$, and BaF$_2$ were fit to a third-order Birch-Murnaghan equation of state and the results are shown in Fig. 5 and Tables IV and V. It is well known that volume compression data may suffer from trade-offs in constraining the three zero-pressure parameters of the equation of state, volume $V_0$, bulk modulus $K_0$, and pressure derivative of the bulk modulus $K_0'$. In order to better constrain $K_0$, we fixed $V_0$ or $K_0'$. Most of the uncertainty in the fit comes from poor constraint on $V_0$. Fixing the zero-pressure volume of the high-pressure phases to various values based on previous experimental or theoretical results (Tables IV and V) results in a range of values for $K_0$ and $K_0'$. This range illustrates the error in our constraint of these zero-pressure equation of state parameters due to parameter trade-offs. Alternatively, $K_0'$ may be fixed to a reasonable value based on previous work. Previous experimental and theoretical work on CaF$_2$, SrF$_2$, and BaF$_2$ found that $K_0'$ is 4.67–4.7 for all phases of BaF$_2$, 4.75 for the fluorite phase of SrF$_2$, and 4.38–4.83 for all phases of CaF$_2$, suggesting that $K_0'$ may have little variation with structure or cation for the alkaline earth fluorides. We therefore chose a $K_0'$ of 4.7 when using a fixed value for this parameter in our fits.

**1. Cotunnite-type phase**

The results of equation of state fits for the cotunnite phases of CaF$_2$ and SrF$_2$ are compared with earlier studies in Table IV. With $K_0'$ fixed at 4.7, the zero-pressure volumes of the cotunnite-type phases of CaF$_2$ and SrF$_2$ are 6–10% less than $V_0$ of the corresponding fluorite phases at ambient con-
diations. For CaF$_2$, this is consistent with density-functional theory$^{5,10,11}$ and with the measured volume of cotunnite-type CaF$_2$ synthesized at ambient conditions$^{59}$ or recovered from shock compression.$^{58}$ It is also consistent with the volume difference between cotunnite and fluorite obtained in recent work on BaF$_2$.$^{12}$

With a zero-pressure bulk modulus of 74(5) GPa, the cotunnite phase of CaF$_2$ is slightly more compressible than the fluorite phase. The same relationship was recently found between the cotunnite and fluorite phases of BaF$_2$ by Smith et al.$^{12}$ A previous static compression experiment$^{15}$ on CaF$_2$ yielded a much higher bulk modulus for the cotunnite phase ($K_0=170$ GPa). The presence of differential stress is known to lead to overestimation of the bulk modulus in static compression studies,$^{59}$ this is the most likely explanation for the discrepancy as the results of Ref. 15 were obtained from an unannealed sample in a methanol-ethanol medium at up to 45 GPa, well above the pressure limit of the hydrostaticity of this medium.$^{60}$ Similar results are found in the case of BaF$_2$, where a more recent experiment$^{12}$ conducted with a quasihydrostatic He pressure medium yielded a much lower bulk modulus for the cotunnite-type phase than earlier work of Leger et al.$^{16}$ with a silicone grease medium. For the cotunnite phase of SrF$_2$, fewer data and the narrower pressure stability range give a poorer constraint on $K_0$, but the fit is consistent with the trend seen in CaF$_2$ and BaF$_2$. The bulk modulus of 74(8) GPa is within uncertainty from the bulk modulus of the fluorite phase of SrF$_2$. The fit value of $V_0$ for the cotunnite phase yields a volume relative to the fluorite phase of $V_0$(cotunnite)/$V_0$(fluorite)=0.90(1), which is lower than the values for either CaF$_2$ or BaF$_2$. If $V_0$ is fixed to a value of 150.5 Å$^3$ [$V_0$(fluorite)/$V_0$(cotunnite)=0.92 between the relative volumes for CaF$_2$ and BaF$_2$], then the fit value of $K_0$ becomes 62(1) GPa, between the $K_0$ values for CaF$_2$ and BaF$_2$.$^{12}$

The similar compressibility of fluorite and cotunnite forms of CaF$_2$ is consistent with recent density-functional theory calculations$^{5,10,11}$ for which generalized gradient approximation (GGA) calculation gives better quantitative agreement with $K_0$ than the local-density approximation.

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TABLE II. Observed and calculated $d$ spacings for the cotunnite-type phase of CaF$_2$ at 35 GPa and 300 K. These peaks are fit to an orthorhombic unit cell with $a=5.3869(10)$ Å, $b=6.5955(13)$ Å, $c=3.3149(7)$ Å, and $V=117.78(3)$ Å$^3$. 

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TABLE III. Observed and calculated $d$ spacings for the Ni$_3$In-type phase of CaF$_2$ at 92 GPa and 300 K. These peaks are fit to a hexagonal unit cell with $a=3.5230(5)$ Å, $c=4.4337(10)$ Å, and $V=47.66(2)$ Å$^3$. 

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with a discontinuous change in the axial compressibilities. Above 55 GPa, the c lattice parameter expands with increasing pressure, but a more rapid increase in compressibility of the a parameter results in a net increase in volumetric compressibility (Fig. 5). Figure 7 shows a direct comparison of interplanar spacings across the cotunnite-Ni2In phase transition for the three alkaline earth fluorides. This phenomenon was also observed by Smith et al.12 in BaF2 and predicted by Ayala19 in BaF2 and Kunc et al.51 in Li2O (anticotunnite). Consistent with the group-subgroup relationship between the cotunnite and Ni2In-type structures, we observe a continuous evolution of the orthorhombic structure toward the hexagonal structure near the phase transition. However, the hysteresis without laser heating and the 5% volume change with heating observed across the transition to the hexagonal phase for all three alkaline earth fluorides indicate that this phase transition is first order.

2. Ni2In-type phase

Table V summarizes equation of state parameters for the Ni2In phase of CaF2, SrF2, and BaF2. The Ni2In phase of BaF2 is constrained over the widest range of experimental data from its transition pressure at 12 GPa (Ref. 16) to our maximum pressure of 133 GPa. The equation of state described by our annealed data (shown in Fig. 5) from 42–133 GPa matches well with the measurement in a He pressure medium by Smith et al. from 15–33 GPa: K0 is 67(9) GPa and V0 is 202(4) Å3, 85% of the fluorite V0. This bulk modulus is comparable to Smith et al.’s theoretical and experimental values12 but significantly lower than values measured by Leger et al.16 and earlier theoretical calculations.8,9,18 The Ni2In-phase of BaF2 has the same zero-pressure bulk modulus as the cotunnite-type phase within experimental error.

Because the Ni2In-type phases of CaF2 and SrF2 are stable only at higher pressures and become amorphous or transform to the cotunnite-type phase upon decompression, the zero-pressure equation of state parameters for these phases are more difficult to constrain. A wide range of values for V0, K0, and K’0 reproduce the high-pressure data. Fitting results with either V0 or K’0 fixed are shown in Table V. Constraints on V0 and K’0 are based on theoretical work and analogous experiments on BaF2. The choice of these constraints strongly controls K0. It is difficult to compare fit values for V0 or K0 to theoretical work5,10,11 as most studies do not report K0. Our fit for CaF2 agrees with theoretical values for V0 and K0 only if K0 is high, about 5.9. Our results for SrF2 are not consistent with theoretical work.6 Either K0 or K’0 must be higher for the Ni2In-type phase than the cotunnite phase to fit the CaF2 and SrF2 data, unlike BaF2, for which neither K0 nor K’0 were significantly different for the fluorite, cotunnite, and Ni2In-type phases. Theoretical studies5,6,10,11 did not predict an increase in bulk modulus for the Ni2In-type phase; instead, the bulk modulus was predicted to be less than or similar to that of the cotunnite phase, as in BaF2. The compositional trend in the zero-pressure bulk modulus roughly shows higher K0 for smaller cations but cannot be unambiguously resolved due to the parameter trade-offs.
TABLE IV. Birch-Murnaghan equation of state parameters for fluorite and cotunnite phases of alkaline earth fluorides from this and previous studies. Moduli from Brillouin scattering and ultrasonic studies have been corrected from adiabatic to isothermal values. $V_0$ for fluorite-type CaF$_2$, SrF$_2$, and BaF$_2$ are 163.6 ± 0.2 Å$^3$, 195.7 ± 0.17 Å$^3$, and 238.3 ± 0.2 Å$^3$, respectively.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$K_0$(fluorite) (GPa)</th>
<th>$K'_0$(fluorite)</th>
<th>$K_0$(cotunnite) (GPa)</th>
<th>$K'_0$(cotunnite)</th>
<th>$V_0$(cotunnite)/$V_0$(fluorite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>74 ± 5</td>
<td>4.7$^a$</td>
<td>0.94 ± 0.01</td>
<td></td>
<td></td>
</tr>
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<td>X-ray diffraction:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. 4</td>
<td>81 ± 1.2</td>
<td>5.22 ± 0.35</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ref. 15</td>
<td>87 ± 5</td>
<td>5 ± 1</td>
<td>169 ± 8</td>
<td>4.7$^{a,b}$</td>
<td>0.86</td>
</tr>
<tr>
<td>Ref. 57</td>
<td>82.0 ± 0.7</td>
<td>4.83 ± 0.13</td>
<td></td>
<td></td>
<td>0.937</td>
</tr>
<tr>
<td>Brillouin scattering$^{22}$</td>
<td>77–103</td>
<td>4–4.92</td>
<td>66–153.8</td>
<td>4.1–4.38</td>
<td>0.863–0.937</td>
</tr>
<tr>
<td>Theory$^{5,7,10,11,19}$</td>
<td>50–80</td>
<td>4.67–4.91</td>
<td>4.7 $\pm 0.01$</td>
<td>0.86–0.937</td>
<td></td>
</tr>
<tr>
<td>SrF$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>74 ± 8</td>
<td>4.7$^a$</td>
<td>0.90 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultrasons$^{20,21}$</td>
<td>70–71</td>
<td>4.76 ± 0.06</td>
<td></td>
<td></td>
<td>0.793–0.868</td>
</tr>
<tr>
<td>Theory$^{8,7}$</td>
<td>66–90</td>
<td></td>
<td>117–127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaF$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray diffraction:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. 12</td>
<td>51 ± 4</td>
<td>4.7$^a$</td>
<td>0.92 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. 16</td>
<td>79 ± 10</td>
<td>4$^a$</td>
<td></td>
<td></td>
<td>0.907 ± 0.005</td>
</tr>
<tr>
<td>Ultrasons$^{23}$</td>
<td>56.9</td>
<td></td>
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<tr>
<td>Theory$^{9,12,18}$</td>
<td>50–80</td>
<td>4.67–4.91</td>
<td>52–98</td>
<td>4.7$^c$</td>
<td>0.876–0.937</td>
</tr>
</tbody>
</table>

$^a$Parameter fixed in fit.
$^b$Birch-Murnaghan equation fit to reported diffraction data.
$^c$Only Ref. 12 provides a value for $K'_0$.

To more directly compare the compressibilities of CaF$_2$, SrF$_2$, and BaF$_2$ in the same pressure regime as our data, we examine the bulk modulus, $K$, calculated at high pressures. Differentiation of the Birch-Murnaghan equation yields a third-order finite strain expression of the variation in $K$ with compression.$^{62}$ Results for the three compositions under consideration here are calculated with the parameters given in Table V with $K'_0$ fixed at 4.7 and shown in Fig. 8. The change in bulk modulus across the cotunnite-Ni$_2$In-type transition is 0–2.5% for these materials. For CaF$_2$ and SrF$_2$, the change in the bulk modulus across the transition is greater than for BaF$_2$; the cotunnite-Ni$_2$In-type transition results in a 20–40% (CaF$_2$) to 45–65% (SrF$_2$) increase in the bulk modulus. At 100 GPa, the Ni$_2$In-type phase has a bulk modulus of 240 GPa for BaF$_2$, 330 GPa for SrF$_2$, and 320 GPa for CaF$_2$. The higher bulk modulus values for SrF$_2$ relative to CaF$_2$ may reflect experimental uncertainty and require further investigation.

In previous experimental and theoretical studies on the Ni$_2$In-type phase of BaF$_2$, CaF$_2$, and SrF$_2$, an anomalously high value of the bulk modulus has been shown to be linked with a systematically high value of the $c$ lattice parameter and hence $c/a$ ratio. Leger et al.$^{16}$ observed an increase in the $c/a$ ratio with pressure, but their pressure transmitting medium, silicone grease, is nonhydrostatic above 0.9 GPa.$^{50}$ Theoretical work$^{18}$ predicted a decrease in $c/a$ ratio with pressure and suggested that differential stress resulted in the $c$ lattice parameter being less compressible than under hydrostatic conditions. Recent x-ray diffraction experiments by Smith et al.$^{12}$ comparing quasihydrostatic compression in a He medium to nonhydrostatic compression with no pressure medium confirm this. Measured volumes in a nonhydrostatic...
sample were as much as 10% greater than in a quasihydrostatic sample, creating the appearance of a much less compressible phase. The volume difference between the two experiments is due almost entirely to the behavior of the $c$ parameter.

In our experiments on all three compounds we find the $c/a$ ratio of the Ni$_2$In-type phase decreased with pressure as long as the sample was well annealed. The $c/a$ ratio increased significantly if differential stress was allowed to accumulate. We heated our BaF$_2$ sample at approximately 10–15 GPa intervals. The $c$ parameter appears less compressible in these intervals than immediately after heating, as can be observed from the open symbols in Fig. 9. The $c/a$ ratio of the Ni$_2$In-type phase correlates well with diffraction peak widths and the normalized differential stress $t/P$ measured in platinum (Fig. 10): the linear correlation coefficient $\rho = 0.69$. This correlation is strong enough to suggest that the $c/a$ ratio of BaF$_2$ could be used to calibrate differential stress above 12 GPa. While the differential stress in Pt could not be measured in SrF$_2$ experiments above 60 GPa due to overlap between Pt and sample diffraction peaks, peaks were slightly wider in this experimental run than other well-annealed runs, which may indicate less hydrostatic conditions, resulting in a higher $c/a$ ratio and volume. However, the decrease in $c/a$ ratio with pressure measured in both CaF$_2$ and SrF$_2$ may be evidence that the bulk modulus has not been overestimated here due to differential stress.

Experimental data provide an important test for theoretical studies. Theoretical calculations for the alkaline earth fluorides have used a variety of techniques from atomistic to $ab$ initio simulations involving different levels of sophistica-

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**TABLE V. Birch-Murnaghan equation of state parameters for Ni$_2$In-type phases of alkaline earth fluorides from this and previous studies.**

<table>
<thead>
<tr>
<th>Reference</th>
<th>$K_0$ (GPa)</th>
<th>$K'_0$</th>
<th>$V_0$(Ni$_2$In-type)/$V_0$(fluorite)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CaF$_2$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>118 ± 11</td>
<td>4.7$^a$</td>
<td>0.82 ± 0.01</td>
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<td></td>
<td>95 ± 5</td>
<td>5.1 ± 0.3</td>
<td>0.85$^a$</td>
</tr>
<tr>
<td></td>
<td>60 ± 5</td>
<td>5.9 ± 0.5</td>
<td>0.90$^a$</td>
</tr>
<tr>
<td>Theory (Refs. 5, 10, and 11)</td>
<td>61–91</td>
<td>4.8$^b$</td>
<td>0.890–0.925</td>
</tr>
<tr>
<td><strong>SrF$_2$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>125 ± 9</td>
<td>4.7$^a$</td>
<td>0.80 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>64 ± 5</td>
<td>7.0 ± 0.6</td>
<td>0.85$^a$</td>
</tr>
<tr>
<td></td>
<td>32 ± 4</td>
<td>10 ± 1.4</td>
<td>0.90$^a$</td>
</tr>
<tr>
<td>Theory (Ref. 6)</td>
<td>43.8</td>
<td></td>
<td>0.633</td>
</tr>
<tr>
<td><strong>BaF$_2$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>67 ± 9</td>
<td>4.7$^a$</td>
<td>0.85 ± 0.02</td>
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<tr>
<td>X-ray diffraction</td>
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</tr>
<tr>
<td>Ref. 12</td>
<td>56 ± 5</td>
<td>4.67$^a$</td>
<td>0.86 ± 0.02</td>
</tr>
<tr>
<td>Ref. 16</td>
<td>133 ± 16</td>
<td>$4^a$</td>
<td>0.829 ± 0.012</td>
</tr>
<tr>
<td>Theory (Refs. 8, 9, 12, and 18)</td>
<td>69–142</td>
<td>4.67$^c$</td>
<td>0.753–0.864</td>
</tr>
</tbody>
</table>

$^a$Parameter fixed in fit.  
$^b$Only Ref. 11 provides a value for $K'_0$.  
$^c$Only Ref. 12 provides a value for $K'_0$.  

---

**FIG. 6.** Lattice parameters of the cotunnite-type phase of alkaline earth fluorides. Open triangles are from previous work in He medium (Ref. 12). Linear fits are shown as a guide to the eye. Near the upper stability limit, the structure distorts continuously toward the hexagonal phase: the $a$ parameter becomes more compressible while $c$ increases in magnitude.
tion. Among density-functional theory calculations, we find that results for CaF$_2$ by Wu et al.\textsuperscript{5} using GGA most closely matched our transition pressures. However, studies using the GGA method have produced a wide range of pressures for the cotunnite-Ni$_2$In-type transition in CaF$_2$, and all predict bulk moduli lower than those we observe for the Ni$_2$In-type phases of CaF$_2$ and SrF$_2$. Theoretical studies on BaF$_2$ had previously reported zero-pressure bulk moduli for the Ni$_2$In-type phase of over 133 GPa, until Smith et al.\textsuperscript{12} reported an experimental value of 56 GPa and confirmed a higher compressibility with their own GGA calculations. This highlights the importance of experimental confirmation of theoretical predictions.

IV. DISCUSSION

A. Static vs shock compression

CaF$_2$ and BaF$_2$ have both been examined to above 250 GPa using shock compression techniques.\textsuperscript{37,58,63,64} These studies have identified phase transitions under dynamic loading and determined the equation of state along the Hugoniot. For both CaF$_2$ and BaF$_2$, x-ray examination of samples recovered from shock loading to 12–50 GPa showed partial transformation to the cotunnite-type phase.\textsuperscript{58} The volume of the recovered cotunnite-type material was about 10% less than that of the fluorite phase, consistent with the static data reported in Table IV. In Fig. 11, Hugoniot data for CaF$_2$ and BaF$_2$ are plotted together with our and previous static measurements.\textsuperscript{4,12} The shock data for CaF$_2$ at pressures below 100 GPa are qualitatively consistent with the transformation to the cotunnite-type phase: due to thermal effects along the Hugoniot, shock states lie at higher pressure for a given volume compared with static data. Below 25 GPa, the BaF$_2$ shock data similarly accord with the static data. Above 100 GPa, the shock data suggest that CaF$_2$ transforms to a highly incompressible phase.\textsuperscript{37} It was proposed that this change in compressibility is associated with a transformation to a phase with 11-fold or 12-fold coordination.\textsuperscript{38,58} The transition to the Ni$_2$In-type phase occurs in CaF$_2$ at 72 GPa, which might be compatible with the shock data if the transition is kinetically delayed under dynamic loading. However, the comparison of our static compression data with the shock compression data (Fig. 11) shows that the Ni$_2$In-type phase is much more compressible than the observed shock compression data. Furthermore, the transition to the Ni$_2$In-type phase of BaF$_2$ near 14 GPa does not appear to be associated with an incompressible phase in shock or static data. Thus, the highly incompressible behavior in CaF$_2$ under shock loading cannot be linked with the...
Ni$_2$In-type phase, which does not have a notably high bulk modulus (Table V, Fig. 8).

The shock compression data for BaF$_2$ (Ref. 64) do reveal similarly incompressible behavior above 100–150 GPa, the same or higher pressure than observed under shock loading in CaF$_2$. In our static experiments, we find no additional phase transitions in CaF$_2$ or BaF$_2$ in this pressure range. It is not known whether additional phases appear in this system at the higher temperatures associated with shock loading.

The similarity of the pressures at which CaF$_2$ and BaF$_2$ become incompressible under shock loading suggest that, rather than a phase transition, thermal pressure may be responsible for the shock behavior of these compounds. Further shock compression studies of alkaline earth fluorides above 1 Mbar are needed to better understand their dynamic response, and efforts should also be directed to identification of other high-pressure solid or liquid phases that may be responsible for the observed behavior.

### B. Phase-transition systematics

Figure 12 is a synthesis of the stable pressure ranges of known AF$_2$ phases from this and other experimental and theoretical studies. The fluoride system exhibits a remarkably systematic dependence of the structure on pressure.
symmetric transition to a Co$_2$Si-type structure.\textsuperscript{71} This could possibly be due to the differences between the electronic structures of alkaline earth and transition-metal cations. As the evidence for an isosymmetric transition appears similar to the nonlinear compression behavior associated with the cotunnite-Ni$_2$In-type transition, further work should be undertaken to confirm whether Ni$_2$In-type PbF$_2$ can be synthesized.

A recent experiment\textsuperscript{72} reported synthesis of an AlB$_2$-type phase with coordination number 12 in BaH$_2$ at 50–65 GPa. This phase then is a plausible candidate for a higher-pressure polymorph in the fluoride system. Based on cation radius considerations, BaF$_2$ would likely transform to this phase at the lowest pressure among fluorides. In addition, an insulator-metal transition\textsuperscript{8} has also been predicted to occur in BaF$_2$. Recent theoretical calculations\textsuperscript{12} predict the AlB$_2$ phase would not be stable below 250 GPa and the insulator-metal transition would occur above 500 GPa. Our experimental study demonstrates that no further structural transformation in BaF$_2$ occurs up to 133 GPa, and further experimental studies at ultrahigh pressures are necessary.

V. SUMMARY

To explore the systematic variation in phase-transition pressures and compressibility of high-pressure phases as a function of cation size for the alkaline earth fluorides, we performed x-ray diffraction experiments on CaF$_2$, SrF$_2$, and BaF$_2$ in the diamond-anvil cell at pressures up to 146 GPa, 89 GPa, and 133 GPa, respectively. These compounds undergo a common sequence of structural transitions from fluorite to cotunnite at 9 GPa, 5 GPa, and 3 GPa, respectively, and from cotunnite to Ni$_3$In-type structure at 72 GPa, 29 GPa, and 14 GPa, respectively. For all three fluorides, the zero-pressure bulk modulus of the cotunnite-type phase is the same or slightly less than that of the fluorite phase. At the transition pressure, the bulk modulus of the Ni$_3$In-type phase is more strongly dependent on cation size. While for BaF$_2$, the transition to the Ni$_3$In-type phase results in a 10–20% increase in bulk modulus, for CaF$_2$ it increases the bulk modulus by 20–40%. At 1 Mbar, the bulk moduli of the Ni$_3$In-type phases of CaF$_2$, SrF$_2$, and BaF$_2$ are 320 GPa, 330 GPa, and 240 GPa, respectively. Phase-transition pressures and bulk moduli for these high-pressure phases are within the wide range of theoretical predictions. Although the Ni$_3$In-type phase of CaF$_2$ had been suggested by dynamic compression results to be a possible ultra-incompressible material, our data do not support this.

The AF$_2$ system exhibits a systematic relationship between structure and cation/anion size ratio. Due to its large cation size and associated low phase-transition pressures, BaF$_2$ had been the only compound in the AF$_2$ system, demonstrated to transform to a Ni$_3$In-type phase. This work is an experimental confirmation of the Ni$_3$In-type structure in CaF$_2$ and SrF$_2$. AF$_2$ compounds with smaller cations than Ca, Sr, and Ba may undergo analogous cotunnite-Ni$_3$In-type transitions at higher pressures than those explored in this work. The Ni$_3$In-type structure may also be a common post-cotunnite phase among other AX$_2$ systems including materi-
als relevant to planetary science such as SiO₂ and possible superhard or super-incompressible materials such as TiO₂.

Because the compressibility of the Ni₂In-type phase is more strongly dependent on cation than the cotunnite-type phase, further experimental work will be needed to determine the compressibility of Ni₂In-type phases in other systems.

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†Present address: University of Texas, Austin.
‡Present address: Sumitomo Corporation.
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