

Phase transitions beyond post-perovskite in NaMgF₃ to 160 GPa

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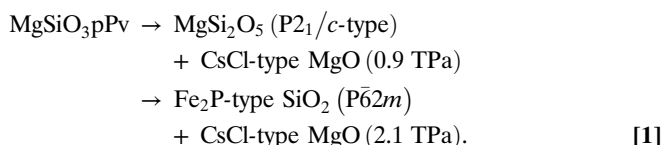
Neighborite, NaMgF₃, is used as a model system for understanding phase transitions in ABX₃ systems (e.g., MgSiO₃) at high pressures. Here we report diamond anvil cell experiments that identify the following phases in NaMgF₃ with compression to 162 GPa: NaMgF₃ (perovskite) → NaMgF₃ (post-perovskite) → NaMgF₃ (Sb₂S₃-type) → NaF (B2-type) + NaMg₂F₅ (P2₁/c) → NaF (B2) + MgF₂ (cotunnite-type). Our results demonstrate the existence of an Sb₂S₃-type post-post-perovskite ABX₃ phase. We also experimentally demonstrate the formation of the P2₁/c AB₂X₅ phase which has been proposed theoretically to be a common high-pressure phase in ABX₃ systems. Our study provides an experimental observation of the full sequence of phase transitions from perovskite to post-perovskite to post-post-perovskite followed by 2-stage breakdown to binary compounds. Notably, a similar sequence of transitions is predicted to occur in MgSiO₃ at ultrahigh pressures, where it has implications for the mineralogy and dynamics in the deep interior of large, rocky extrasolar planets.

post-post-perovskite | high pressure | analog

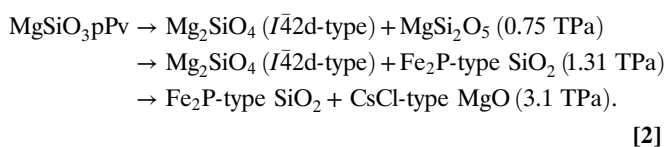
MgSiO₃ perovskite (bridgmanite, Pv, *Pbnm*) is expected to be the most abundant mineral in the Earth's lower mantle. At pressure and temperature conditions (~125 GPa, >2,000 K) of the lowermost ~150 km of the mantle (D'' layer), bridgmanite undergoes a phase transition into the CaIrO₃-type structure (*Cmcm*) known as post-perovskite (1, 2) (pPv). Although pPv is expected to be the final ABO₃ silicate phase in the Earth's interior, additional higher pressure "post-post-perovskite" (ppPv) phases may play an important role in the interiors of large terrestrial exoplanets (3, 4). Recent advances in astronomy have led to discoveries of many large rocky planets up to ~10 Earth masses in size (5). These exoplanets are expected to have very high internal pressures and temperatures (up to ~4,000 GPa, ~10,000 K). Laboratory experiments attempting to replicate such conditions are extremely challenging and generally beyond the reach of even state-of-the-art experimental techniques for static compression. Our understanding of the mineralogy of rocky exoplanets is therefore based largely on quantum mechanical computations, but these require experimental verification. One approach to testing the theoretical results is to compare analog materials that display a similar sequence of phase transitions as expected in silicate minerals but at lower pressures.

NaMgF₃ (neighborite) is both isostructural and isoelectronic to bridgmanite, crystallizing in the orthorhombic Pv (*Pbnm*) structure at ambient conditions. Neighborite undergoes a pressure-induced phase transition to the pPv structure at pressures as low as 19 GPa at room temperature (6) (compared to ~125 GPa, 2,000 K in MgSiO₃). Based on comparison of structural parameters (e.g., axial ratios, polyhedral volume, octahedral tilt, etc.) of several analogs, it was concluded that NaMgF₃ pPv is likely an excellent analog for MgSiO₃ pPv (6–8) (*SI Appendix, Table S1*).

Earlier theoretical calculations on MgSiO₃ pPv predict a 2-stage (9) dissociation process under compression as follows:



A more recent update (4) supports a 3-step breakdown:



Another computational study (10) has instead proposed a temperature-dependent 3-stage dissociation pathway. At relatively low temperatures (<6,400 K), the above sequence (Eq. 2) is followed. Under higher temperatures (>6,600 K), MgSiO₃ pPv is predicted to instead decompose into Mg₂SiO₄ and MgSi₂O₅, followed by decomposition of Mg₂SiO₄ into MgO and MgSi₂O₅ and finally into the simple oxides. Current experiments (11) on MgSiO₃ extending up to 265 GPa find that the pPv phase remains stable to this pressure and none of the proposed higher-pressure phases have yet been observed experimentally.

In the case of pPv NaMgF₃, a 2-stage dissociation (12) analogous to Eq. 1 has been proposed: from pPv into NaMg₂F₅ (P2₁/c-type) + B2-NaF (29 GPa) and then into B2-NaF + cotunnite-MgF₂ (71 GPa). Additional ppPv ABX₃ structures that have also been proposed theoretically in this system include an

Significance

The high-pressure behavior of NaMgF₃ is of interest due to its role as a low-pressure analog for phase transitions in the MgSiO₃ system. In this work, we have used the diamond anvil cell and synchrotron X-ray diffraction techniques to study structural transitions in NaMgF₃ to 1.6 Mbars. Our work has identified a sequence of high-pressure phases beyond post-perovskite in this ABX₃ system. We report the presence of a post-post-perovskite phase, followed by a partial and then complete dissociation into binary fluorides. A similar sequence of high-pressure phase transitions in MgSiO₃ at very high pressure-temperature conditions has implications for understanding the interiors of large rocky exoplanets.

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La_2S_3 -type (*Pnma*, 51 GPa, ref. 13), an Sb_2S_3 -type (*Pnma*, 44 GPa, ref. 14), and a $P6_3/mmc$ -type (223 GPa, ref. 14) structure. The La_2S_3 -type ppPv phase was predicted to be stable not only in NaMgF_3 but also in a wide range of ABX_3 compounds, with the notable exception of MgSiO_3 (13). However, both the La_2S_3 - and Sb_2S_3 -type phases were found to be energetically unfavorable with respect to $\text{NaF} + \text{MgF}_2$ above 48 GPa (15).

In the ABX_3 pPv structure (*Cmcm*), BX_6 octahedra share edges and corners and form layers oriented perpendicular to the most-compressible *b* axis. With increasing compression, X anions enter the primary coordination polyhedra of B cations in the octahedral sheets. This increases the B coordination number to 7 and links alternating pairs of edge-sharing, 8-fold-coordinated Mg-polyhedra leading to the Sb_2S_3 -type structure (*Pmnc* setting). The AB_2X_5 ($P2_1/c$ -type) structure is also of interest as a possible decomposition product of ABX_3 compounds (9). In AB_2X_5 , there are 2 types of B atoms, one 7-coordinated and the other 8-coordinated, while the coordination of the A cation also increases to 9. The $P2_1/c$ - AB_2X_5 structure may occur commonly at high pressures (9).

In addition to NaMgF_3 , pPv and ppPv phases have been synthesized in related compositions with transition elements (e.g., Fe, Ni, and Co) substituting for Mg in the B site (16, 17). These compounds show varied high-pressure behavior. In NaFeF_3 , a transition from the pPv phase to the Sb_2S_3 -type structure has been reported at 22 GPa (16). NaCoF_3 pPv dissociated into a mixture of unknown, unquenchable phases on laser heating above 26 GPa (17), while no disproportionation or phase transition of pPv was observed in NaNiF_3 at least up to 54 GPa (17).

The search for ppPv phases has also extended to oxide systems including FeSiO_3 , FeGeO_3 , MnTiO_3 , and FeTiO_3 . In the case of both FeSiO_3 (18) and FeGeO_3 (19), neither Pv nor pPv phases are observed and a mixture of $\text{FeO} + \text{SiO}_2/\text{GeO}_2$ is stable at least up to 149 and 127 GPa, respectively. In MnTiO_3 , the Pv phase was found to decompose into $\text{MnO} + \text{MnTi}_2\text{O}_5$ above 38 GPa (20). Several decomposition pathways (21–23) have been proposed for FeTiO_3 , but no pPv or ppPv phases have been observed. Both MnTi_2O_5 and FeTi_2O_5 were reported to have orthorhombic (20, 23) symmetry, but the structure is not known. The $P2_1/c$ -type AB_2X_5 structure, although monoclinic, has only a small monoclinic distortion from an orthorhombic cell and may account for these structures (9).

In this work, the high-pressure behavior of NaMgF_3 , a low-pressure analog of MgSiO_3 , was examined to explore the stability of phases beyond pPv. Laser-heated diamond anvil cell experiments coupled with synchrotron X-ray diffraction (Xrd) techniques were applied. We show that pPv NaMgF_3 undergoes multiple pressure-induced phase transitions and eventually decomposes into a mixture of binary fluorides.

Results

In the first experimental run (Exp. 1; *SI Appendix*, Table S2), room-temperature Xrd patterns were collected on an NaMgF_3 sample at several compression steps up to a peak pressure of 87 GPa (Fig. 1). At 13 GPa, the diffraction pattern can be indexed using the Pv structure in agreement with previous studies (24) (*SI Appendix*, Fig. S1). The measured unit cell volume of 199.8 (2) $\text{\AA}^3$ at this pressure is consistent with that reported by Hustoft et al. (24) (198.1 $\text{\AA}^3$ at 13 GPa). Upon further compression to 40 GPa, the diffraction pattern changed, indicating a pressure-induced phase transition. The observed pattern (*SI Appendix*, Fig. S2) is consistent with the CaIrO_3 -type pPv structure. Our measured cell volume [167.2 (2) $\text{\AA}^3$] is slightly higher than the expected volume based on the equation of state (EOS) parameters reported in an earlier study (24) (163.8 $\text{\AA}^3$ at 40 GPa). It should be noted that the present experiment used no pressure-transmitting medium, whereas argon was used as a medium in the

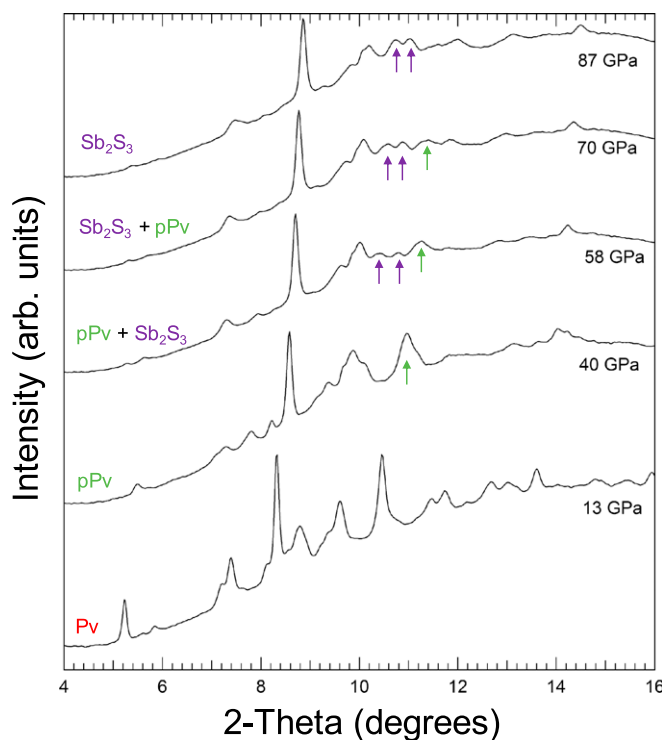


Fig. 1. Xrd patterns of NaMgF_3 compressed at room temperature. Green and purple arrows indicate the positions of the pPv (004), (113), (132) and Sb_2S_3 -type (013), (311) peaks, respectively. See *SI Appendix* for further details on peak identification.

previous work. A pressure medium was not used here in order to maximize the signal from the weakly scattering sample at higher pressures.

At 58 GPa, the diffraction pattern can no longer be indexed solely using the pPv structure (*SI Appendix*, Fig. S3). With increasing pressure, the intensity of the pPv peaks (004, 113, and 132; indicated by green arrow in Fig. 1) decreases and new peaks (indicated by purple arrows) grow near 2-theta of 10 to 11° . At ~ 87 GPa, the observed spectrum no longer shows any evidence of the pPv peaks and the new peaks identified previously are now the most intense peaks of the pattern, indicating the presence of a new phase. We attempted to index the diffraction pattern using the theoretically proposed La_2S_3 -type (13) and Sb_2S_3 -type (14) structures, using the theoretically determined structures as starting models. The Sb_2S_3 -type structure can explain all of the major peaks in the observed pattern, while the former cannot. The appearance of the Sb_2S_3 -type structure beginning from around 58 GPa is consistent with theoretical predictions (14, 15). Under further compression at room temperature, this phase was found to remain stable up to at least 160 GPa.

Computational studies predict that while the Sb_2S_3 -type phase may have lower energy than pPv, it would still be unstable with respect to $\text{MgF}_2 + \text{NaF}$ at all pressures (14, 15), suggesting that the phase that we observed may be metastable. In the next runs, we directly compressed the sample to 90 GPa (Exp. 2a, with Ne) and 87 GPa (Exp. 2b, without Ne) and heated it to peak temperatures of $\sim 1,810$ K and $\sim 2,710$ K for ~ 30 and ~ 20 min, respectively. Fig. 2 (Exp. 2a) and *SI Appendix*, Fig. S4 show the diffraction pattern obtained on quenching the sample after heating to 1,810 K (temperature-quenched pressure [P] = 91 GPa). It can be seen that the Sb_2S_3 -type phase remains stable even after prolonged laser heating. Our experiments thus indicate that the Sb_2S_3 -type phase is likely stable with respect to breakdown at these conditions and not a metastable phase.

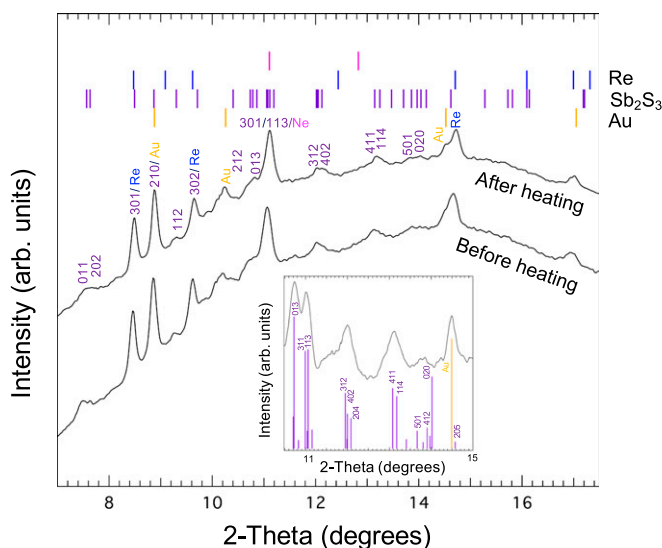


Fig. 2. Xrd pattern obtained before and after heating NaMgF₃ at ~1,810 K and 90 GPa followed by quenching to room temperature (quenched P = 91 GPa). The ticks at the top indicate Sb₂S₃-type NaMgF₃ (purple), Re (blue), Ne (pink), and Au (yellow) peaks, respectively. (Inset) A magnified view of a diffraction pattern (87 GPa) obtained in a separate run (unheated) conducted without Ne medium because Ne (111) overlaps with (311) and (113) peaks from the Sb₂S₃-type phase. Atomic positions from the theoretical calculations were used for calculating the intensities of the diffraction peaks in the inset.

Fig. 3 shows the pressure–volume behavior of the pv, pPv, and Sb₂S₃-type phases of NaMgF₃ based on this and previous work (see *SI Appendix, Fig. S5* for the variation of lattice parameters with pressure). Using a third-order Birch–Murnaghan EOS fit to the data (Sb₂S₃-type), the resulting parameters are $V_0 = 214$ (9) Å³, $K_0 = 88$ (16) GPa, and $K'_0 = 4$ (fixed), where V , K , and K' are the unit cell volume, bulk modulus, and its pressure derivative, respectively; the subscript 0 indicates ambient-pressure conditions. These values are consistent with the results of theoretical calculations (15) [$V_0 = 218.7$ (3) Å³, $K_0 = 78$ (4) GPa, and $K'_0 = 4.3$]. The EOS parameters are also comparable with those reported (24) for the Pv [$V_0 = 225.1$ Å³, $K_0 = 81$ (4) GPa, and $K'_0 = 3.6$ (4)] and pPv phases [$V_0 = 223$ Å³, $K_0 = 54$ (3) GPa, and $K'_0 = 5.7$ (4)]. Our EOS results suggest the transition from pPv to Sb₂S₃-type structure will have a small (~0.5%) volume change (at 55 GPa), which is less than the corresponding decrease in volume (~4%) at ~28 GPa during the Pv-to-pPv transition (25). The small volume change is consistent with observations of the same transition in NaFeF₃ at 22 GPa, where no detectable volume change was reported (16). However, it should be noted that these pressure–volume measurements were performed in absence of a pressure-transmitting medium and/or without laser annealing. Further experiments are necessary for more accurate determination of the EOS parameters of this phase.

In Exp. 2b, the sample was again compressed to near 90 GPa, but in this case the heating extended to higher temperatures. New diffraction peaks appeared after heating to ~2,590 K for ~5 min. The new peaks were retained on quenching to ambient temperature (quenched P = 88 GPa; Fig. 4). The most marked difference between the 2 patterns in Exps. 2a and 2b is the presence of the strong peak at $2\theta = 11.38^\circ$. The peak is consistent with the (110) reflection of NaF in the B2-type (cesium chloride) structure. The measured unit cell volume of CsCl-type NaF (54.19 Å³) at 88 GPa is in reasonable agreement with predictions from a theoretical EOS (15) (55.4 Å³). The presence of an NaF peak in our diffraction pattern suggests the sample has

dissociated into a phase assemblage such as NaMg₂F₅ + NaF as predicted by theoretical calculations (12). This phase mixture is indeed consistent with the observed diffraction pattern (Fig. 4). The differences between the calculated and observed d -spacings for peaks of the NaMg₂F₅ phase are <0.002 Å, indicating a good fit to the structure (*SI Appendix, Table S4*). The difference between the results of Exps. 2a and 2b can be explained in 2 ways. One possibility is that the Sb₂S₃-type phase is stable at relatively lower temperatures and dissociates into NaMg₂F₅ + NaF at higher temperatures. Alternatively, high temperatures may be required to overcome the kinetic barrier for the transition and the Sb₂S₃-type structure is instead a metastable phase. We consider the former to be more likely given that the Sb₂S₃-type phase remained stable for nearly 30 min of heating at moderately high temperatures, but further studies at high temperature are needed.

In the next experiment (Exp. 3, no pressure medium), the sample was directly compressed to 134 GPa and then laser-heated. The diffraction pattern obtained on quenching the sample to room temperature after heating to ~2,600 K at 134 GPa (quenched P = 137 GPa) can also be indexed using NaMg₂F₅ + NaF (*SI Appendix, Fig. S6*; see *SI Appendix* for detailed discussion). In the absence of experimental/theoretical data on unit cell parameters of NaMg₂F₅ at high pressure, direct comparisons of lattice parameters with literature data are not possible. However, the experimental unit cell dimensions are in fair agreement with our theoretical calculations (*SI Appendix, Fig. S4*). The unit cell volume of NaF (48.8 Å³) at 137 GPa is consistent with the prediction of a theoretically calculated EOS (15) (49.7 Å³) at this pressure.

In the fourth run (Exp. 4), the sample was compressed directly to 162 GPa at room temperature. The sample was then heated

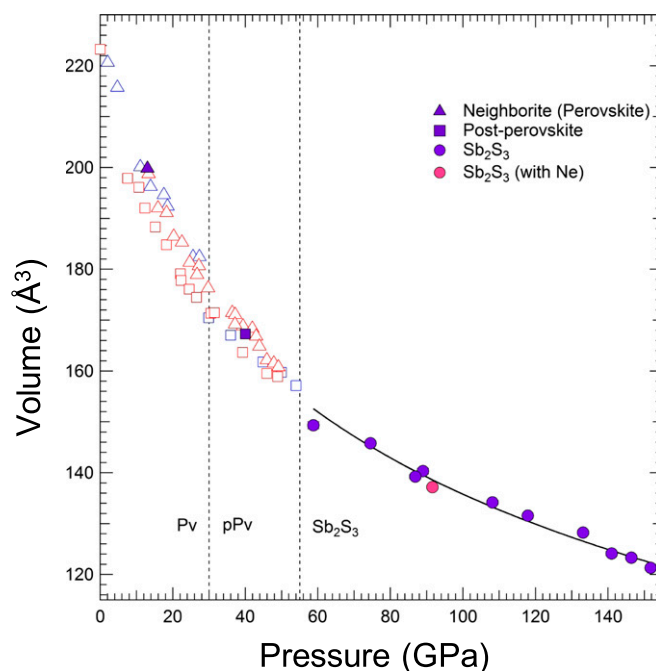


Fig. 3. Pressure variation of unit cell volume for Pv (triangles), pPv (squares), and Sb₂S₃-type (circles) phases of NaMgF₃ at ambient temperature. Solid and open symbols represent this study (purple) and literature data (red, ref. 24. and blue, ref. 25), respectively. The pink symbol shows the volume of the Sb₂S₃-type phase compressed in a neon pressure-transmitting medium and quenched after laser heating. The solid black line is Birch–Murnaghan EOS fit to the Sb₂S₃-type phase (excluding the pink datum). The dashed black lines indicate the pv–pPv and pPv–Sb₂S₃ phase boundaries (15, 25).

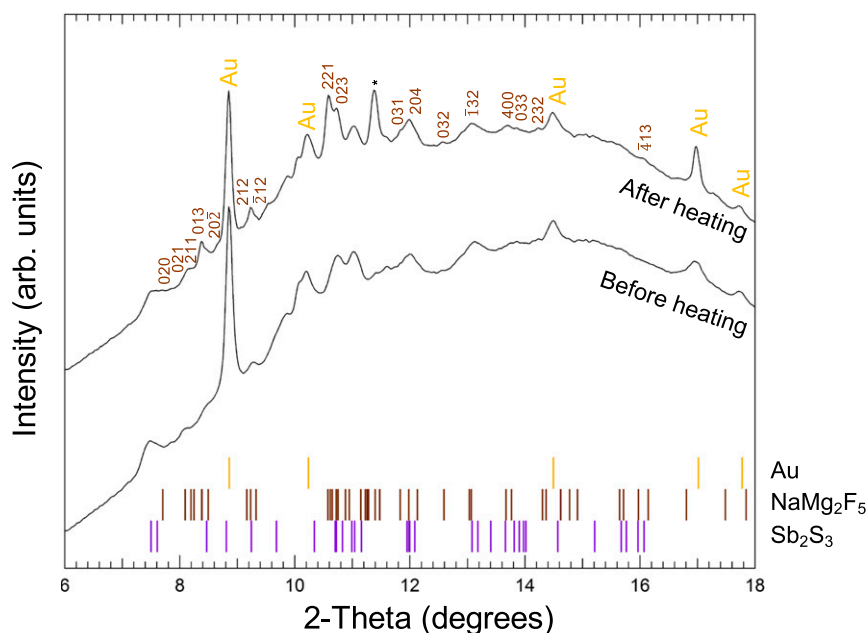


Fig. 4. Xrd pattern before and after heating NaMgF₃ to $\sim 2,700$ K at 87 GPa (quenched P after heating = 88 GPa). The ticks at the bottom indicate diffraction peaks positions of Sb₂S₃-type NaMgF₃ (purple), NaMg₂F₅ (brown), and Au (yellow), respectively. Miller indices of the NaMg₂F₅ peaks are listed above the observed pattern. An asterisk indicates the (110) peak of NaF in the CsCl-type structure.

for 20 min to a peak temperature of $\sim 2,260$ K, with the temperature being increased steadily during the heating cycle. New diffraction peaks appeared at $\sim 1,830$ K (in situ P = 172 GPa; Fig. 5) and were retained upon temperature quench. The Xrd pattern can be indexed using a mixture of cotunnite-type MgF₂ and CsCl-type NaF. The difference between the observed and calculated d -spacings of the cotunnite-type phase of MgF₂ was less than 0.005 Å (*SI Appendix, Table S6*), indicating a good fit between

the two. The unit cell volumes of cotunnite-type MgF₂ (69.9 Å³) and CsCl-type NaF (46.9 Å³) are consistent with the respective volumes predicted from the EOS reported in previous experiments (15) (MgF₂ = 69.1 Å³, NaF = 47.8 Å³ at 160 GPa). An additional peak of unknown origin at $2\theta = 9.75^\circ$ (marked by an asterisk in Fig. 5) was observed. The peak may be due to formation of gold fluoride (Au₂F) as predicted from theoretical calculations (26) (see *SI Appendix, section S5* for details). The same

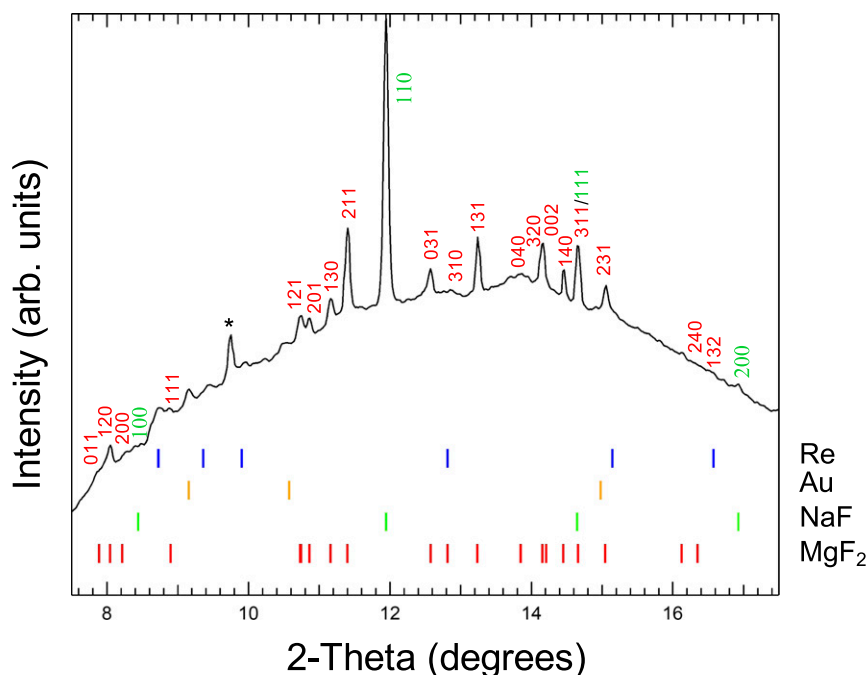


Fig. 5. Xrd pattern obtained on heating NaMgF₃ to $1,830$ K at 160 GPa (in situ P = 172 GPa). The ticks at the bottom indicate cotunnite-type MgF₂ (red), NaF-B2 (green), Re (blue), and Au (yellow), respectively. An asterisk indicates an unindexed peak (*SI Appendix*).

phase transition from Sb_2S_3 to MgF_2 and NaF was also observed in an additional experiment (Exp. 5) for a sample that was directly compressed to 150 GPa and then heated to $\sim 2,200$ K.

Discussion

The high-pressure transition pathways of pPv phases are of interest for understanding the possible mineralogy and evolution of super-Earth planets. Dissociation of pPv is important for understanding mantle convection in large, rocky exoplanets (27). Dissociation transitions (4) may affect layering and viscosity which will, in turn, affect heat flow and long-term thermal evolution. Thus, an understanding of such transitions in pPv materials is fundamentally important for developing plausible evolutionary models for super-Earths.

Because of the extremely high-pressure and -temperature conditions necessary for the ppPv phase transitions in MgSiO_3 , our understanding of these transitions is entirely based on theoretical calculations (4, 9, 10). While laser-driven dynamic ramp compression techniques combined with Xrd (28) can reach pressures close to the terapascal range, such methods are generally limited to high-symmetry and/or high-atomic-number solids at present. To probe the ppPv phases, static experimental studies in the diamond anvil cell have focused on analog compounds which display lower transition pressures compared to MgSiO_3 . In the case of oxides, experiments have not identified direct analogs for the expected transition sequence in MgSiO_3 . In MgGeO_3 , the pPv phase is experimentally observed up to 200 GPa (29). ABO_3 oxides with transition elements in the A site such as FeSiO_3 (18), FeGeO_3 (19), MnTiO_3 (20), and FeTiO_3 (22) do not exhibit either the Pv and/or the pPv phase.

NaMgF_3 , on the other hand, is a very good structural analog for both the Pv and pPv phases of MgSiO_3 (7, 30) (SI Appendix, Table S1). Fig. 6 shows a schematic phase diagram of the NaMgF_3 system summarizing available experimental data. Based on our study, the observed phase transition sequence in NaMgF_3 neighborite is



[3]

Although this is in many respects consistent with theoretical predictions (12, 15), there are important differences. As previously mentioned, the Sb_2S_3 -type phase is predicted to be metastable, while our experiments indicate it may be a stable ppPv phase at low to moderate temperatures. Our study provides experimental evidence for a 2-stage dissociation of a pPv-forming ABX_3 compound. We also provide experimental evidence for formation of $P2_1/c$ -type NaMg_2F_5 , a structure type that has been proposed to be a common high-pressure form in AB_2X_5 -type compounds at high pressures (12). Our work also confirms the theoretical predictions (4, 9, 10, 12) that a mixture of $\text{AX} + \text{BX}_2$ is the final product of ABX_3 systems. However, our experiments show that the binary fluorides are stabilized only above ~ 150 GPa, which is much higher than the theoretically predicted transition pressure [71 GPa (12) or 48 GPa (15)].

The dissociation transitions in MgSiO_3 are predicted to have large negative Clapeyron slopes (9), which would promote stratification in the mantles of super-Earth planets (27, 31). The transitions to a Sb_2S_3 -type ppPv phase, on the other hand, may only have minor effects on dynamic behavior due to the very small volume change. Other pressure- and temperature-dependent properties like viscosity may dramatically change across phase transitions, which could also significantly affect the mantle dynamics. The high-pressure behavior of NaMgF_3 is important as an analog system for understanding possible phase transitions and their effects in the interiors of super-Earths.

Methodology

NaMgF_3 Pv starting material was synthesized by heating stoichiometric proportions of NaF and MgF_2 . The powdered sample was mixed with 10 wt % Au as a pressure calibrant and loaded into symmetric diamond anvil cells with 75- to 200- μm -diameter culets. Samples were compressed up to a peak pressure

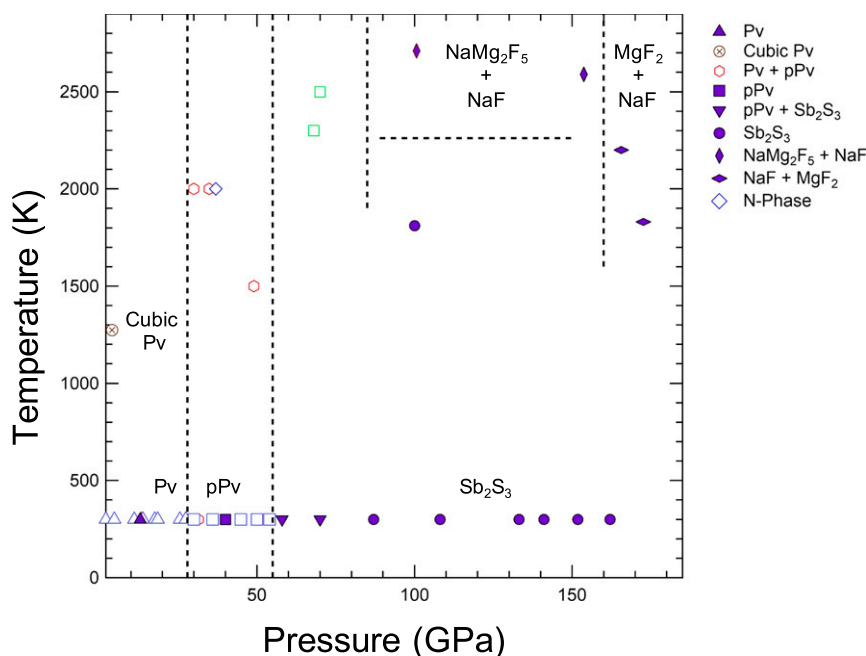


Fig. 6. Summary of constraints on the high-pressure and -temperature phase diagram of NaMgF_3 . The solid symbols (triangles: Pv, star: pPv, circles: Sb_2S_3 , inverted triangle: pPv + Sb_2S_3 , vertical diamonds: $\text{NaMg}_2\text{F}_5 + \text{NaF}$, horizontal diamonds: $\text{NaF} + \text{MgF}_2$) represent the present experimental data. Open symbols (red, ref. 24; blue, ref. 25; and green, ref. 32) show experimental literature data for the respective phases. The brown open circle indicates the high-temperature cubic phase (33, 34). The dashed black lines are schematic phase boundaries.

of 160 GPa. Double-sided pulsed-laser heating was used to heat the sample up to ~2,700 K and temperatures were measured by spectroradiometry. Angle-dispersive synchrotron Xrd was carried out at beamline 13-ID-D of the Advanced Photon Source using a monochromatic X-ray beam ($\lambda = 0.3344 \text{ \AA}$) focused to dimensions of $\sim 3 \mu\text{m} \times 3 \mu\text{m}$ with Kirkpatrick-Baez mirrors. A 2D charge-coupled device (Mar165) or a CdTe 1M Pilatus detector was used to collect the diffraction patterns. The Xrd patterns were fit using background-subtracted Voigt line shapes. Lattice parameters were calculated by least-squares refinement of the fitted peak position. LeBail refinements were carried out on selected data using the programs GSAS/EXPGUI. Further details are provided in *SI Appendix, section S2*.

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Supplementary Material

Phase transitions beyond post-perovskite in NaMgF₃ to 160 GPa.

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S1. Comparison of structural parameters.

Table S1. Comparison of the structural parameters of post-perovskite (pPv) ABX₃ compounds

(A = Mg, Na; B = Si, Mg and X = O, F) based on theoretical calculations (1, 2).

Parameter	MgSiO ₃ pPv	NaMgF ₃ pPv
<i>c/a</i>	2.48	2.48
<i>b/a</i>	3.27	3.13
Ay	0.253	0.2515
X1y	0.927	0.929
X2y	0.363	0.3604
X2z	0.441	0.4399
A-X/B-X	1.17	1.16
Poly A/B	2.08	2.03
X2-B-X2 angle (Degrees)	93.4	94.4
B-X1/B-X2	0.97	0.97
Octahedral tilt (Degrees)	138	140

a, *b* and *c* refer to unit cell parameters; Poly A/B is the ratio of AX₈ and BX₆ polyhedral volumes.

Atomic positions of pPv are: A (0, *y*, 3/4), B (0, 0, 0), X1 (0, *y*, 3/4) and X2 (0, *y*, *z*).

MgSiO₃ pPv: 120 GPa, 0 K (Tsuchiya et al., 2004, Ref (1)).

NaMgF₃ pPv: 30 GPa, 0 K (Umemoto and Wentzcovitch, 2006, Ref. (2)).

S2a. Experimental Methodology

The starting sample was synthesized according to established procedures (3). Stoichiometric proportions of NaF and MgF₂ were ground in an agate mortar under acetone for 2 hours. The mixture was then pressed to form pellets which were sintered in covered alumina crucibles for 48 hours at 1023 K. The synthesized polycrystalline aggregate was then re-ground and characterized by x-ray diffraction and Raman spectroscopy. The x-ray diffraction data were fit to an orthorhombic perovskite structure with lattice parameters in good agreement with literature data.

The sample was mixed with 10 wt% gold which served as both the pressure calibrant and laser absorber. The sample + Au mixture was then pressed into ~ 7-10- μ m thick pellets. Rhenium gaskets were pre-indented to ~20-25 μ m thickness and 20-100 μ m diameter holes were drilled to form the sample chamber. The sample disks were then loaded into symmetric diamond anvil cells with 75-200 μ m culet diamond anvils mounted on WC or cubic BN seats. In one experiment (Exp 2a), neon was loaded into the sample chamber as pressure-transmitting medium using the gas-loading system at the GeoSoilEnviroCARS sector of the Advanced Photon Source (APS).

Angle-dispersive x-ray diffraction was carried out at beamline 13-ID-D of the APS using a monochromatic x-ray beam ($\lambda = 0.3344 \text{ \AA}$) focused to dimensions of ~3 μ m x 3 μ m with Kirkpatrick-Baez mirrors. A two-dimensional CCD (Mar165) or a CdTe 1M Pilatus detector was used to collect the diffraction patterns. A lanthanum hexaboride (LaB₆) standard was used to calibrate the detector position and orientation. High temperatures were attained by double-sided heating (4) with diode pumped fiber lasers with ~15 μ m spot size (5). Temperatures were measured from both sides of the sample using spectroradiometry (6). The laser power incident on

each side were adjusted independently so that the temperature differences across the sample was typically less than 100 K. Pressures were determined using the (111) diffraction peak and the EOS of Au (7, 8).

The x-ray diffraction patterns were fit using background-subtracted Voigt line shapes. Lattice parameters were calculated by least-squares refinement of the fitted peak positions (9). LeBail refinements were carried out on selected patterns using the programs GSAS/ EXPGUI (10). Structures based on density functional theory calculations were used as the starting model for the refinements (section S2b). The parameters for all the observed phases were initially refined separately and then simultaneously. The lattice parameters were refined first, followed by the profile function (pseudo-Voigt with Finger-Cox-Jephcoat asymmetry and Stephens anisotropic strain broadening) and finally the background (Chebyshev polynomial, 8 terms).

Table S2. Experimental conditions and observed phases.

Experiment	Pressure Range (GPa)	Peak Temperature (K)	Phase(s) present
Exp 1	0 - 13	300	Pv
Exp 1	40	300	pPv
Exp 1	58 - 70	300	pPv + Sb ₂ S ₃
Exp 1	87	300	Sb ₂ S ₃
Exp 2a*	90	1810	Sb ₂ S ₃
Exp 2b	87	2710	NaMg ₂ F ₅ + NaF
Exp 3	134	2590	NaMg ₂ F ₅ + NaF
Exp 4	162	2260	MgF ₂ + NaF
Exp 5	150	2200	MgF ₂ + NaF

*Ne used as a pressure transmitting medium.

All phases were retained upon quenching to ambient temperature.

S2b. Computational Details

Theoretical calculations were performed to obtain values for the lattice parameters of the NaMg_2F_5 and Sb_2S_3 -type NaMgF_3 phases to be used as starting values in the least-squares refinements. The calculations were performed using the plane wave implementation of density functional theory (DFT) (11, 12) as implemented in the CASTEP (13) code. The exchange-correlation energies were treated using the local density approximation (LDA). We used a kinetic energy cutoff of 410 eV for the basis set. The Brillouin zone was sampled using a Monkhorst-Pack (14) $2 \times 5 \times 2$ and $3 \times 3 \times 2$ k -point grid for the Sb_2S_3 -type NaMgF_3 and NaMg_2F_5 respectively. Ultrasoft (15) pseudopotentials were used to treat the electron-ion interactions. The geometry optimizations were carried out using the Broyden-Fletcher-Goldfarb-Shanno (16) algorithm and were considered complete when the forces on atoms were less than 0.03 eV/Å and the energy change was less than 1×10^{-5} eV/atom. Both atomic positions and lattice parameters were optimized at each pressure step.

S3. NaMgF₃ Neighborite (Perovskite) and Post-Perovskite

Figure S1. X-ray diffraction pattern of NaMgF₃ at 13 GPa and room temperature. The ticks at the bottom indicate the expected peak positions of perovskite (Pv, Red), gold (yellow) and rhenium (blue). Peaks for perovskite are indicated by their Miller indices. The lattice parameters are $a = 5.069(5) \text{ \AA}$, $b = 5.355(4) \text{ \AA}$ and $c = 7.361(4) \text{ \AA}$.

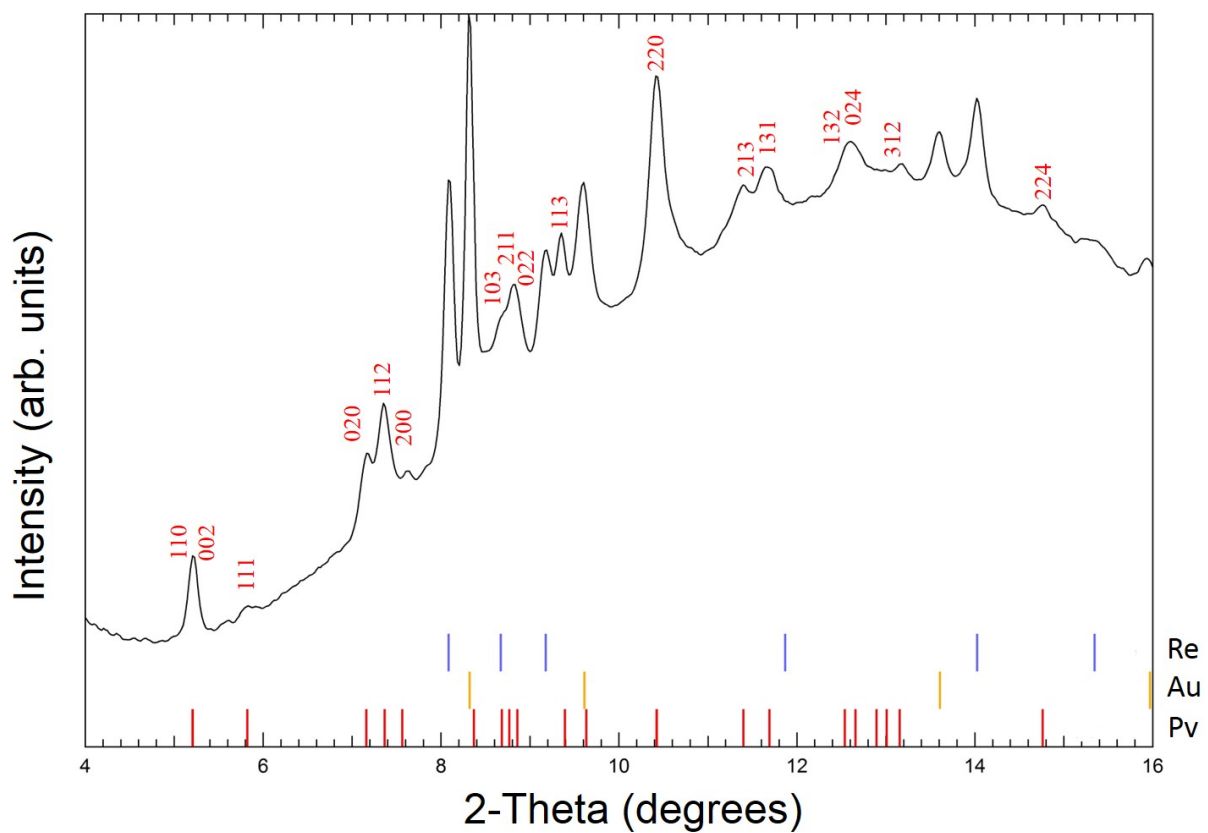
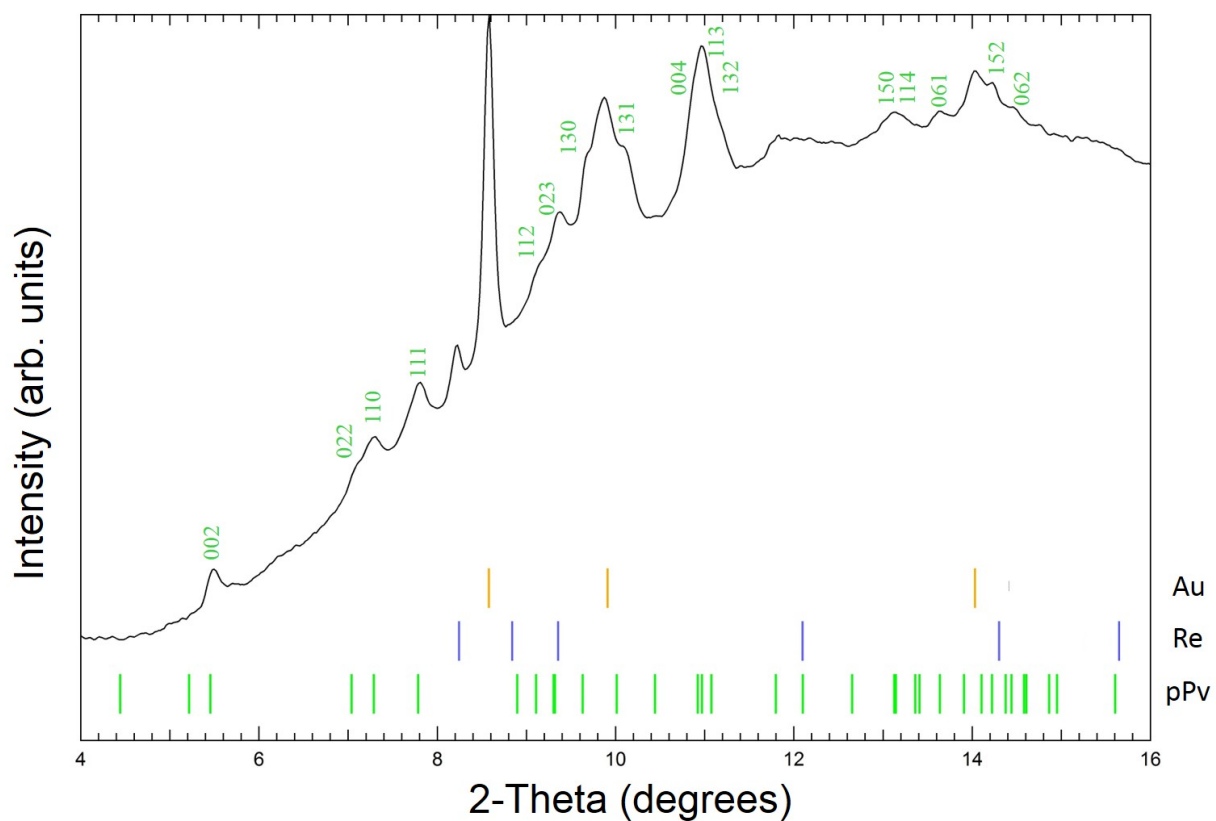


Figure S2. X-ray diffraction pattern for NaMgF₃ at 40 GPa (300 K). The ticks at the bottom indicate the calculated peak positions of post-perovskite (green), gold (yellow) and rhenium (blue). Post-perovskite peaks are labeled with their Miller indices. The unit cell dimensions are $a = 2.761$ (1) Å, $b = 8.622$ (3) Å and $c = 7.026$ (5) Å.



S4. Sb₂S₃-type Phase

Figure S3. X-ray diffraction pattern of NaMgF₃ at 58 GPa and 300 K. The ticks at the bottom indicate the calculated peak positions of Sb₂S₃-type NaMgF₃ (purple), post-perovskite (green) and gold (yellow). The Miller indices of the Sb₂S₃-type ($a = 7.276$ (7) Å, $b = 2.818$ (2) Å and $c = 7.282$ (5) Å) and post-perovskite ($a = 2.731$ (2) Å, $b = 8.322$ (9) Å and $c = 6.823$ (3) Å) phases of NaMgF₃ are indicated.

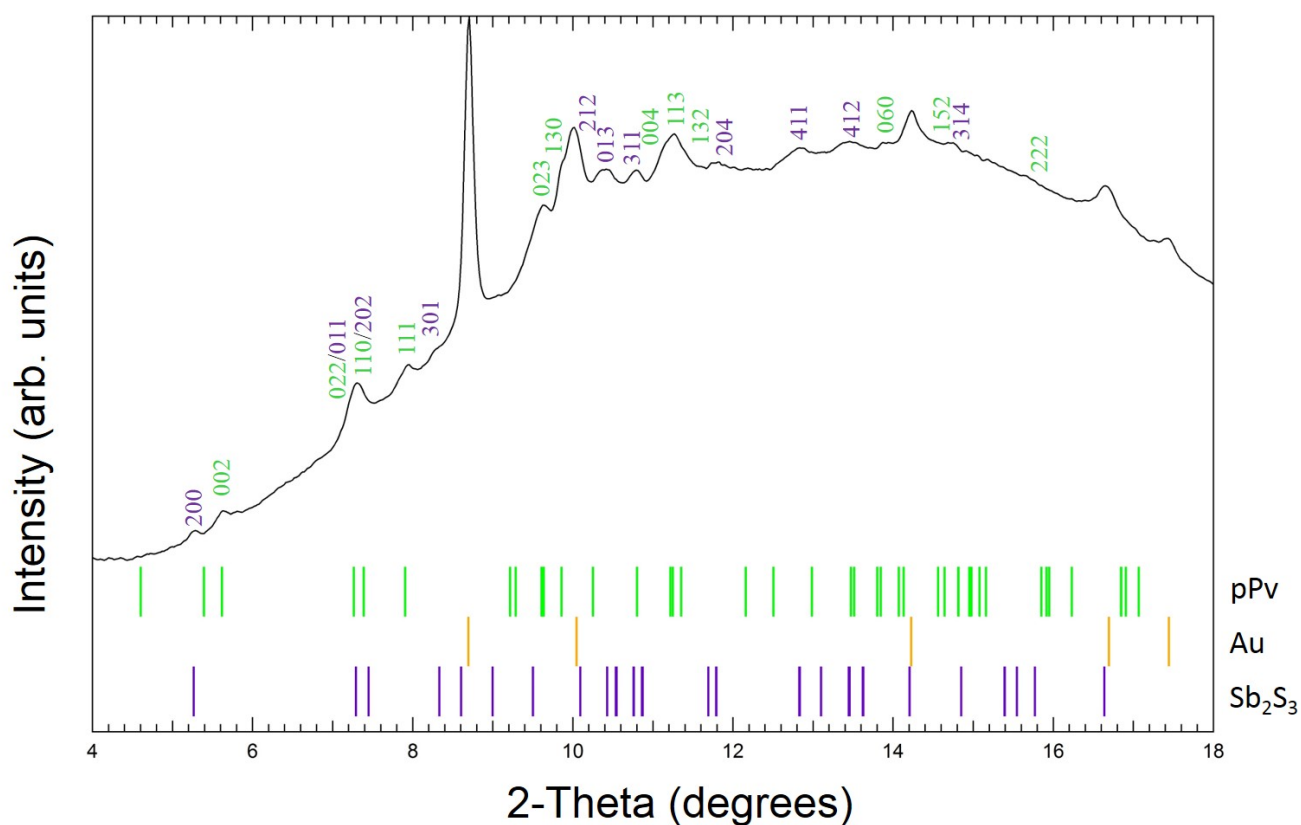


Figure S4. LeBail refinement of the diffraction pattern shown in Figure 2. The lattice parameters of the Sb_2S_3 -type phase are $a = 7.149 (2) \text{ \AA}$, $b = 2.716 (1) \text{ \AA}$, and $c = 7.065 (5) \text{ \AA}$. The red, green and blue lines indicate the calculated pattern, background and the difference between the simulated and observed patterns, respectively. Peaks indicated by the star symbol were masked out in Figure 2 on textural grounds. Inset shows the caked diffraction pattern with orange circles indicating the spots give rising to the above-mentioned peaks.

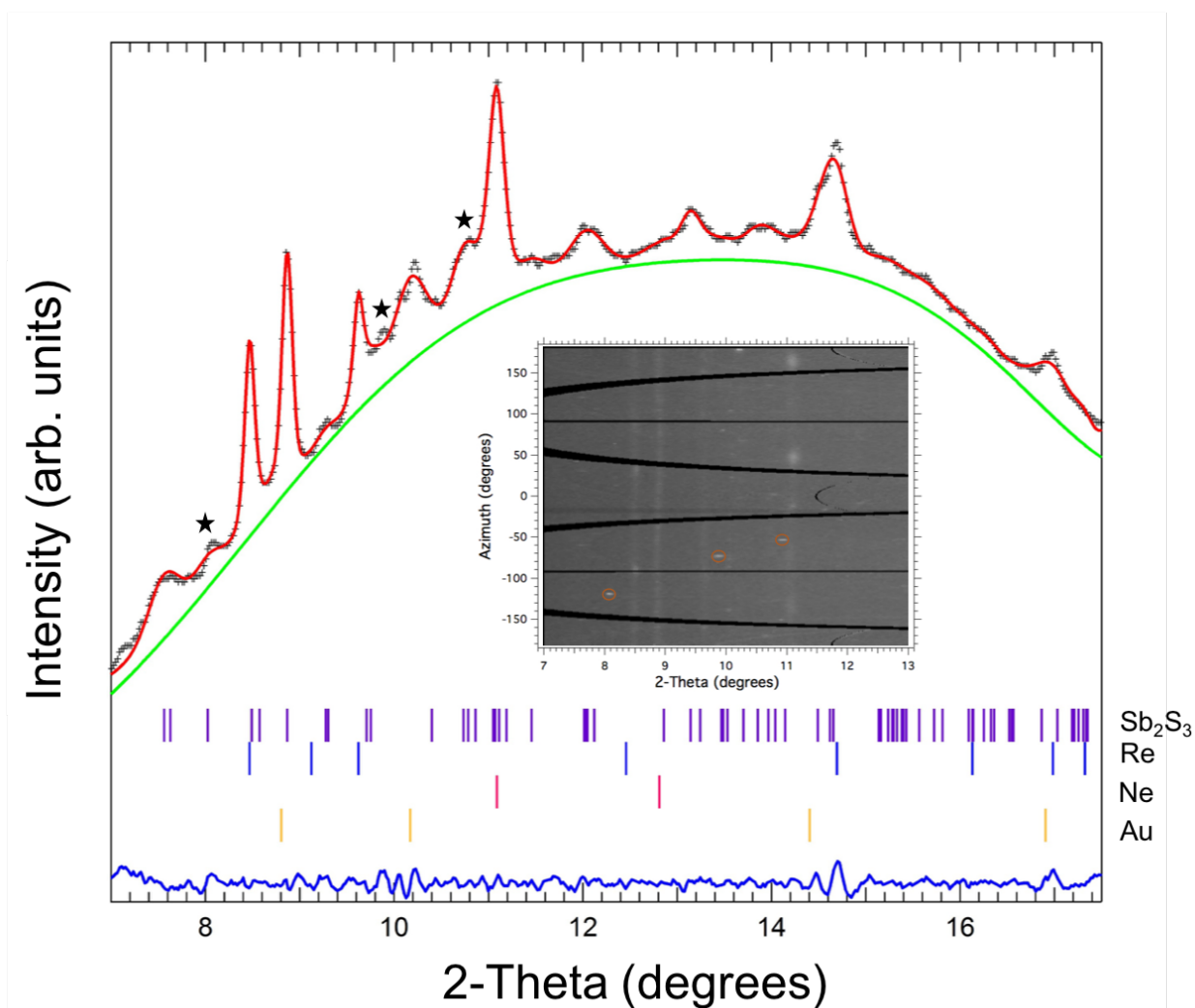


Figure S5. Lattice parameters of the Sb_2S_3 -type phase as a function of pressure at 300 K. The pink datum represents the experiment where the sample was quenched from laser heating in a neon pressure medium. It should be noted that the $Pnma$ setting has been adopted in this study for the Sb_2S_3 -type phase [$Pnma(a, b, c) = Pmcn(b, c, a)$]. Solid lines are linear fits to the data.

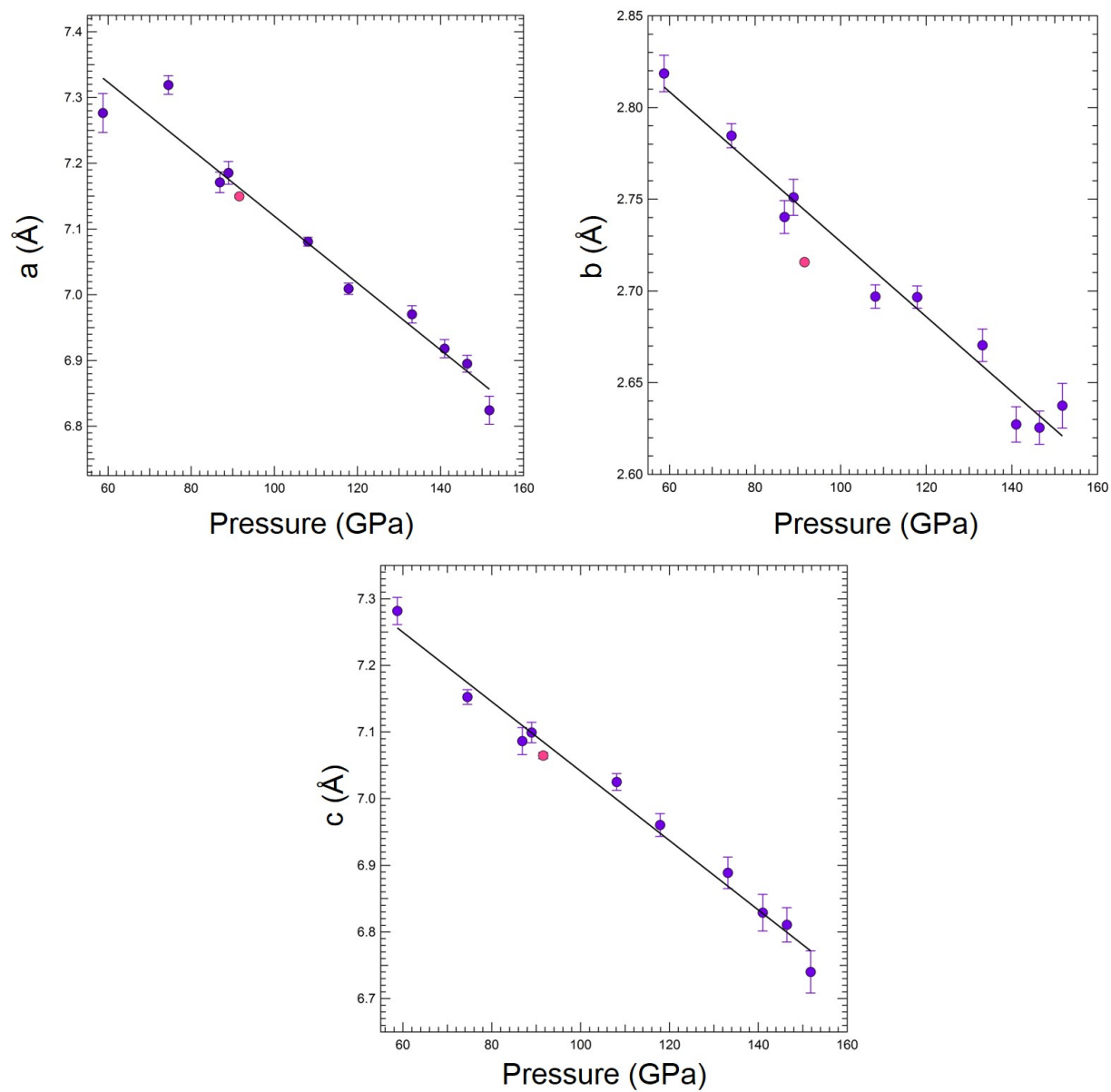


Table S3. Calculated and observed d -spacings of Sb₂S₃-type NaMgF₃ at 87 GPa (xrd pattern shown in inset of figure 2). The lattice parameters are $a = 7.163$ (4) Å, $b = 2.741$ (2) Å, $c = 7.094$ (4) Å.

h	k	l	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)
0	1	1	2.56250	2.55689	0.00561
1	1	2	2.07138	2.07585	-0.00447
0	1	3	1.78710	1.79048	-0.00338
1	1	3	1.73864	1.73704	0.00160
4	0	2	1.59860	1.59857	0.00003
1	1	4	1.45921	1.45784	0.00137

Since some of the assigned peaks (e.g. 113 and 311; 114 and 411) are closely spaced, peak assignments can be ambiguous. It should be noted that the a and c dimensions obtained from both experiments and theoretical calculations (2) ($a = 7.296$ Å and $c = 7.289$ Å at 50 GPa) are within 0.1% of each other. Thus, swapping the h and l indices does not significantly affect the results.

S5. NaMg₂F₅ + NaF

Two temperature-quenched x-ray diffraction patterns were obtained in experiment 2b (91 GPa) and 3 (137 GPa). The patterns are similar (accounting for differences in pressure) and so we discuss only one of them in detail here. Fig S6 shows diffraction patterns before and after heating at 134 GPa. We observe the presence of a strong peak at $\sim 11.78^\circ$ in the quenched pattern that is not present in the unheated one. This peak is consistent with the expected position of the strongest reflection (110) of NaF in the CsCl-type (B2) structure. That only a single NaF peak is observed in the spectrum is not surprising as all other peaks of the CsCl-type phase in the relevant 2θ range are expected to have relative intensities of $< 10\%$ of the (110) peak.

The presence of NaF requires that another phase such as MgF₂ or NaMg₂F₅ ($P2_1/c$) must be present for chemical balance. The cotunnite-type phase of MgF₂ is expected to be stable above 64 GPa (17), but the observed diffraction peaks are not consistent with this phase. To examine the possible presence of NaMg₂F₅, we first optimized the structure at the required pressures using density functional theory calculations. The parameters reported in a computational study (18) at lower pressure (50 GPa) were used as the starting model for the optimization. The lattice parameters at 135 GPa obtained from our theoretical calculation ($a = 5.454 \text{ \AA}$, $b = 4.780 \text{ \AA}$, $c = 7.408 \text{ \AA}$ and $\beta = 89.89^\circ$) were then used to compare expected peak positions with the measured pattern. We found that the assemblage NaMg₂F₅ + NaF can account for all the major peaks (some of which overlap with Sb₂S₃-type) in the pattern (Fig. S6). The lattice parameters obtained from least-squares fitting of our experimental data are in fair agreement with our calculated value at both 88 and 137 GPa. NaMg₂F₅ + NaF thus provides the best fit to the current data (Tables S4 and S5).

We also examined whether our interpretation could be affected by the possible presence of diffraction peaks from the Re gasket. The observed peak at $\sim 8.56^\circ$ two-theta could potentially be assigned to the (002) peak from rhenium. However, we do not observe any evidence for the stronger Re peak (101) in the measured pattern or any evidence for Re at all in the unheated pattern recorded prior to heating. Examination of the two-dimensional CCD image shows that the diffraction ring at 8.56° does not show the characteristic hexagonal texture typical of the rhenium gasket reflection, but rather displays a spotty texture similar to other rings from the sample. This indicates that the presence of Re is not a viable explanation for this peak.

One other feature in the diffraction pattern that should be mentioned is the offset of the Au (111) and (200) peaks. The pressure determined from the Au (111) peak is 137 GPa but the corresponding pressure from the Au (200) peak is only 111 GPa. In terms of two-theta values, the expected position of Au (200) at 137 GPa is $2\theta = 10.48^\circ$, while the observed position is 10.36° ($\Delta d = d_{\text{expected}} - d_{\text{observed}} = 0.02 \text{ \AA}$). This difference is larger than expected based on the expected strength of gold at this pressure. In FCC crystals, the presence of stacking faults (19) can cause the (111) and (200) peaks to shift in opposite directions i.e. (111) to higher angle and (200) to lower angle, with the (200) peak shifting more than (111). A combination of differential stress and stacking faults may be an explanation for the observed offset.

Figure S6. Observed x-ray diffraction pattern before (bottom) and after laser heating (top) to 2600 K at 134 GPa (*in situ* P = 137 GPa). The predicted peak positions of gold (yellow) and NaMg₂F₅ (brown) are shown at the bottom. Asterisk shows the position of the NaF (110) peak. Miller indices of the NaMg₂F₅ phase are indicated next to the quenched xrd pattern.

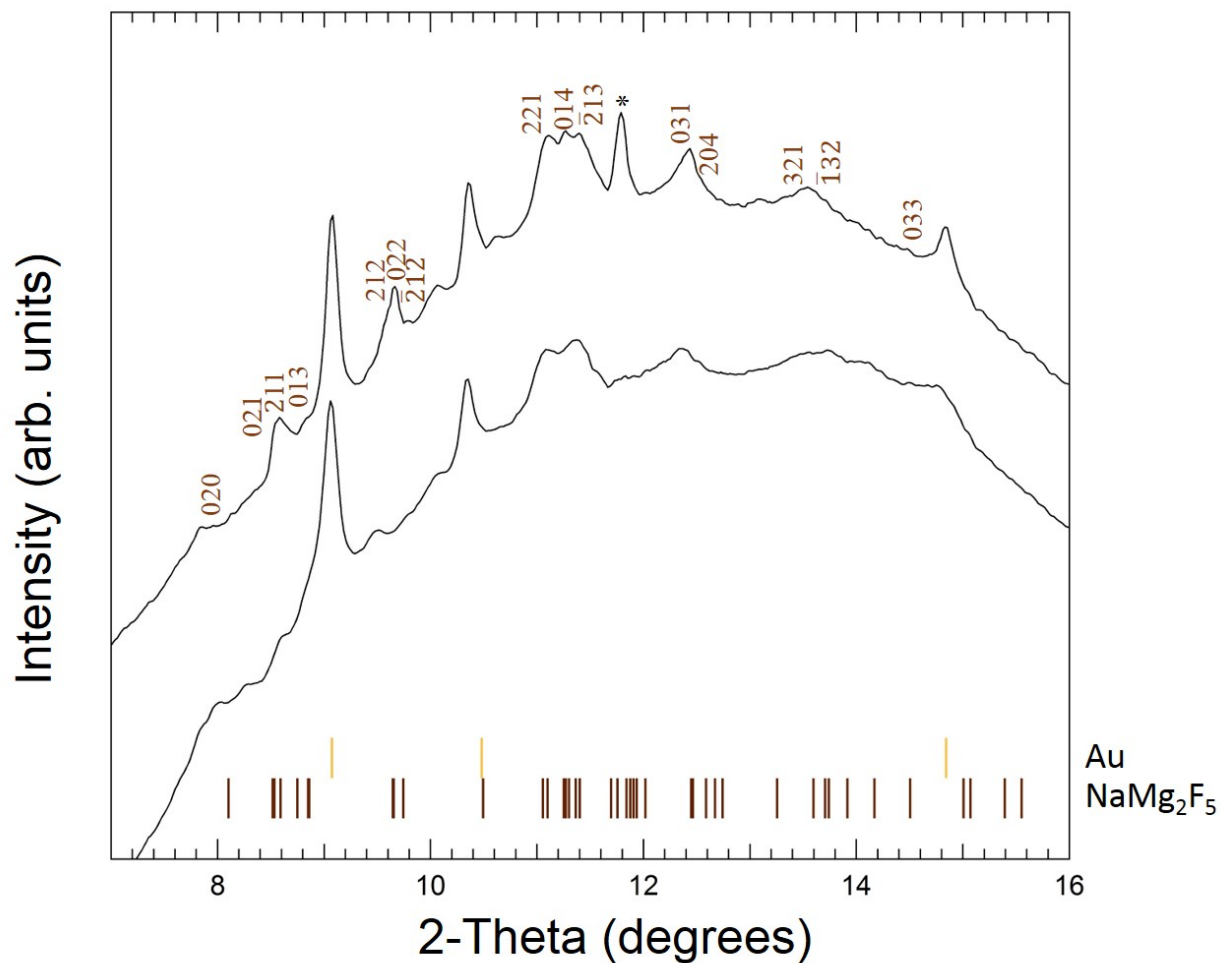


Table S4. Calculated and observed d -spacings of NaMg₂F₅ at 88 GPa. The lattice parameters are $a = 5.618$ (3) Å, $b = 4.977$ (3) Å, $c = 7.729$ (7) Å and $\beta = 89.23$ (9) degrees.

h	k	l	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)
0	1	3	2.28763	2.2879	-0.00026
2	1	2	2.07593	2.0778	-0.00188
2	2	1	1.81338	1.81442	-0.00104
0	2	3	1.78868	1.7898	-0.00112
0	3	1	1.62284	1.62195	0.00089
2	0	4	1.6029	1.60191	0.00099
-1	3	2	1.46938	1.46923	0.00015
4	0	0	1.40478	1.40449	0.00029

Table S5. Calculated and observed d -spacings of NaMg₂F₅ at 137 GPa. The lattice parameters are $a = 5.423$ (16) Å, $b = 4.732$ (6) Å, $c = 7.312$ (13) Å and $\beta = 89.2$ (2) degrees.

h	k	l	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)
0	2	1	2.24533	2.25136	-0.00602
0	1	3	2.1698	2.16677	0.00303
2	1	2	1.99061	1.98851	0.0021
0	2	2	1.98377	1.9865	-0.00273
2	2	1	1.73316	1.73544	-0.00228
0	1	4	1.70389	1.70515	-0.00125
-2	1	3	1.68358	1.68314	0.00044
0	3	1	1.5454	1.54207	0.00334

S5. NaF + MgF₂

The major peaks in the diffraction pattern at 160 GPa shown in Fig. 4 can be attributed to cotunnite-type MgF₂ (Table S6), Au and CsCl-type NaF except for a peak marked with an asterisk in the figure ($2\theta = 9.75^\circ$, $d = 1.97 \text{ \AA}$). Fig. S7 shows diffraction patterns recorded at different temperatures during this heating cycle. The unexplained peak is absent in the room-temperature diffraction pattern before heating. It first appears in the pattern at $\sim 1750 \text{ K}$, before the appearance of any evidence of peaks of the binary fluorides, which only appear at higher temperature ($\sim 1830 \text{ K}$). This observation suggests that the peak may be from a reaction product possibly involving carbon from the anvils which have been observed in other laser-heated DAC experiments (17) but its origin requires further investigation.

Alternatively, this peak could be from a gold fluoride. A recent theoretical study (20) proposed stable gold fluorides with variable oxidation states to be stable at high-pressure. Under pressures comparable to our experimental conditions, we find Au₂F ($P4/nmm$, $a = 2.641 \text{ \AA}$ and $c = 8.565 \text{ \AA}$ at 160 GPa) is broadly consistent with the concerned peak.

Figure S7. X-ray diffraction patterns of NaMgF₃ on heating at 162 GPa. The asterisk indicates the unexplained diffraction peak. In the upper three patterns, all other major peaks can be assigned to MgF₂ + NaF + Au (refer Fig. 4 for indexing). The red and blue arrows indicate the peak positions of MgF₂ and NaF respectively. The lower two diffraction patterns can be indexed using Sb₂S₃-type NaMgF₃.

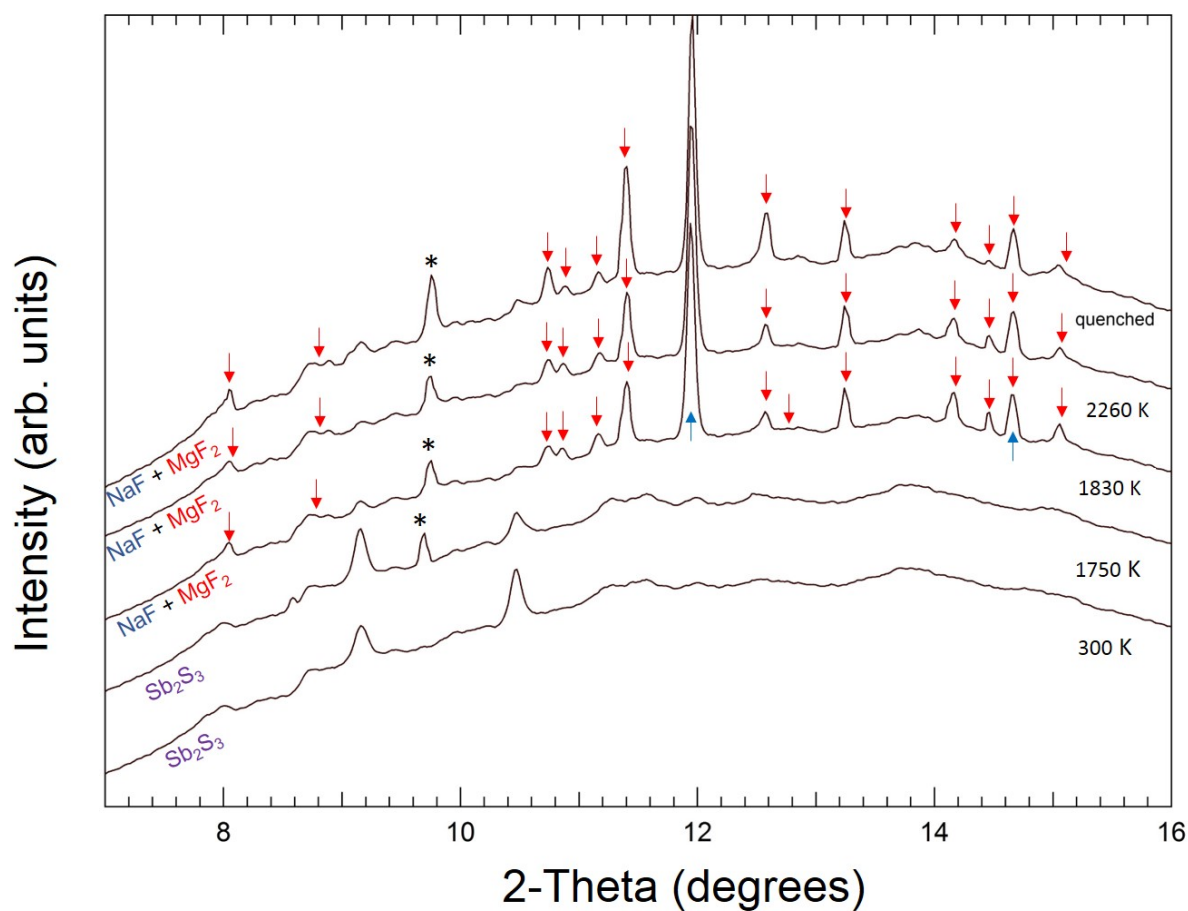


Table S6. Calculated and observed d -spacings of cotunnite-type MgF_2 at 160 GPa. The lattice parameters are $a = 4.667$ (2) Å, $b = 2.704$ (1) Å and $c = 5.545$ (1) Å.

h	k	l	d_{obs} (Å)	d_{calc} (Å)	Δd (Å)
1	0	2	2.38411	2.38382	0.00029
1	1	2	1.78722	1.78815	-0.00093
2	1	0	1.76692	1.76674	0.00018
1	0	3	1.71923	1.7186	0.00062
2	1	1	1.68342	1.68337	0.00005
0	1	3	1.52734	1.52598	0.00136
1	1	3	1.44967	1.45043	-0.00077
3	0	2	1.35685	1.35684	0.00001
1	0	4	1.32856	1.32897	-0.00041
3	1	1	1.3104	1.31036	0.00004

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