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| As Published     | http://dx.doi.org/10.1029/2010GL043645 |
| Publisher        | American Geophysical Union |
| Version          | Final published version |
| Accessed         | Sat Dec 22 01:12:31 EST 2018 |
| Citable Link     | http://hdl.handle.net/1721.1/61369 |
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Stability of the MgSiO$_3$ analog NaMgF$_3$ and its implication for mantle structure in super-Earths

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Received 16 April 2010; revised 31 May 2010; accepted 7 June 2010; published 28 July 2010.

First-principles calculations on MgSiO$_3$ suggested a breakdown into MgO + SiO$_2$ at pressure above 1000 GPa with an extremely large negative Clapeyron slope, isolating the lowermost mantles of larger super-Earths ($\sim 10 M_\oplus$) from convection. Similar calculations predicted the same type of breakdown in NaMgF$_3$ to NaF + MgF$_2$ at 40 GPa, allowing for experimental examination. We found that NaMgF$_3$ is stable to at least 70 GPa and 2500 K. In our measurements on MgF$_2$ (an SiO$_2$ analog), we found a previously unidentified phase ("phase X") between the stability fields of pyrite-type and cotunnite-type (49–53 GPa and 1500–2500 K). A very small density increase (1%) at the pyrite-type → phase X transition would extend the stability of NaMgF$_3$ relative to the breakdown products. Furthermore, because phase X appears to have a cation coordination number intermediate between pyrite-type (6) and cotunnite-type (9), entropy change ($\Delta S$) would be smaller at the breakdown boundary, making the Clapeyron slope ($dP/dT = \Delta S/\Delta V$) much smaller than the prediction. If similar trend occurs in MgSiO$_3$ and SiO$_2$, the breakdown of MgSiO$_3$ may occur at higher pressure and have much smaller negative Clapeyron slope than the prediction, allowing for large-scale convection in the mantles of super-Earth exoplanets. Citation: Grocholski, B., S.-H. Shim, and V. B. Prakapenka (2010), Stability of the MgSiO$_3$ analog NaMgF$_3$ and its implication for mantle structure in super-Earths, Geophys. Res. Lett., 37, L14204, doi:10.1029/2010GL043645.

1. Introduction

Among recently discovered exoplanets, some may have compositions similar to that of the Earth, i.e., super-Earths [Rivera et al., 2007]. Most of these planets have much larger sizes (5 – 10 $M_\oplus$), with their internal pressures (P) far in excess of Earth [Seager et al., 2007; Valencia et al., 2007]. Therefore, in order to understand the heat transport, thermal evolution, and internal structure of super-Earths, we need to study the phase relations of silicates to extremely high pressures.

Recent first-principles calculations by Umemoto et al. [2006a] suggested that the post-perovskite form of MgSiO$_3$ breaks down to an oxide mixture (MgO + SiO$_2$) at $\sim$1000 GPa, corresponding to the core-mantle boundary pressure in 10$M_\oplus$ super-Earths. They predicted a strongly negative Clapeyron slope ($dP/dT = -30$ MPa/K) of the breakdown — at least an order of magnitude larger than the post-spinel transition. Such a large negative Clapeyron slope would make the breakdown boundary impermeable for mantle convection, resulting in drastically different internal structure and thermochemical evolution of larger super-Earths [Tackley, 1995; van den Berg et al., 1996].

[4] While our current static compression techniques, such as the diamond-anvil cell, are not capable of reaching the predicted breakdown pressure, the prediction can be examined by studying analog materials which undergo the same sequence of phase transitions as MgSiO$_3$ but at much lower pressures. Umemoto et al. [2006b] have also predicted a breakdown of NaMgF$_3$ to NaF + MgF$_2$ at 40–48 GPa. NaMgF$_3$ is both isoelectronic and isostructural with MgSiO$_3$, and undergoes a perovskite (Pv) → post-perovskite (PPv) transition at $\sim$30 GPa [Martin et al., 2006], compared to $\sim$120 GPa in MgSiO$_3$. Furthermore, the unit-cell axis ratios of the Pv and PPv phases in NaMgF$_3$ are close to those in MgSiO$_3$, making it an excellent analog material [Kubo et al., 2008].

[5] The breakdown product of NaMgF$_3$ (NaF and MgF$_2$) are also analogs of MgO and SiO$_2$. According to Umemoto et al. [2006a] a large decrease in enthalpy at the pyrite-type → cotunnite-type transition in SiO$_2$ stabilizes the breakdown products with respect to MgSiO$_3$, due mainly to the higher density of the cotunnite-type SiO$_2$ + B$_2$-MgO than MgSiO$_3$-PPv. NaMgF$_3$ is a good analog material for MgSiO$_3$ because its breakdown occurs from the same thermodynamic driving force [Umemoto et al., 2006b]. The predicted large negative Clapeyron slope ($dP/dT = \Delta S/\Delta V$) can be explained by a large increase in the coordination number of cation at the breakdown (6 → 9 for Si), which would induce a large increase in entropy ($\Delta S$). This highlights in particular the importance of the polymorphic transitions of SiO$_2$.

[6] The high-P transition sequence for SiO$_2$ has been experimentally determined to be: quartz → coesite → rutile-type → CaCl$_2$-type → $\alpha$-PbO$_2$-type → pyrite-type, with the pyrite type appearing at 270 GPa [Kawamura et al., 2005]. MgF$_2$ has the same sequence except the sequence starts from the rutile type, the transition to the pyrite type occurs at 14 GPa, the $\alpha$-PbO$_2$-type phase only appears upon decompression [Haines et al., 2001]. Previous studies reported that MgF$_2$ undergoes a phase transition to the cotunnite type at 35 GPa [Haines et al., 2001; Kanchana et al., 2003; Umemoto et al., 2006a]. The cotunnite type has been seen in many SiO$_2$ analogs at high P and is predicted be the stable phase of SiO$_2$ above 750 GPa at 0 K [Oganov et al., 2005]. Although Umemoto et al. [2006a] predicted that the pyrite-type SiO$_2$ transforms directly to the cotunnite-type, similar compounds have structures with seven-fold coordination that appear before the cotunnite type, such as

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2. Experimental Method

[8] Synthetic NaMgF$_3$ was used in this study. Detailed information on the sample is given by Hustoft et al. [2008]. MgF$_2$ was obtained at 99.99% purity (Alfa-Aesar). Thin foils (10 μm) of NaMgF$_3$ or MgF$_2$ mixed with 10 wt% platinum or gold used as a pressure calibrant and laser absorber were loaded into the diamond-anvil cells with 200 μm culets using argon as a pressure medium, with the exception of one NaMgF$_3$ sample loaded with MgO plates. Rhenium gaskets were used for all experiments with a sample chamber of 120 μm. Pressures were determined in situ from the equations of state for platinum [Holmes et al., 1989] or gold [Tsuchiya, 2003]. We loaded a total of four samples of NaMgF$_3$ and two samples of MgF$_2$. Experiments were performed at the GSECARS sector at the Advanced Photon Source using x-rays with an energy of 40 keV, MAR-345 ccd detector and CeO$_2$ to calibrate the detector.

[9] The sample was brought to pressure at room temperature and laser heated at 1500–2500 K for at least 30 minutes while simultaneously collecting X-ray diffraction patterns every 2–3 minutes during the heating cycle, with temperature determinations made using spectral radiometry. Lattice parameters were calculated using the UnitCell program [Holland and Redfern, 1997]. We found all samples loaded with platinum react with the diamond culets at $P > 53$ GPa when heated at $T > 2000$ K, consistent with Ono et al. [2005]. The PtC diffraction intensities approach those of platinum after several minutes of laser heating, allowing for ready identification of the contaminating phase in this experiment. Care must be taken not to mistake these for sample peaks, although the strong diffraction intensities could be useful as a secondary pressure calibrant.

3. Results

[10] We heated four different samples of NaMgF$_3$ a total of 15 times at $T \geq 2000$ K for between 20–70 minutes to 74 GPa. The best diagnostic for determining if NaMgF$_3$ breakdown occurs is the most intense lines of the high-$P$ polymorphs of MgF$_2$. This line is between 1.80–1.85 Å for both “phase X” (see below) and cotunnite type. Calculations based on Hustoft et al. [2008] show that no diffraction lines of the Pv or PPv phases exist in this region. As shown in Figure 1d, we found the appearance of PPv, but no evidence of MgF$_3$ up to 74 GPa. We do not find evidence for the “N-phase” reported by Martin et al. [2006].

[11] Previous measurements of MgF$_2$ found the pyrite-type phase (Pa3) stable to 35 GPa and the cotunnite-type phase (Pnma) stable above this pressure after laser heating at $T < 1500$ K [Haines et al., 2001]. We find a new phase (“phase X”) at pressures between the stability fields of the pyrite- and cotunnite-type phases (Figures 1a–1c). Phase X is stable between 49 and 55 GPa upon compression at $T \geq 1500$ K, and stable upon decompression at 300 K to 26 GPa. Once formed, phase X is metastable to at least 71 GPa and temperatures 2000 K, near the maximum pressure of this experiment. When cold compressed to 64 GPa and then heated to 1700 K, MgF$_2$ converts directly to the cotunnite type as reported by Haines et al. [2001] (Figures 1a–1c). Above 55 GPa, heating the previously synthesized phase X results in the growth of the most intense line of the cotunnite-type phase. We were able to convert the cotunnite-type phase back to phase X at ~50 GPa and 2000 K upon decompression. The back transformation is sluggish, taking a full 30 min of laser heating at 2000 K before sudden recrystallization of the sample to phase X with an accompanying drop in pressure by 4 GPa. This demonstrates that phase X is a thermodynamically stable high-$P$ polymorph in MgF$_2$ whose stability field exists between those of the pyrite- and cotunnite-type phases.

[12] We investigated the crystal structure of phase X using the powder diffraction patterns combined with the CRYSFIRE and DICVOL programs [Shirley, 1999; Boultif and Lauer, 2004]. Among many high-$P$ polymorphs found in SiO$_2$ analogs, the two most likely crystal structures found between the stability fields of pyrite type and cotunnite type are the baddeleyite type ($P2_1/c$) and SrI$_2$ type (Pbca). These

Figure 1. Diffraction patterns of the (a) pyrite-type, (b) phase X, (c) cotunnite-type MgF$_2$, and (d) NaMgF$_3$ collected with 40 keV x-ray energy. The broad peaks Figure 1a are the result of no laser annealing post-conversion. The baddeleyite crystal structure is consistent with most of the diffraction intensities of phase X as shown in Figure 1b. Example of the product of a heating run far in excess of the expected breakdown pressure of NaMgF$_3$ shown in Figure 1d. The diffraction pattern can be indexed as a combination of post-perovskite and platinum carbide. The grey box shows the range where we expect the most intense line expected for MgF$_2$. The absence of major line at the angular range shows the stability of PPv.

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the baddeleyite type and SrI$_2$ type [Shieh et al., 2006; Leger et al., 1993].

[7] Here, we report a new high-$P$ phase transition in MgF$_2$ and find the stability of NaMgF$_3$ to pressures well above the predicted breakdown pressure.
are both distorted versions of the fluorite structure with well-constrained axial ratios. Equation of state parameters for phase X and other MgF$_2$ phases are given in Figure 2, but fail to help determine if phase X is monoclinic or orthorhombic.

[13] According to the reported sequence of phase transitions in SiO$_2$ analogs, the SrI$_2$ type is most likely structure for phase X [Moriwaki et al., 2006; Vajeeston et al., 2006; Lowther et al., 1999]. However, no orthorhombic solutions satisfied the expected axial ratios for the SrI$_2$-type: $a:b:c \approx 1:2:2$. We found the fit to the monoclinic baddeleyite structure provides reasonable lattice constants (Table 1). However, this solution cannot fit two diffraction lines at 2.529 Å and 1.900 Å, which appear in the diffraction patterns using both types of pressure calibrants and are therefore unlikely to be contamination (Figure 1b).

[14] The baddeleyite-type phase is normally found instead of pyrite type, with both of these phases transforming to the SrI$_2$-type phase before transforming to cotunnite at higher $P$ [Ohtaka et al., 2005]. However, systematic high resolution investigation of SiO$_2$ analogs at high temperature and quasihydrostatic conditions is lacking. Further, phase X could be an unidentified low-symmetry crystal structure not yet seen in any SiO$_2$ analogs or a mixture of two (or even more) polymorphs. Mixed phases may be experimentally inevitable if the phase stability fields are narrow in pressure. In addition, computer simulations of SiO$_2$ analogs usually find numerous phases within small energy differences of each other at 0 K [Lowther et al., 1999; Oganov et al., 2005; Moriwaki et al., 2006].

[15] The measured volumes for pyrite-type MgF$_2$ are consistent with Haines et al. [2001] (Figure 2). If baddeleyite-type is assigned to phase X, at the pyrite-type → phase X transition, we found a small volume decrease (1%), which appears to be reasonable given that the coordination number of cation increases by 1 ($6 \rightarrow 7$). In addition, examples of direct transformation from the pyrite structure to the cotunnite structure are rare and intermediate phases are not surprising.

[16] Our measurements on cotunnite-type MgF$_2$ are consistent with the axial ratios of other cotunnite-type SiO$_2$ analogs: $a/b \approx 0.86$ and $(a+b)/c \approx 3.76$ [Dewhurst and Lowther, 2001; Morris et al., 2001]. Our a lattice parameter for cotunnite-type MgF$_2$ is 3% higher than the previous result [Haines et al., 2001]. We attribute this difference to overlapped diffraction intensities of phase X and cotunnite type of Haines et al. [2001], resulting in misidentified peak positions. In particular, we do not observe peaks at 1.88 and 1.78 Å in our diffraction patterns on cotunnite-type – both of these could be from phase X. The mixed phase in the earlier study [Haines et al., 2001] could be due to pressure gradients, insufficient laser heating, and a relatively large X-ray beam size. We note, however, that the volume difference between the pyrite- and cotunnite-type, which is 7%, is consistent with computations on MgF$_2$ [Kanchana et al., 2003] and experimental results on cotunnite types in other SiO$_2$ analogs [Morris et al., 2001]. If the baddeleyite-type is assigned to phase X, our data indicate a large volume decrease for the phase X → cotunnite-type transition, 6%.

### Table 1. Observed and Calculated d-Spacing for the Baddeleyite and Orthorhombic Solutions for Phase X

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$^a$Both are not able to fit all the diffraction lines, which could be due to other phases (including cotunnite-type MgF$_2$). The baddeleyite-type MgF$_2$ ($Z = 4$) has lattice parameters of $a = 4.587(3)$ Å, $b = 4.324(3)$ Å, $c = 4.769(3)$ Å, $\beta = 98.38(5)^\circ$. The orthorhombic solution ($Z = 8$) has $a = 7.172(6)$ Å, $b = 5.840(4)$ Å, $c = 4.471(3)$ Å. Texturing in the sample and the potential for mixed phases make determining the crystal structure difficult. Attempts were made to fit the diffraction intensities to the orthorhombic SrI$_2$ structure with $a:b:c \approx 1:1:2$, but was found to not fit the diffraction peak positions very well. This phase or mixture of phases may be a quenchable high temperature phase as it is synthesized above ~1500 K in these experiments.
which appears to be consistent with a larger increase in the coordination number of cation (7 → 9) (Figure 2).

4. Discussion and Planetary Implications

[17] The stability of NaMgF$_3$ (a MgSiO$_3$ analog) to the $P$–$T$ conditions well above those of the breakdown predicted by the simulation of Umemoto et al. [2006b] can be explained by insufficient understanding on phase transitions in MgF$_2$ (an SiO$_2$ analog) at high $P$–$T$. The breakdown reaction is predicted to be driven by the significant enthalpy reduction at the pyrite-type → cotunnite-type phase transition that stabilizes the breakdown products relative to NaMgF$_3$–PPv [Umemoto et al., 2006b].

[18] However, our study reveals that MgF$_2$ may not transform directly from pyrite type to cotunnite type. In fact, the pyrite-type → cotunnite-type transition requires a drastic increase in the coordination number of cation from 6 to 9. Intermediate phases (baddelyrite type, SrI$_2$ type, or other structures) between the pyrite type and cotunnite type may have a coordination of 7 or 8. Therefore, the stability of the new phase in MgF$_2$ would not make the breakdown products energetically more favorable until higher $P$, which may explain our observation of the stability of the PPv phase to higher $P$.

[19] The discrepancy between our experiments and the computation [Umemoto et al., 2006b] could be due in part to the instability of the quasi-harmonic approximation (QHA) to properly account for thermal effects. The computational results indicate the breakdown occurs at lower pressures at higher temperatures based on a QHA of the change in entropy with temperature [Umemoto et al., 2006b]. The QHA used to estimate the slope only works well to temperatures at which the thermal expansivity starts to deviate from linear behavior, in the case of NaF this limit is under 1000 K, possibly invalidating the results above these temperatures. The newly identified phase X synthesized at high $P$–$T$ should be a good test for the QHA in the MgF$_2$ system as it should be valid to ~1500 K, while current computational results do not find another phase between pyrite- and cotunnite-types at 0 K [Kanchana et al., 2003; Umemoto et al., 2006b].

[20] Failure to observe the breakdown could be due to kinetic effects, as we cannot rule out insufficient heating duration to overcome activation barriers. Higher temperature heating is helpful [Catalli et al., 2009], but the low melting temperature of NaMgF$_3$ limits the temperature during experiments to $T \leq 2300$ K. We note that we conducted heating up to ~1 hr, which should help reducing kinetic effects.

[21] We observe the pyrite → phase X transition, and the phase X → cotunnite-type transition together with its reverse transition, documenting the stability of phase X in MgF$_2$. Together with small volume difference between pyrite type and phase X, the new phase may not be dense enough to energetically stabilize the breakdown products over the PPv phase.

[22] Assuming neighborite and MgF$_2$ are good analogs for the silicate and oxide systems, this is of particular importance for the phase relations in MgSiO$_3$ and SiO$_2$. Although at zero K the cotunnite-type is stable over pyrite at ~750 GPa, the enthalpy of the SrI$_2$-type SiO$_2$ is close enough that it may be the stable phase at high $T$ [Oganov et al., 2005]. Further, other structures such as orthorhombic Pbc2$_1$ have been found to be computationally stable between the stability fields of α-PbO$_2$ and cotunnite in MgH$_2$ [Morivaki et al., 2006]. If SrI$_2$, baddelyite, or other structures with the coordination number of cations smaller than nine are stable before the stability field of cotunnite type, this will likely stabilize MgSiO$_3$–PPv over breakdown products at all pressures inside super-Earths, because the predicted breakdown pressure is already close to the core-mantle boundary pressure of larger super-Earths (10$M_E$). Therefore, no major barrier for the mantle convection would exist in super-Earths. If even larger Earth-like exoplanets would exist (>10$M_E$) and have sufficient internal mantle pressures for the breakdown, the boundary may have a much smaller negative Clapeyron slope, as entropy change would be smaller due to a smaller increase in the coordination number of Si (7 or 8 → 9, instead of 6 → 9). Therefore, our finding implies that the mantles of super-Earths would not be strongly stratified, unlike the first-principles predictions [Umemoto et al., 2006b].

[23] Acknowledgments. The authors would like to thank K. Catalli for experimental assistance and Justin Hustoft for helpful discussions. We would like to thank the two anonymous reviewers for helpful comments that improved this manuscript. This work was performed in the GeoSoilEnviRO-CARS sector of the Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviRO-CARS is supported by the NSF and the DOE. Use of the APS is supported by the DOE. This work was supported in NSF to S.-H. S. (EAR0738655).

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