



NaMgF₃: A low-pressure analog of MgSiO₃

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Received 19 March 2006; revised 14 June 2006; accepted 21 June 2006; published 3 August 2006.

[1] Using first principles computations we show that NaMgF₃ perovskite undergoes the same series of phase transitions as MgSiO₃ perovskite, that is, the post-perovskite transition and the dissociation into CsCl-type NaF and cotunnite-type MgF₂. These fluorides also undergo the same series of phase transitions as MgO and SiO₂, the dissociation products of MgSiO₃. Since the phase transformations in NaMgF₃ are not accompanied by any soft mode, we compute quasi-harmonic free energies and the respective phase boundaries. They have positive and negative Clapeyron slopes, respectively, like MgSiO₃. However, the transition pressures in NaMgF₃ are much lower and could be easily achieved in diamond anvil experiments. Therefore NaMgF₃ should be a good low-pressure analog of MgSiO₃. **Citation:** Umemoto, K., R. M. Wentzcovitch, D. J. Weidner, and J. B. Parise (2006), NaMgF₃: A low-pressure analog of MgSiO₃, *Geophys. Res. Lett.*, 33, L15304, doi:10.1029/2006GL026348.

1. Introduction

[2] Since the discovery of the transition from perovskite (PV) to CaIrO₃-type post-perovskite (PPV) phase in MgSiO₃ near the core-mantle boundary of the Earth (at ~125 GPa and 2500 K) [Murakami *et al.*, 2004; Tsuchiya *et al.*, 2004; Oganov and Ono, 2004], this transition has been attracting great interest. Very recently we have predicted the dissociation of MgSiO₃ PPV into CsCl-type MgO and cotunnite-type SiO₂ at ultrahigh pressure and temperature (PT) typical of solar giants, Jupiter and Saturn, and newly-found extrasolar planets [Umemoto *et al.*, 2006]. Unfortunately, the predicted dissociation pressure is too high (~1 TPa) to be achieved experimentally today. Therefore low-pressure analogs of MgSiO₃ are highly desired for experimental investigation of properties of the CaIrO₃-type structure. NaMgF₃ PV, neighborite, is one of the best candidates. It is a stable *Pbnm* perovskite phase at ambient condition and undergoes a transition to a cubic phase by elevating temperature. The temperature dependence of structural parameters has been studied in detail [Zhao *et al.*, 1993a, 1993b, 1994; Zhou *et al.*, 1997; Smith *et al.*, 2000]. The PPV transition occurs also in NaMgF₃ under pressure [Parise *et al.*, 2004; Liu *et al.*, 2005]. However, the pressure dependence of NaMgF₃'s structural properties has been reported in detail only at

low pressure [Zhao *et al.*, 1994], not near the PPV transition. If NaMgF₃ is a good low-pressure analog of MgSiO₃, then the ternary system of Na, Mg, and F could be useful for comparison at higher pressures as well. It would be particularly important for investigations of the CaIrO₃-type structure and its dissociation into the elementary fluorides NaF and MgF₂, which are also low-pressure analogs of MgO and SiO₂ [Yagi *et al.*, 1983; Haines *et al.*, 2001].

[3] In this paper, we investigate NaMgF₃ under pressure by first-principles and demonstrate that NaMgF₃ should undergo the same types of pressure-induced phase transitions as MgSiO₃: the transition from the PV to PPV phase and the dissociation of the PPV phase into CsCl-type NaF and cotunnite-type MgF₂.

2. Computational Method

[4] Calculations were performed using the local-density approximation (LDA) and the generalized-gradient approximation (GGA) [Perdew and Zunger, 1981; Perdew *et al.*, 1996]. The valence electronic configurations used for the generation of Vanderbilt ultrasoft pseudopotentials [Vanderbilt, 1990] are 2s² 2p⁶ 3s¹ 3p⁰ 3d⁰, 2s² 2p⁶ 3s² 3p⁰ 3d⁰, and 2s² 2p⁵ 3d⁰, for Na, Mg, and F, respectively. Their cutoff radii are 1.6 a.u. for all quantum numbers *l* in each atom. The plane-wave cutoff energy is 60 Ry. We used variable-cell-shape molecular dynamics [Wentzcovitch,

Table 1. Calculated Parameters of the Third-Order Birch-Murnaghan Equations of States by LDA and GGA for Perovskite NaMgF₃, Post-Perovskite NaMgF₃, NaCl-type NaF, and Rutile-type MgF₂^a

	V_0 , a.u. ³ /f.u.	B_0 , GPa	B'_0
<i>NaMgF₃ PV at 0 GPa</i>			
Calc. (static)	358.07 (397.30)	86.9 (67.5)	3.7 (4.1)
Calc. (300 K)	366.98 (409.02)	80.1 (59.1)	3.8 (4.3)
Exp. ^b	380.27	67.6	
<i>NaCl-type NaF at 0 GPa</i>			
Calc. (static)	154.05 (175.20)	61.6 (45.1)	4.7 (4.5)
Calc. (300 K)	159.05 (182.31)	53.9 (37.9)	4.8 (4.7)
Exp. ^c	166.33	48.5	
<i>Rutile-type MgF₂ at 0 GPa</i>			
Calc. (static)	211.38 (230.55)	111.8 (90.4)	4.7 (4.6)
Calc. (300 K)	213.74 (234.57)	108.3 (83.4)	4.8 (4.6)
Exp. ^d	220.33	101	4.2
<i>NaMgF₃ PPV at 0 GPa</i>			
Calc. (static)	350.30 (391.47)	77.6 (60.8)	4.7 (4.5)
Calc. (300 K)	359.87 (403.75)	69.1 (54.6)	4.8 (4.5)

^aThe GGA results are in parentheses.

^bAt ambient temperature [Zhao *et al.*, 1994].

^cAt 300 K [Cortona, 1992].

^dAt ambient temperature [Haines *et al.*, 2001].

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Table 2. Calculated Transition Pressures by LDA and GGA for NaF and MgF₂^a

	Static-calc.	300 K-calc.	Exp.
<i>NaF</i>			
NaCl→CsCl	22.8 (27.1)	21.7 (26.0)	27 ^b
<i>MgF₂</i>			
Rutile→CaCl ₂	5.8 (6.7)	7.5 (10.3)	9.1 ^c
CaCl ₂ →Pyrite	9.0 (14.5)	8.6 (14.1)	14 ^c
Pyrite→Cotunnite	33.5 (42.5)	32.9 (41.0)	36 ^c

^aThe GGA results are shown in parentheses. The unit is GPa.

^bAt room temperature [Yagi *et al.*, 1983].

^cAt ambient temperature [Haines *et al.*, 2001].

1991; Wentzcovitch *et al.*, 1993] for structural optimization under arbitrary pressures. Dynamical matrices were computed at wave vectors \mathbf{q} using density-functional perturbation theory [Giannozzi *et al.*, 1991; Baroni *et al.*, 2001]. The numbers of formula units in the unit cells, \mathbf{k} points in the irreducible wedge, and \mathbf{q} points are (4, 4, 8) for NaMgF₃ PV, (2, 6, 6) for NaMgF₃ PPV, (1, 10, 8) for NaCl-type NaF, (1, 20, 10) for CsCl-type NaF, (2, 6, 6) for rutile-type MgF₂, (2, 8, 8) for CaCl₂-type MgF₂, (4, 1, 4) for pyrite-type MgF₂, and (4, 2, 8) for cotunnite-type MgF₂. Force constants are extracted to build dynamical matrices at arbitrary phonon \mathbf{q} vectors. Vibrational contributions to the free energy due to the zero-point motion (ZPM) and finite temperature are taken into account by the quasi-harmonic approximation (QHA) [Wallace, 1972].

[5] Comparisons between our calculated structural parameters (Table 1) and transition pressures (Table 2) with experimental values in Tables 1 and 2 confirm the reliability of our computational method. Notice that experimental data appear bracketed between LDA and GGA results, except the transition pressure from NaCl-type to CsCl-type NaF, where the experimental value is slightly larger than the GGA value but very close to it. Hence, the two series of calculations, one using the LDA and other the GGA should provide good predictions for the behavior of NaMgF₃ under pressure.

3. Results and Discussion

[6] Static LDA (GGA) enthalpy calculation shows NaMgF₃ PV transforms to PPV at 17.5 (22.5) GPa (blue line in Figure 1). Around the PPV transition pressure no phonon instability is found both in the PV and PPV phases, indicating that the PPV transition is enthalpically driven (Figure 2). At 0 GPa, all phonon frequencies in NaMgF₃ PPV are real and there is no dynamical instability. This is consistent with the experimental result that the PPV phase can be recovered at ambient pressure and room temperature [Liu *et al.*, 2005]. But imaginary phonon frequencies (soft mode) occur at negative pressure, ~ -7 GPa (~ -4 GPa) by LDA(GGA) (Figure 2). The lowest acoustic phonon branch along the Δ line goes soft entirely. Since this is a typical sign of amorphization, NaMgF₃ PPV should amorphize upon decompression at high temperatures (annealing), which is somewhat analogous to decompressing to negative pressures at 0 K.

[7] Next we investigate the dissociation of NaMgF₃ PPV into NaF and MgF₂. NaCl-type and CsCl-type NaF and pyrite-type and cotunnite-type MgF₂ are the relevant phases for the dissociation, because they are the stable phases beyond the PPV transition pressure (Table 2). Figure 1 shows that NaMgF₃ PPV dissociates into CsCl-type NaF and cotunnite-type MgF₂ at 40 GPa (LDA). The GGA dissociation pressure is 48 GPa. This dissociation pressure is much smaller than that of MgSiO₃ (~ 1 TPa) [Umamoto *et al.*, 2006] and can be easily achieved by diamond anvil experiments. There is no soft mode in CsCl-type NaF and cotunnite-type MgF₂ beyond the dissociation pressure and these phases are dynamically stable. NaMgF₃ PPV is also dynamically stable around the dissociation pressure; the dissociation as well as the PPV transition are enthalpically driven. Table 3 gives calculated structural parameters of NaMgF₃ PPV at 30 GPa and CsCl-type NaF and cotunnite-type MgF₂ at 50 GPa. They should be useful for the experimental identification of these phases.

[8] We have also investigated possible structures of post-PPV NaMgF₃: LiSbO₃-type BaNiO₃-type, hexagonal BaTiO₃-type, and *P6₃/mmc* NaMgF₃. The former three structures are described by Wyckoff [1965] and Hyde and Andersson [1989]. The LiSbO₃-type structure consists of MgF₆ octahedra interconnected in an α -PbO₂-like network; this is a likely higher connectivity. In BaNiO₃-type structure, MgF₆ octahedra share their faces and form separate columns. In the hexagonal BaTiO₃-type structure, MgF₆ octahedra share their faces and apices. In these two structures, MgF₆ octahedra have a higher degree of connectivity than the PPV structure. The last *P6₃/mmc* structure, to our knowledge, has not been observed experimentally so far. Its space group is a supergroup of *Cmcm*, the space group of the PPV structure. This structure has been found by a static compression of NaMgF₃ PPV to 150 GPa. Magnesium is 8-fold coordinated and the MgF₈ polyhedra share edges and apices. The MgF₈ network is related to Ni₂In-type structure. We found that all four phases have higher enthalpies than NaMgF₃ PPV around the dissociation pressure. At 50 GPa,

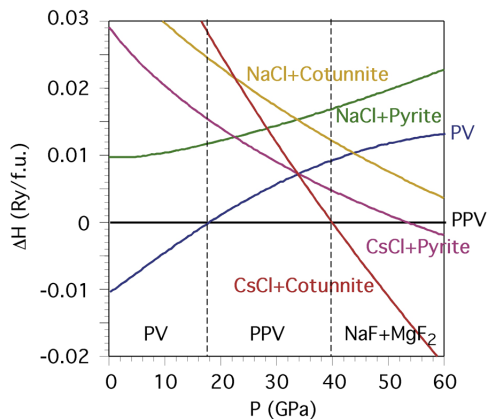


Figure 1. Pressure dependence of static-LDA enthalpies of NaMgF₃ PV and aggregations of NaF and MgF₂ with respect to NaMgF₃ PPV (ΔH).

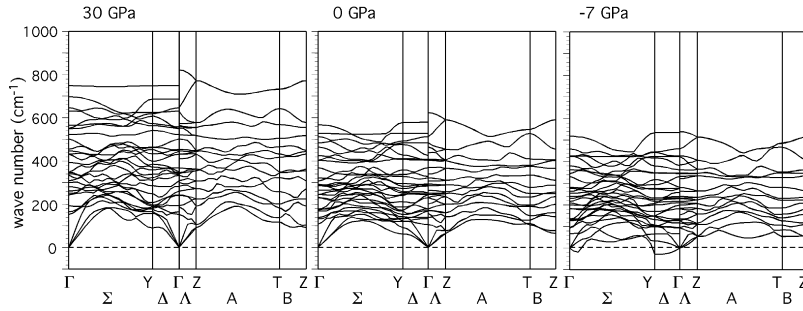


Figure 2. Phonon dispersion of NaMgF₃ PPV. Pressures are static-LDA values.

LDA calculations show that ΔH (Ry/f.u.) of these four structures with respect to NaMgF₃ PPV are 0.092, 0.173, 0.128, and 0.033, respectively.

[9] Using the QHA in conjunction with the computed phonon density of states (Figure 3), we obtain phase boundaries of the PPV transition and the dissociation (Figure 4). Empirically, the QHA works well below the temperature at which the thermal expansivity α (P , T) starts to deviate from linear behavior [Karki *et al.*, 1999]. Dashed lines in Figure 4 represent P - T conditions on which $d^2 \alpha/dT^2 = 0$ for the investigated phases; the QHA should be valid at least up to these lines. The experimental PPV transition pressure at room temperature (19.7 GPa) [Liu *et al.*, 2005] is bracketed by LDA (19.4 GPa) and GGA (24.0 GPa) values at 300 K. The unit cell volume decreases through the PPV transition by $\sim 2.5\%$. The shortest covalent Mg-F bond length also decreases through the transition by $\sim 1\%$. These decreases induce higher phonon frequencies (Figure 3a) and consequently lower vibrational entropy in the PPV phase than those in the PV phase. Hence, ZPM energy increases the PPV transition pressure from the static value. The Clapeyron slope ($dP/dT = \Delta S/\Delta V$) of the PPV transition is positive, 6 (5) MPa/K at 500 K by LDA (GGA).

[10] Throughout the dissociation, the volume decreases by ~ 5 – 6% , while the covalent Mg-F bond length increases

accompanied by an increase in the Mg coordination number (6 to 9). These longer covalent bonds give rise to smaller high (optical) phonon frequencies in general (Figure 3b). Hence, ZPM energy decreases the dissociation pressure from the static value. The Clapeyron slope is negative above ~ 300 K because of the overall increase in entropy: -1.7 (-1.8) MPa/K at 500 K and -3.3 (-3.6) MPa/K at 1000 K by LDA (GGA). On the other hand, the volume shrinkage increases the lowest (acoustic) phonon frequencies ($< \sim 200$ – 300 cm^{-1} ~ 300 – 400 K in Figure 3b). Since this effect compensates that of the longer bond lengths, the Clapeyron slope below ~ 300 K is almost independent on temperature. The same type of Clapeyron slope occurs in the transition of NaCl-type to CsCl-type NaF and pyrite-type to cotunnite-type MgF₂. In both cases there are increases in covalent bond lengths and cation coordination numbers and decrease of volumes.

[11] The present results show that NaMgF₃ PV undergoes the same sequence of phase transitions as MgSiO₃ PV: the PPV transition and the dissociation into NaF and MgF₂. The Clapeyron slopes of these transitions are positive and negative respectively, like the case of MgSiO₃. Transition pressures in NaMgF₃ are much smaller than those in MgSiO₃. Therefore, NaMgF₃ should be a good low-pressure analog of MgSiO₃ and serve as an alternative

Table 3. Calculated Lattice Constants and Atomic Wyckoff Positions of NaMgF₃ PPV at Static 30 GPa and CsCl-type NaF and Cotunnite-type MgF₂ at Static 50 GPa

	LDA	GGA
<i>NaMgF₃ PPV (Space Group: Cmc₂m)</i>		
(a, b, c) , a.u.	(5.238, 16.407, 12.995)	(5.343, 16.907, 13.240)
Na (4c)	(0, 0.252, 0.75)	(0, 0.252, 0.75)
Mg (4a)	(0, 0, 0)	(0, 0, 0)
F ₁ (4c)	(0, 0.071, 0.25)	(0, 0.071, 0.25)
F ₂ (8f)	(0, 0.360, 0.060)	(0, 0.362, 0.060)
<i>CsCl-type NaF (Space Group: Pm$\bar{3}$m)</i>		
a , a.u.	4.626	4.729
<i>Cotunnite-type MgF₂ (Space Group: Pbnm)</i>		
(a, b, c) , a.u.	(11.016, 9.377, 5.527)	(11.195, 9.547, 5.648)
Mg (4c)	(0.118, 0.248, 0.25)	(0.116, 0.249, 0.25)
F ₁ (4c)	(0.429, 0.353, 0.25)	(0.428, 0.354, 0.25)
F ₂ (4c)	(0.667, 0.978, 0.25)	(0.667, 0.979, 0.25)

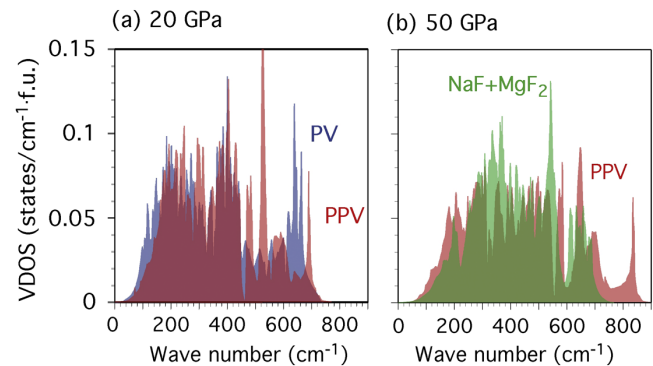


Figure 3. Vibrational density of states (VDOS) of (a) NaMgF₃ PV and PPV at 20 GPa and (b) NaMgF₃ PPV and aggregation of CsCl-type NaF and cotunnite-type MgF₂ at 50 GPa. Pressures are static-LDA values.

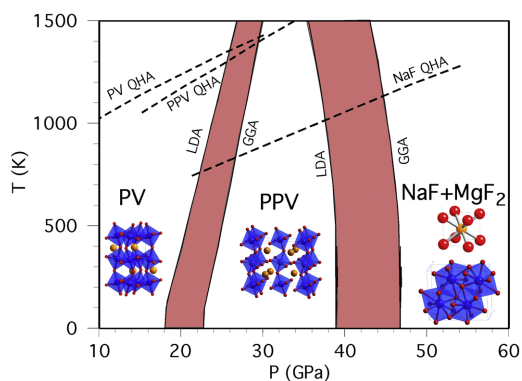


Figure 4. Calculated phase boundaries of NaMgF₃. NaF is CsCl-type and MgF₂ is cotunnite-type. Solid lines denote phase boundaries by LDA and GGA; real phase boundaries are expected to occur in red bands between them. Dashed lines represent the upper temperature limits in which QHA should be valid (see text); MgF₂'s limit occurs over 1,500 K.

route to investigate properties of the PPV structure, including its dissociation.

[12] **Acknowledgments.** Calculations have been carried out using the Quantum-ESPRESSO package (<http://www.pwscf.org>). Research was supported by NSF grants EAR-0135533, EAR-0230319, EAR-0510501, and ITR-0428774 (VLab).

References

- Baroni, S., S. de Gironcoli, A. Dal Corso, and P. Giannozzi (2001), Phonons and related crystal properties from density-functional perturbation theory, *Rev. Mod. Phys.*, **73**, 515.
- Cortona, P. (1992), Direct determination of self-consistent total energies and charge densities of solids: A study of the cohesive properties of the alkali halides, *Phys. Rev. B*, **46**, 2008.
- Giannozzi, P., S. de Gironcoli, P. Pavone, and S. Baroni (1991), Ab initio calculation of phonon dispersions in semiconductors, *Phys. Rev. B*, **43**, 7231.
- Haines, J., J. M. Leger, F. Gorelli, D. D. Klug, J. S. Tse, and Z. Q. Li (2001), X-ray diffraction and theoretical studies of the high-pressure structures and phase transitions in magnesium fluoride, *Phys. Rev. B*, **64**, 134130.
- Hyde, B. G., and S. Andersson (1989), *Inorganic Crystal Structures*, John Wiley, Hoboken, N. J.
- Karki, B. B., R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni (1999), First-principles determination of elastic anisotropy and wave velocities of MgO at lower mantle conditions, *Science*, **286**, 1705.
- Liu, H.-Z., J. Chen, J. Hu, C. D. Martin, D. J. Weidner, D. Husermann, and H.-K. Mao (2005), Octahedral tilting evolution and phase transition in

orthorhombic NaMgF₃ perovskite under pressure, *Geophys. Res. Lett.*, **32**, L04304, doi:10.1029/2004GL022068.

- Murakami, M., K. Hirose, K. Kawamura, N. Sata, and Y. Ohishi (2004), Post-perovskite phase transition in MgSiO₃, *Science*, **304**, 855.
- Oganov, A. R., and S. Ono (2004), Theoretical and experimental evidence for a post-perovskite phase of MgSiO₃ in Earth's D' layer, *Nature*, **430**, 445.
- Parise, J., K. Umemoto, R. M. Wentzcovitch, and D. Weidner (2004), Post-perovskite transition in NaMgF₃, *Eos Trans. AGU*, **85**(47), Fall Meet. Suppl., Abstract MR23A-0188.
- Perdew, J. P., and A. Zunger (1981), Self-interaction correction to density-functional approximations for many-electron systems, *Phys. Rev. B*, **23**, 5048.
- Perdew, J. P., K. Burke, and M. Ernzerhof (1996), Generalized gradient approximation made simple, *Phys. Rev. Lett.*, **77**, 3865.
- Smith, R. W., W. N. Mei, J. W. Flocken, M. J. Dubik, and J. R. Hardy (2000), Polymorphic phase transitions in mixed alkali magnesium fluoride solid solutions, *Mater. Res. Bull.*, **35**, 341.
- Tsuchiya, T., J. Tsuchiya, K. Umemoto, and R. M. Wentzcovitch (2004), Phase transition in MgSiO₃ perovskite in the Earth's lower mantle, *Earth Planet. Sci. Lett.*, **224**, 241.
- Umemoto, K., R. M. Wentzcovitch, and P. B. Allen (2006), Dissociation of MgSiO₃ in the cores of gas giants and terrestrial exoplanets, *Science*, **311**, 983.
- Vanderbilt, D. (1990), Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, *Phys. Rev. B*, **41**, R7892.
- Wallace, D. (1972), *Thermodynamics of Crystals*, John Wiley, Hoboken, N. J.
- Wentzcovitch, R. M. (1991), Invariant molecular-dynamics approach to structural phase transitions, *Phys. Rev. B*, **44**, 2358.
- Wentzcovitch, R. M., J. L. Martins, and G. D. Price (1993), Ab initio molecular dynamics with variable cell shape: Application to MgSiO₃, *Phys. Rev. Lett.*, **70**, 3947.
- Wyckoff, R. W. G. (1965), *Crystal Structures*, vol. 2, Wiley-Interscience, Hoboken, N. J.
- Yagi, T., T. Suzuki, and S. Akimoto (1983), New high-pressure polymorphs of sodium halides, *J. Phys. Chem. Solids*, **44**, 135.
- Zhao, Y., D. J. Weidner, J. B. Parise, and D. E. Cox (1993a), Thermal expansion and structural distortion of perovskite—Data for NaMgF₃ perovskite. Part I, *Phys. Earth Planet. Inter.*, **76**, 1.
- Zhao, Y., D. J. Weidner, J. B. Parise, and D. E. Cox (1993b), Critical phenomena and phase transition of perovskite—Data for NaMgF₃ perovskite. Part II, *Phys. Earth Planet. Inter.*, **76**, 17.
- Zhao, Y., et al. (1994), Perovskite at high P-T conditions: An in situ synchrotron X ray diffraction study of NaMgF₃ perovskite, *J. Geophys. Res.*, **99**, 2871.
- Zhou, L. X., J. R. Hardy, and H. Z. Cao (1997), Molecular dynamics simulation of superionicity in neighborite, NaMgF₃, *Geophys. Res. Lett.*, **24**, 747.

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