Phase transitions and compressibility of $NaMgF_3$ (Neighborite) in perovskite- and post-perovskite-related structures

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[1] Monochromatic x-ray diffraction data collected in-situ within the diamond anvil cell show perovskite structured Neighborite ($NaMgF_3$) transforms to the $CaIrO_3$-type post-perovskite structure between 28 and 30 GPa. Upon laser heating, the $CaIrO_3$-type structure transforms further to an unknown structure (*Pnnm*, designated N-phase). Upon pressure release, N-phase $NaMgF_3$ becomes x-ray amorphous. A structure transformation in post-perovskite $MgSiO_3$ and $MgGeO_3$ to N-phase may account for previous observations of extra x-ray reflections during high pressure experiments and tomographic observations of an additional boundary in the lower mantle below the D'' discontinuity. **Citation:** Martin, C. D., W. A. Crichton, H. Liu, V. Prakapenka, J. Chen, and J. B. Parise (2006), Phase transitions and compressibility of $NaMgF_3$ (Neighborite) in perovskite- and post-perovskite-related structures, *Geophys. Res. Lett.*, *33*, L11305, doi:10.1029/2006GL026150.

1. Introduction

[2] Recently, a post-perovskite structure of $MgSiO_3$ has been observed at pressures in excess of 120 GPa and 2500 K, conditions thought to coincide with the onset of the D'' layer [*Murakami et al.*, 2004; *Oganov and Ono*, 2004]. The post-perovskite structure is orthorhombic (*Cmcm*) and rarely adopted among oxides and sulfides (Figure 1). Having significant axial anisotropy, this layered structure may provide a suitable explanation for both the sharp horizontal discontinuity marking the onset of D'' and the zones of strong anisotropy observed within the layer [*Garnero*, 2004; *Murakami et al.*, 2004; *Oganov and Ono*, 2004; *Tsuchiya et al.*, 2004].

[3] Neighborite ($NaMgF_3$) [*Chao et al.*, 1961] is a well studied analog for $MgSiO_3$ perovskite, helpful in demonstrating the effects of pressure and temperature as well as cation substitution on the perovskite structure [*Liu et al.*, 2005; *Martin et al.*, 2005; *Zhao et al.*, 1993]. $NaMgF_3$ perovskite

has a bulk modulus less than one third that of $MgSiO_3$ and nearly half that of $MgGeO_3$ perovskite. Thus $NaMgF_3$ may require a lower pressure to stabilize post-perovskite, and thereby facilitate Rietveld structural modeling.

[4] Previous work [*Liu et al.*, 2005] finds evidence for a post-perovskite phase transition in $NaMgF_3$ at just 19 GPa, however the data quality is not sufficient for further analysis. Later, enthalpy calculations [*Parise et al.*, 2004] support the work of *Liu et al.* [2005], finding $NaMgF_3$ should transform to the $CaIrO_3$ structure around 35 GPa, before dissociating to constituent fluorides at even higher pressures and temperatures.

[5] In the current study, we report results of x-ray diffraction as we observe high pressure structural phase transformation of $NaMgF_3$ perovskite to post-perovskite. Utilizing laser heating within the diamond anvil cell we overcome kinetic transition barriers and observe the formation of an unknown post-$CaIrO_3$-type phase of $NaMgF_3$ (designated N-phase).

2. Experiment

[6] Polycrystalline samples of perovskite analog $NaMgF_3$, synthesized using conventional solid state techniques [*Zhao et al.*, 1993], were ground and loaded in diamond anvil cells (DACs) fitted with 350 μm culets. Anvil gaskets (Tungsten or stainless steel) were pre-indented to 80 μm thickness. The transparent sample was mixed with a dark material (platinum or graphite) to absorb the laser radiation before loading into the DAC. Samples were sandwiched between layers of insulating material (NaCl or MgO). By conducting multiple experiments with several different combinations of gasket, laser absorber, and insulator material, we distinguish possible chemical reactions from structural transitions. The equation of state of NaCl [*Decker*, 1971], or MgO [*Speziale et al.*, 2001] with Pt [*Holmes et al.*, 1989] was used as an internal pressure marker.

[7] Data were collected using monochromatic radiation at several synchrotron beamlines; at GeoSoilEnviroCARS (GSECARS) 13-ID-D with $\lambda = 0.3344(2)$ Å, and at the High Pressure Collaborative Access Team (HPCAT) 16-ID-B with $\lambda = 0.4018(2)$ Å [*Shen et al.*, 2005], both at the Advanced Photon Source (APS). At the European Synchrotron Radiation Facility (ESRF) data were collected at ID-27 [*Mezouar et al.*, 2005] with $\lambda = 0.3738(2)$ Å. Data at HPCAT and ESRF were collected by a MAR345 imaging plate, while that at GSECARS was collected by a Bruker CCD. Raw 2-D data were integrated to 1-D powder patterns suitable for Rietveld structure refinement using program FIT2D [*Hammersley et al.*, 1996].

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Post-Perovskite NaMgF$_3$
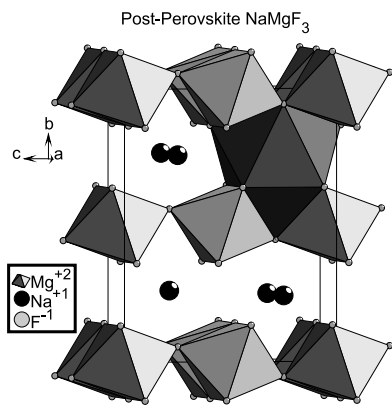
Figure 1. The orthorhombic (Cmcm, Z = 4) post-perovskite structure of NaMgF$_3$. Sodium moves from 4-fold coordination in the perovskite structure to 9-fold (tri-capped trigonal prism) in the post-perovskite structure.

[8] Double-sided infrared laser heating was performed in-situ during each experiment [*Schultz et al.*, 2005]. X-ray diffraction data were collected before during and after heating to temperatures of 2000 K ± 200 K [*Benedetti and Loubeyre*, 2004].

3. Results

[9] High pressure x-ray diffraction data show a complete transformation of NaMgF$_3$ perovskite (Pbnm) to a phase resembling CaIrO$_3$-type post-perovskite (*Cmcm*) at room temperature between 28 and 30 GPa (Figure 2); pressures much higher than that found previously [*Liu et al.*, 2005]. Heating is not required to drive the transition, which is accompanied by a 4% increase in density. This result is in contrast with the ~1% change reported for CaIrO$_3$ [*Hirose and Fujita*, 2005], MgSiO$_3$ [*Murakami et al.*, 2004; *Oganov and Ono*, 2004], MgGeO$_3$ [*Hirose et al.*, 2005], and Fe$_2$O$_3$ [*Ono and Ohishi*, 2005]. The larger change in density may reduce kinetic barriers to transform NaMgF$_3$ perovskite,

Compressibility of perovskite and post-perovskite NaMgF$_3$
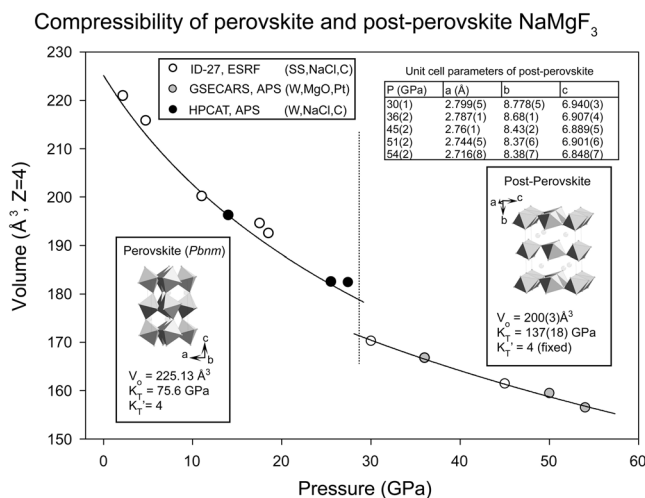
Figure 2. The 2nd order Birch-Murnaghan equations of state (EoS) of NaMgF$_3$ are compiled from three high pressure runs. Each high pressure run contained different materials to preclude reaction with the sample (SS, stainless steel; C, graphite).

while significant heating is required in the case of the oxides [*Duffy et al.*, 2005; *Murakami et al.*, 2004; *Oganov and Ono*, 2004].

[10] Our pressure-volume data for NaMgF$_3$ perovskite are consistent with previous estimates of zero pressure bulk modulus [*Liu et al.*, 2005; *Zhao et al.*, 1994], where K$_T$ = 76.5 GPa. Fitting pressure-volume data of the post-perovskite phase to a 2nd order Birch-Murnaghan equation of state yields a zero pressure bulk modulus of 137(18) GPa. The significant error in this value stems from uncertainty in the volume of the unit cell at 1 bar, 200(3) Å^3.

[11] Contributing to error in unit cell axis measurements of post-perovskite is the presence of an unknown phase (N-phase) which appears upon laser heating in the post-perovskite region (Figure 3). This phase transition is reproducible and observed in 3 different sample loadings with different pressure markers, laser absorber, and gasket from data collected at both GSECARS and ESRF. The new peaks are not those expected of both MgF$_2$ (cotunnite) [*Haines et al.*, 2001] and NaF (B2) as dissociation of NaMgF$_3$ would imply [*Parise et al.*, 2004]. Solutions derived from indexing the new reflections favor an orthorhombic unit cell with 6 formula units (Z). The Inorganic Crystal Structure Database (ICSD) contains no orthorhombic ABX$_3$ structures with Z = 6, and few with Z = 12. Considering monoclinic and triclinic structure entries with these criteria are scarce in the ICSD, in addition to the quality of our Le Bail refinement (*Pnnm*, Figure 3), we believe the structure of N-phase NaMgF$_3$ (a = 8.353(3) Å, b = 5.265(2), c = 5.857(3), V = 257.58(3) Å^3 at 37(1) GPa) may be new and need not belong space group *Pnnm* necessarily. The density
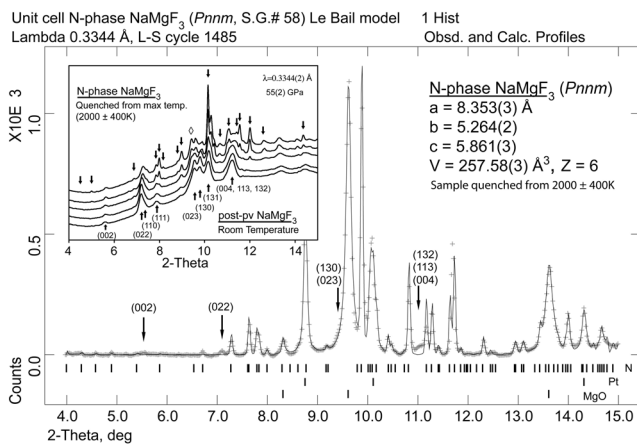
Figure 3. X-ray diffraction pattern of N-phase NaMgF$_3$ after laser heating at 37(1) GPa with Pt and MgO internal standards. The N-phase unit cell (*Pnnm*), Pt, and MgO are fit with a Le Bail model. Arrows pointing down indicate residual CaIrO$_3$-type NaMgF$_3$. The inset shows X-ray diffraction patterns of NaMgF$_3$ at 55(2) GPa before and after laser heating. This data series (inset) was obtained by stepping the x-ray beam position away from the position of the heating laser, allowing the collection of x-ray diffraction patterns from sample heated to temperatures consecutively less than the maximum to room temperature. Arrows pointing up show indexed peak positions of the post-perovskite structure, while arrows pointing down highlight peaks of N-phase NaMgF$_3$. Sample also contains NaCl (open diamond) and graphite (no diffraction).

difference between N-phase and CaIrO$_3$-type NaMgF$_3$ is smaller than that between perovskite and post-perovskite, about 1%, yet a value is difficult to derive since relaxing stress in post-perovskite requires heating, driving the phase transition to N-phase. Upon decompression to the perovskite field, diffraction peaks broaden suggesting the onset of amorphization of N-phase at low pressure.

4. Discussion

[12] It is possible the topology of N-phase NaMgF$_3$ is also layered, containing cations in coordination schemes other than that existing in the CaIrO$_3$-type structure. While more work is necessary to identify a structure for N-phase NaMgF$_3$, we can gain insight to possible high pressure structures through comparative analysis of other high pressure fluoride phases. While sodium in post-perovskite NaMgF$_3$ is contained within a tri-capped trigonal prism, at 38 GPa MgF$_2$ (Sellaite) is reported to form a structure based on mineral cotunnite [*Haines et al.*, 2001], where magnesium also resides in a tri-capped trigonal prism. Thus, N-phase NaMgF$_3$, or further high pressure forms of NaMgF$_3$, could contain both sodium and magnesium in these 9-fold coordination units, and perhaps adopt structures [*Caracas and Cohen*, 2005] expected for A$_2$X$_3$ compounds as opposed to dissociation [*Parise et al.*, 2004; *Umemoto et al.*, 2006].

[13] A transformation in CaIrO$_3$-type NaMgF$_3$ to N-phase has possible implications for MgSiO$_3$ and the lower mantle. A post-post-perovskite phase such as N-phase may account for previous observations of extra x-ray reflections during studies of MgSiO$_3$ and MgGeO$_3$ post-perovskite [*Guignot et al.*, 2005] and several recent studies of lower mantle tomography [*Flores and Lay*, 2005; *Hernlund et al.*, 2005; *Thomas*, 2005] suggest a seismic discontinuity below the D″. Recent rationale invokes a double-crossing of the post-perovskite phase boundary by the geotherm at two different depths. NaMgF$_3$ has proven to be a satisfactory analogue material for MgSiO$_3$ thus, solid-solid transformation in silicate post-perovskite via N-phase may be possible within the lower mantle considering geotherms [*Boehler*, 2000; *Zerr et al.*, 1998] above the core-mantle boundary as well as within rocky interiors of extraterrestrial bodies.

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