Octahedral Tilting Evolution in Orthorhombic NaMgF₃ Perovskite Under Pressure

H.-Z. Liu,[1, 2] J. Chen,[3] J. Hu,[2] D. J. Weidner,[3] D. Häusermann,[1] H.-K. Mao[1, 2]

[1]HPCAT, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA;
[2]Geophysical Laboratory, Carnegie Institution of Washington, Washington DC, USA;
[3]Mineral Physics Institute, State University of New York at Stony Brook, NY, USA

Introduction

The driving force to low or high symmetry crystal structure in perovskite under pressure is of great interest due to the significant change in the physical properties during structural phase transitions. The fundamental understanding of the stable mechanisms of various perovskite structures upon compression has been a problem of long standing interest in condensed state physics, solid state chemistry, materials science and Earth science. In this report, NaMgF₃ perovskite (neighborite) was chosen to study the hydrostatic pressure effect on the tilting of its MgF₆ octahedra because neighborite has gained significant attention as an analogue of MgSiO₃ perovskite, which was believed to dominate in the Earth's lower mantle.

Systematic studies of NaMgF₃ structure for its temperature-induced phase transition at room pressure as well as under high pressure conditions were performed by Zhao et al,[1-5] following which O'Keeffe and Bovin pointed out the structural similarity between NaMgF₃ and MgSiO₃.[6] However, no systematic structural refinement have been done for a sample maintained under hydrostatic high pressure conditions to study the pressure effect on the structure distortion from microstructure viewpoint. Most previous high pressure studies were carried out using energy dispersive x-ray diffraction, and only one structural refinement result for NaMgF₃ at 4.9 GPa was reported based on monochromatic synchrotron x-ray diffraction experimental data.[5]

Methods and Materials

The synthetic sample used in the present study was identical to that used in the previous studies by Zhao et al,[1-5] which was prepared by solid state reaction of NaF and MgF₂. The crystal structure has been determined at ambient conditions using X-ray diffraction. The high pressure experiments were carried out in a diamond anvil cell (DAC) apparatus. The sample was loaded in a sample hole of T301 stainless steel gasket. Helium was used as pressure transmitting medium which can generate hydrostatic pressure conditions. The pressure was calibrated by the ruby luminescence method. The angle-dispersive X-ray diffraction (ADXRD) experiments (λ = 0.4028 Å) in a DAC were performed at room temperature at the beam line ID-B, HPCAT, Advanced Photon Source, Argonne National Laboratory. Diffraction patterns were recorded on a MAR345 image plate and then integrated by using the program FIT2D.

Results and Discussion

The Rietveld refinements were carried out using the GSAS program package for all of the ADXRD patterns collected at hydrostatic pressure conditions. A structural model at ambient conditions cited from Ref. [1] was used as a starting structure. Fig. 1 shows the atomic displacements as a function of pressure, in which the fractional atomic coordinates of the *Pbnm* orthorhombic perovskite are defined with reference to a *Pm-3m* cubic perovskite structure.[2]
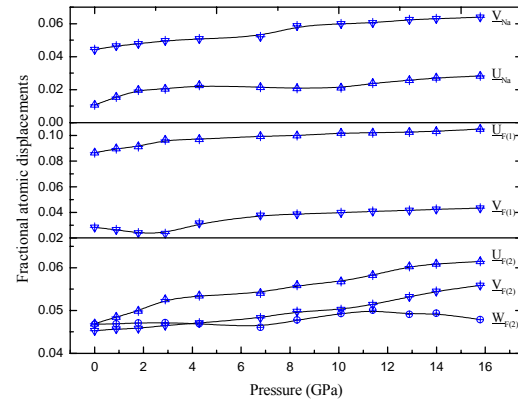

Fig. 1 Fractional atomic displacements (referred to cubic *Pm-3m* perovskite) of orthorhombic NaMgF₃ change as a function of pressure. Top: Na⁺ cation moves straight along the *a*- and *b*-axis of the orthorhombic cell. Middle: The fractional displacements F(1) are related to the anti-phase tilting. Bottom: The displacements of F(2) are related to the in-phase tilting ($\underline{U}_{F(2)}$ and $\underline{V}_{F(2)}$) and anti-phase tilting ($\underline{W}_{F(2)}$). The lines are a guide to the eye.

The lattice parameters of orthorhombic perovskite with space group *Pbnm* (Z=4) could be expressed in terms of a pseudo-cubic prototype cell (*Pm-3m*, Z=1).[1] The previous heating experiments showed the continuous convergence of the pseudo-cubic lattice axes with increasing temperature at ambient condition,[1, 2] as well as under high pressure,[4] to a cubic structure. In this study, the axes of the pseudo-cubic unit cell was found continuously diverge with increasing pressure, indicating pressure enhances the orthorhombic structural distortion. Thus, role of pressure on the structural distortion is opposite to that of temperature in NaMgF₃. This trend is in agreement with the compression behavior of MgSiO₃.

The centrosymmetrically distorted orthorhombic perovskite with space group *Pbnm* is distorted by two independent octahedral tilting θ and φ, where θ is an anti-phase tilt about the pseudo-cubic $\langle 110 \rangle_{pc}$ axes, and φ is an in-phase tilt about the pseudo-cubic $\langle 001 \rangle_{pc}$ axis of the octahedron. It can also be conceived as the tilting Φ about the threefold $\langle 111 \rangle_{pc}$ axes of the regular octahedra (see Fig. 2 insertion for detail). The octahedral tilting of the NaMgF₃ perovskite could be quantitatively derived from the cell parameters (macro-approach) as well as from the positional parameters of atoms (micro-approach).[1, 2] Fig. 2 shows the octahedral tilting as a function of pressure from both macro and micro methods. The overall trends of the octahedral tilting angles, i. e. increasing with increasing pressure, are similar for both macro and micro approaches, indicating that the structural distortion increases with pressure. The tilting angles which are derived from lattice parameters are underestimated due to the assumed regularity of

the octahedron. It is noticed that the derivation of the octahedral tilting angles from unit cell parameters and atomic positions are only accurate when the assumption of rigid octahedra is valid, and the octahedral tilting angles are small.[1, 2] Since pressure enhances the structural distortion in this orthorhombic perovskite case, these assumptions do not remain valid any more. The octahedral tilting angles under high pressure derived from lattice parameters or from atomic positions (shown in Fig. 2), basically provide the relative values of the octahedral tilting angles.
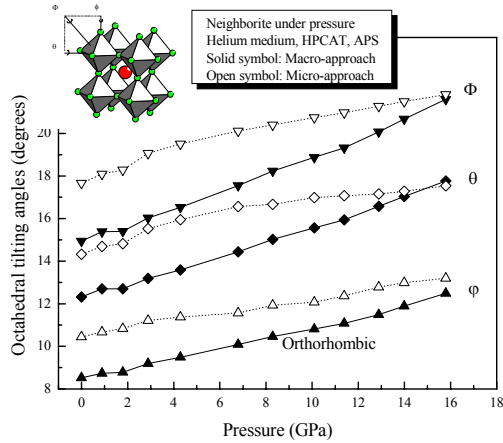

Fig. 2   Pressure evolution of the octahedral tilting angles of NaMgF$_3$ perovskite as derived from lattice parameters (macro-approach), and atomic positions (micro-approach) plotted as solid and open symbols, respectively. Insertion shows the octahedral tilting angles referred to an ideal cubic *Pm-3m* perovskite.

The lattice distortion and thus the ferroelastic feature are the direct results introduced by octahedral tilting. The spontaneous strain is applied to characterize these and its magnitude for this ferroic species of *m3mFmmm* can be expressed as a function of lattice parameters.[2] It increases continuously with increasing pressure. The ADXRD high pressure LVC experiment under 4.9 GPa had been carefully annealed under high pressure to release deviatoric stresses.[5] We believed that this is corroborated by this result in good agreement with our results.

The contribution of octahedral tilting and the octahedral bond length to the volumetric compression could be decoupled as:[1, 4]

$$\beta_V = \beta_{V0} + \beta_{V\Phi} = \frac{-3\partial[Mg-F]}{[Mg-F]\partial P} + \frac{-2\partial\cos\Phi}{\cos\Phi\partial P}$$

This compression mechanism was analyzed in previous high pressure studies, and the compression of octahedral bond length was found to contribute about 70-80% to the overall volumetric compression within about 5 GPa.[4, 5] In this report, the contribution to the volumetric compression from octahedral bond length and tilting were estimated from the unit cell parameters, and Fig. 3 illustrates β_V, β_{V0}, and $\beta_{V\Phi}$ change as a function of pressure. It is shown that volumetric compression was dominated by the shortening of the octahedral Mg-F bond at beginning of compression below 6 GPa. Between 6-12 GPa pressure range, the contribution from the octahedral tilting matches that of bond length compression. This is following by an increasing contribution from the octahedral tilting above 12 GPa. Since the decoupled volumetric compression mechanism is based on the assumption that octahedra remain regular under compression, this model should not work well at higher

pressures where the pressure induced structural distortion increases. This in turn makes the MgF$_6$ octahedra gradually lose their regularity upon compression.
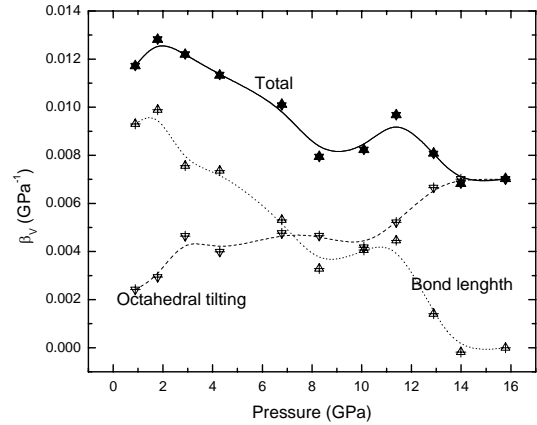

Fig. 3   Total volumetric compression β_V, and the octahedral tilting $\beta_{V\Phi}$ and the octahedral bond length β_{V0} contribution to volumetric compression as a function of pressure.

The equation of state of NaMgF$_3$ could be fitted using a second order Birch equation of state, keeping the pressure derivative of bulk modulus K$_0$' as 4. The zero pressure bulk modulus (K_0) is estimated as 76.0±1.1 GPa, which is in good agreement with the bulk modulus value of 75.6 GPa measured from single crystal Brillouin scattering.[3]

In summary, the structural refinement of NaMgF$_3$ perovskite under hydrostatic pressure up to 16 GPa were carried out using high resolution ADXRD data. The macro and microscopic structural evolution, spontaneous strain, and compression mechanism were quantitatively analyzed. The octahedral tilting angles increased with increasing pressure, and pressure enhance of the structural distortion was observed in this orthorhombic perovskite. These results provide experimental information on the octahedral rotation in orthorhombic perovskite structures, and help to extend the understanding of the structural stability of perovskite phase under high pressure.

Acknowledgements

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