$NaMgF_3$ Perovskite Under Pressure: Octahedral Tilting Evolution and Phase Transition

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A high-pressure test of an analog for a common deep-Earth mineral may allow researchers to estimate the physical properties of materials in the planet's lower mantle. We induced pressures greater than 16 gigapascals (GPa), more than 160,000 times the normal atmospheric pressure on the Earth's surface, on a perovskite material with a similar makeup as the ubiquitous deep-mantle perovskite $MgSiO_3$ and analyzed the change in its physical makeup under the stress. We observed slight changes to its chemical bonds beginning at 6 GPa and a compression that destroyed the perovskite crystal structure at pressures approaching 20 GPa.

Geophysical interest in the perovskite family of materials dates from the 1960s when geologist A.E. Ringwood proposed that the Earth's lower mantle is dominated by iron-bearing $MgSiO_3$ perovskite. A fundamental understanding of the behavior of selected representatives of the perovskite family of structures to high-pressure/high-temperature conditions is valuable for establishing possible behaviors of this family in general. We have chosen to study $NaMgF_3$ perovskite (neighborite) as it has gained significant attention as an analogue material of $MgSiO_3$ perovskite since O'Keeffe et al pointed out their structural similarity in 1970s. Neighborite is isoelectronic with $MgSiO_3$, and they are isostructural, possessing the same type of distortion from the ideal cubic perovskite structure to crystallize in space group *Pbnm*.

We used a diamond anvil cell high-pressure device and synchrotron x-ray micro-diffraction to *in situ* study the crystalline change of the sample under high-pressure conditions. A series of experiments were carried out using various pressure-transmitting media, the focusing beam size and grain size of the sample (at NSLS beamline X17C and the High Pressure Collaborative Access Team facility at the Advanced Photon Source) to optimize the quality of our diffraction data. The structural evolution of $NaMgF_3$ under high pressure, therefore, could be analyzed from the Rietveld refinement of the high-quality x-ray diffraction patterns. The atomic positions could be obtained under high pressure; for example, **Figure 1** demonstrates the crystalline structure of neighborite under 10.1 GPa when helium was used as the pressure medium.

The centrosymmetrically distorted orthorhombic perovskite with space group *Pbnm* is distorted by two independent octahedral tilting angles θ and ϕ, where θ is an anti-phase tilt and ϕ is an in-phase tilt. It can also be conceived as the tilting Φ about the threefold $<111>_{pc}$ axes of the regular octahedra (see **Figure 2** insert). The octahedral tilting of the $NaMgF_3$ perovskite could be quantitatively derived from the cell parameters (macro-approach) as well as from the positional parameters of atoms (micro-approach), as shown in **Figure 2**. The overall trends of the octahedral tilting angles, i.e. increasing with increasing pressure, are similar for both the macro and micro approaches. The volumetric compression was dominated by the shortening of the octahedral Mg-F bond at the beginning of compression below 6 GPa. In the 6-12 GPa pressure range, the contribution from the octahedral tilting matches that of the bond length

Beamline X17C

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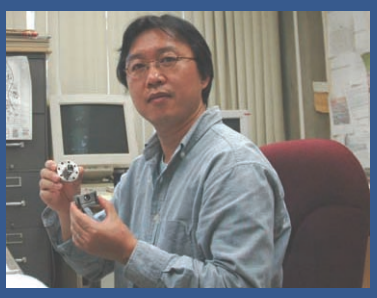

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compression. This is followed by an increasing contribution from the octahedral tilting above 12 GPa.

The octahedral tilting, increasing with pressure, finally destroys the perovskite structure. An experiment was carried out using silicone oil as the pressure medium, which could generate more shear stress to accelerate the phase transition. We observed a phase transition at about 19.4 GPa, and the patterns above this pressure can no longer be indexed by the *Pbnm* perovskite structure, but can be indexed with the layering-type post-perovskite structural model with space group *Cmcm*. This distinct material created under these extremely high-pressure conditions should be further studied to establish its properties. Such research could help scientists better understand the mechanisms of perovskite, including the temperatures and pressures required for it to stabilize near the Earth's core.

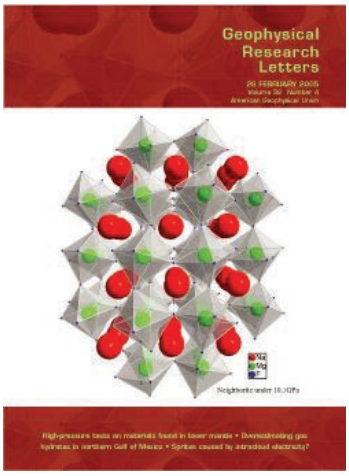

Figure 1. The crystalline structure of $NaMgF_3$ under pressure of 10.1GPa, was featured on the cover of Geophysical Research Letters.

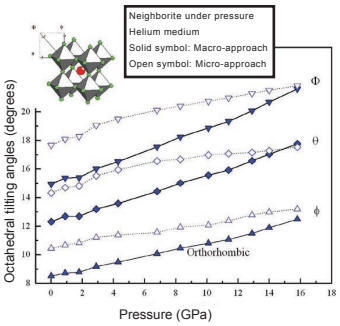

Figure 2. Pressure evolution of the octahedral tilting angles of $NaMgF_3$ perovskite as derived from lattice parameters (macro-approach), and atomic positions (micro-approach) plotted as solid and open symbols, respectively. Insertion shows the octahedral tilting angles referred to an ideal cubic *Pmm* perovskite.