Vibrational Anisotropy of δ-(Al,Fe)OOH

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Hydrous phases in the system (Al,Fe)OOH–$MgSiO_2(OH)_2$ remain stable to pressures and temperatures of Earth's lower mantle and may open pathways to transport H_2O deep into Earth's interior[1,2]. Even small amounts of these high-pressure oxyhydroxide phases can exert a strong control on the H_2O budget of the lower mantle and may have affected the exchange of hydrogen between Earth's mantle, core, and surface in the geological past. In addition to binding H_2O in the crystal structures of high-pressure oxyhydroxides, hydroxyl groups and related hydrogen bonds participate in lattice vibrations. The directional nature of O—H···O interactions together with the low reduced mass of hydroxyl groups may affect the vibrational structure and contribute to vibrational anisotropy. Pressure-induced changes in hydrogen bonding, for example, affect the anisotropic compression behavior of the oxyhydroxide δ-(Al,Fe)OOH (ref. 3), highlighting the effect of hydroxyl groups and their dynamics on physical properties. Since lattice dynamics determine the thermal properties of crystalline solids, understanding the vibrational structure of high-pressure oxyhydroxides promises to provide explanations for the extraordinary stability of their hydroxyl groups.

We studied the anisotropy of lattice vibrations in δ-(Al,Fe)OOH crystals by probing the partial phonon density of states (PDOS) using ^{57}Fe nuclear resonant inelastic X-ray scattering (NRIXS). Crystals of δ-(Al,Fe)OOH with Fe/(Al+Fe) = 0.14(2) were synthesized in a multi-anvil press and mounted on Kapton micro-meshes. NRIXS spectra were recorded at beamline 3-ID-B at the Advanced Photon Source of the Argonne National Laboratory. The crystals of δ-(Al,Fe)OOH were oriented relative to the incident X-ray beam to probe the PDOS for different combinations of phonon polarizations. The energy of the incident X-rays was scanned from −100 meV to 180 meV relative to the resonance energy of ^{57}Fe nuclei to capture inelastic scattering events by acoustic and optical phonons, including high-frequency modes and multi-phonon contributions. NRIXS spectra were processed and analyzed using the software PHOENIX. Crystal orientations were determined using single-crystal X-ray diffraction.

From the NRIXS spectra of δ-(Al,Fe)OOH single crystals, we extracted the partial PDOS, force constants, and sound wave velocities for different crystal orientations. Based on the results, we discuss the vibrational anisotropy of δ-(Al,Fe)OOH crystals with a focus on the effect of hydroxyl groups on vibrational properties. Our findings on the vibrational structure of δ-(Al,Fe)OOH at ambient conditions will contribute to our understanding of the thermal properties and stability of high-pressure oxyhydroxides and guide future experiments on lattice dynamics at high pressures.

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3. Ohira, I. *et al.* Compressional behavior and spin state of δ-(Al,Fe)OOH at high pressures. *Am. Mineral.* in press (2019).