Single crystal synthesis of \(\delta-(\text{Al,Fe})\text{OOH}\)

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ABSTRACT

Single crystals of \(\delta-(\text{Al})\text{OOH}\), \(\delta-(\text{Al}_{0.953},\text{Fe}_{0.047})\text{OOH}\), and \(\delta-(\text{Al}_{0.878},\text{Fe}_{0.122})\text{OOH}\) with dimensions up to \(-0.4 \sim 0.6\) mm were synthesized by the high-pressure hydrothermal method. Synthesis experiments were performed at 21 GPa and 1470 K for 4 h using a Kawai-type multi-anvil apparatus. The crystals of \(\delta-(\text{Al})\text{OOH}\), \(\delta-(\text{Al}_{0.953},\text{Fe}_{0.047})\text{OOH}\), and \(\delta-(\text{Al}_{0.878},\text{Fe}_{0.122})\text{OOH}\) were colorless, yellowish green, and brown, respectively. Mössbauer spectra showed \(95 \sim 100\% \text{ Fe}^{3+}/2\text{Fe}\) at the octahedral site in \(\delta-(\text{Al,Fe})\text{OOH}\). Chemical compositions of \(\delta-(\text{Al}_{0.953},\text{Fe}_{0.047})\text{OOH}\) and \(\delta-(\text{Al}_{0.878},\text{Fe}_{0.122})\text{OOH}\) are homogeneous with \(\text{Fe}/(\text{Al+Fe})\) of 0.0469(8) and 0.122(3), respectively. Unit-cell parameters of \(\delta-(\text{Al})\text{OOH}\) are consistent with those of previous studies, and they increase with \(\text{Fe}/(\text{Al+Fe})\). These results confirm that \(\delta-(\text{Al})\text{OOH}\) can form a solid solution with \(\varepsilon-(\text{Fe})\text{OOH}\). The crystals contained a small number of fluid inclusions. The syntheses of large single crystals of \(\delta-(\text{Al,Fe})\text{OOH}\) will facilitate investigation of their phase stability, physical properties including elasticity and elastic anisotropy, behavior of hydrogen bonding, and spin state of \(\text{Fe}\), which will improve models of the water and oxygen cycles in the deep Earth.

Keywords: \(\delta-(\text{Al})\text{OOH}\), \(\delta-(\text{Al,Fe})\text{OOH}\), water, single crystal, hydrous mineral, high-pressure synthesis, Kawai-type multi-anvil apparatus

INTRODUCTION

\(\delta-(\text{Al})\text{OOH}\) is an important phase in the deep water cycle because: (1) a large amount of water can be incorporated in its crystal structure; (2) this phase is stable in hydrous pyrolite mantle (Ohtani et al. 2001), hydrous basalt (Suzuki et al. 2000a), and hydrous sediment components (Rapp et al. 2008) of slabs descending into the mantle transition zone (MTZ) and lower mantle; (3) this phase can carry water to the core-mantle boundary (Ohira et al. 2014; Sano et al. 2008); (4) chemical reaction between \(\delta-(\text{Al})\text{OOH}\) and Fe-Ni alloy can deliver hydrogen to the Earth’s core (Terasaki et al. 2012). Consequently, the physical and chemical properties of \(\delta-(\text{Al})\text{OOH}\) are of fundamental importance to understanding the water cycle in the MTZ, the lower mantle, and the core.

Previous single-crystal X-ray diffraction (SC-XRD) studies of \(\delta-(\text{Al})\text{OOH}\) and \(\delta-(\text{Al}_{0.878},\text{Fe}_{0.122})\text{OOH}\) include crystal structure refinements (Komatsu et al. 2006; Kudoh et al. 2004) and pressure-induced phase transitions (Kuribayashi et al. 2014). The dimensions of crystals were less than 83 \(\mu\)m in the mentioned studies, however. While such sizes are sufficient for structure determinations, larger crystals (>100 \(\mu\)m) of high quality are required for measurements of physical and chemical properties, for example as prepared by the focused ion beam technique to obtain specific dimensions, shapes, and crystallographic orientations (Marquardt and Marquardt 2012).

The effect of \(\text{Fe}\) substitution on the physical and chemical properties of \(\delta-(\text{Al})\text{OOH}\) has not yet been studied. \(\text{Fe}\) is expected to be accommodated in \(\delta-(\text{Al})\text{OOH}\) as \(\text{Fe}^{3+}\) in the MTZ and the lower mantle because \(\varepsilon-(\text{Fe})\text{OOH}\) is isostructural with \(\delta-(\text{Al})\text{OOH}\) (Chenavas et al. 1973) and stable above 6 GPa at high temperature (Gleason et al. 2008; Nishihara and Matsukage 2016). \(\text{Fe}\)-bearing \(\delta-(\text{Al})\text{OOH}\) might exist in descending slabs and therefore carry \(\text{Fe}^{2+}\) (oxygen) into the deep Earth.

In this study, we synthesized single crystals of \(\delta-(\text{Al})\text{OOH}\), \(\delta-(\text{Al}_{0.953},\text{Fe}_{0.047})\text{OOH}\), and \(\delta-(\text{Al}_{0.878},\text{Fe}_{0.122})\text{OOH}\) with dimensions up to \(-0.4 \sim 0.6\) mm using a high-pressure hydrothermal method. We report results of sample characterization that includes evaluation of crystal quality, the presence of inclusions, chemical composition, and unit-cell parameters. We discuss implications for the stability of \(\delta-(\text{Al,Fe})\text{OOH}\) and the water and oxygen cycles in the MTZ and the lower mantle.

EXPERIMENTAL METHODS

Synthesis experiments

Starting materials were either reagent-grade \(\text{Al(OH)}_{3}\) powder or mixtures of reagent-grade \(\text{Al(OH)}_{3}\), and \(\text{Fe}_{2}\text{O}_{3}\) powders with \(\text{Fe}/(\text{Al+Fe}) = 0.06\) or 0.15 in molar ratios. The \(\text{Fe}_{2}\text{O}_{3}\) powder contained 96.64\% \(?\text{Fe}_{2}\text{O}_{3}.\) The mixtures of \(\text{Al(OH)}_{3}\), and \(\text{Fe}_{2}\text{O}_{3}\)-enriched \(\text{Fe}_{2}\text{O}_{3}\) powders were ground in an agate mortar with acetone for 1 h. The starting material was packed into a \(\text{Au}_{80}\text{Pd}_{20}\) capsule with inner and outer diameters of 0.9 and 1.2 mm, respectively. The lengths of the capsules for the syntheses of \(\text{Fe}-\text{free}\) and \(\text{Fe-bearing}\) \(\delta-(\text{Al})\text{OOH}\) were 3.3 and 2.0 mm, respectively. The capsules were closed by welding.

Synthesis experiments were conducted at 21 GPa using a Kawai-type multi-anvil apparatus with split-sphere type guide blocks (Keppler and Frost 2005; Rubie 1999). The capsule was loaded into a Cr-doped \(\text{MgO}\) octahedron with a 10 mm edge length. We used second-stage anvils made of tungsten carbide (“\(\text{ch}-75\)”, Hawedia, Marklofen, Germany) with 4 mm truncation and pyrophyllite gaskets with a 3.0 mm width. The sample was heated using a \(\text{LaCrO}_{3}\) furnace with inner and outer diameters of 1.8 and 2.5 mm, respectively, surrounded by a \(\text{ZrO}_{2}\) thermal insulator.

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