## Electrical conductivity of diaspore, δ-AlOOH and ε-FeOOH

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## ABSTRACT

Electrical conductivities of diaspore ( $\alpha$ -AlOOH),  $\delta$ -AlOOH, and  $\epsilon$ -FeOOH were measured by impedance spectroscopy with a frequency range from 10<sup>-1</sup> to 10<sup>6</sup> Hz at pressures from 8 to 20 GPa and temperatures from 500 to 1200 K, well below the dehydration temperatures of these phases at the relevant pressures. For diaspore, the relationship between electrical conductivity and reciprocal temperature can be well fitted by the Arrhenius formula:

$$\sigma = \sigma_0 \exp\left[\frac{-(\Delta E + P\Delta V)}{kT}\right],$$

where  $\sigma_0$  is the pre-exponential factor,  $\Delta E$  is the activation energy, and  $\Delta V$  is activation volume of  $56.0 \pm 1.2$  S/m,  $0.55 \pm 0.02$  eV, and  $1.68 \pm 0.12$  cm<sup>3</sup>/mol, respectively. The electrical conductivity of diaspore decreases with increasing pressure ranging from 8 to 12 GPa by a half order of magnitude, whereas the conductivity becomes almost constant in a pressure range above 12 GPa. δ-AlOOH and ε-FeOOH show one and two orders of magnitude higher electrical conductivity than diaspore. Electrical conductivities of  $\delta$ -AlOOH and  $\epsilon$ -FeOOH, which have isostructural CaCl<sub>2</sub>-type hydroxide structure, show the nearly identical activation enthalpies  $(0.38 \pm 0.01, 0.33 \pm 0.05 \text{ eV})$ , which are relatively lower than that of diaspore. The dominant conduction mechanism of AlOOH phases can be regarded as proton conduction. The conductivity difference between diaspore and  $\delta$ -AlOOH attributes to result in the different O<sub>1</sub>H bond lengths of each phase. The reduction of O<sub>1</sub>H bond length with increasing pressure could enhance the proton migration by reducing the potential barrier, thereby raising the electrical conductivity. Small polaron conduction may contribute to the conductivity of  $\varepsilon$ -FeOOH to generate higher conductivity than  $\delta$ -AlOOH. Furthermore, hydrogen bond symmetrization will also play an important role in the conductivity discrepancy of these hydrous minerals with CaCl<sub>2</sub>-type hydroxide structure. For subducted sedimentary rocks, polymorphs of AlOOH and FeOOH are representative hydrous phases. Al-rich sediments show conductivity reduction with increasing depth until phase transformation occurs because diaspore represents negative pressure dependence of conductivity. After transformation to  $\delta$ -AlOOH, the conductivity will jump up around 18 GPa. If  $\varepsilon$ -FeOOH is stable above 5 GPa in an iron-rich lithology, such as banded iron formation (BIF), a high conductivity zone with positive pressure dependence could be observed to the deep lower mantle.

Keywords: Electrical conductivity, diaspore, δ-AlOOH, ε-FeOOH, hydrogen bond