Electrical properties of natural and synthetic nano-crystalline MgTiO$_3$ geikielite at mantle pressure and temperature conditions

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ABSTRACT

Electrical resistivity of synthetic nanocrystalline (30–40 nm crystallite size) and a crystalline natural sample of geikielite MgTiO$_3$ has been measured at simultaneous high pressure and high temperature up to 6 GPa and 800 K, respectively. The temperature dependence of the electrical resistivity of both the synthetic and natural sample obeys the Arrehenius behavior in the temperature range between 3 and 800 K and pressure range up to 6.0 GPa. The activation volume of the electrical conduction for coarse crystalline natural sample of geikielite is almost twice that of the synthetic nanocrystalline geikielite indicating the increase of activation volume with the crystallite size. The activation energy for the electronic conduction decreases from 0.39 eV at room pressure to 0.25 eV at 6.0 GPa for natural geikielite, and 0.68 to 0.225 eV in the same pressure range for synthetic geikielite. The pressure dependence of the activation energy of geikielite sample is found to obey the following expressions

\[ \Delta E (\text{eV}) = 0.39 - 0.026(1) P + 0.0036 P^2 \] for natural sample, and

\[ \Delta E (\text{eV}) = 0.68 - 0.080 (2) P + 0.0007 P^2 \] for synthetic sample,

where \( P \) is pressure in GPa. We observe a crossover from extended state type conduction to hopping conduction at 4.0 GPa and 350 K for nano-crystalline geikielite. However, there is no such change of conduction mechanism observed for the natural geikielite at high pressures and high temperatures. The present study reveals the phase stability of nano-crystalline geikielite and natural geikielite up to mantle pressure and temperature conditions, viz. 6 GPa and 800 K, and no phase transition or decomposition is observed in the sample.

Keywords: Geikielite, electrical resistivity, high pressures, high temperatures, nano-materials

INTRODUCTION

Fe-Mg-titanate minerals (ilmenite, pseudobrookite, ulvospinel, geikielite, etc.) are common accessory minerals in terrestrial metamorphic and igneous rocks, and are especially abundant in the high-Ti environment of the lunar crust (Haggerty 1976). Minerals with intermediate compositions of ilmenite-geikielite solid solution are also known to occur as accessory minerals in kimberlites, with geikielite content ranging from 3 to 70 mol% (Haggerty 1976; Parthasarathy et al. 2002). Geikielite also occurs as inclusions in spinel group minerals formed by exsolution in metasomatic veins of the Bergell contact aureole (Italy) and in granulite facies marbles of Southern India (Reusser et al. 2001). An experimental study on high-pressure phase stability of Ti-based oxides would provide a useful geobarometer for ilmenite-bearing rocks either shocked by a meteorite or exhumed from the Earth’s deep mantle (Okada et al. 2008). There are only few reports on high-pressure behavior of ilmenite FeTiO$_3$ (Linton et al. 1999; Wechsler and Prewitt 1984; Zhang et al. 2006) including the observation of pressure induced irreversible phase transitions from ilmenite to LiNbO$_3$ phase at 15 GPa (Ming et al. 2006). However, the high-pressure data on minerals in the Mg-Ti-O system is limited to synthetic karrooite MgTi$_2$O$_5$, showing pressure-induced cation ordering, and phase stability of karrooite up to 7.5 GPa at room temperature (Hazen and Yang 1997) by neutron diffraction (Lennie et al. 2007). A recent study on the pressure dependence of electrical resistivity of geikielite at high pressures showed the phase stability of geikielite up to 8 GPa at room temperature (Parthasarathy 2007a).

Electrical properties of transition metal oxides attract much attention due to the discovery of temperature and pressure induced semiconductor to metal transition in binary 3d transition metal oxides like V$_2$O$_3$, Ti$_2$O$_3$, and VO$_2$ (Rao and Subbarao 1974; Mott 1990). Cogle et al. (1991) reported a possible superconductivity transition in the Mg-Ti-O spinel system, at 50 K. However, the electrical resistivity and heat capacity studies on the MgTiO$_3$ studies do not show any phase transition up to 1000 K (Parthasarathy 2007b). To the best of our knowledge, there are no previously published data on the high-pressure and high-temperature electrical resistivity of either nano-crystalline geikielite or natural geikielite.

EXPERIMENTAL METHODS

The synthetic nanocrystalline geikielite sample has been prepared by the co-precipitation method (Parthasarathy and Manorama 2007). The formation of geikielite has been confirmed by using a Hitachi S-520 scanning electron