High-temperature Raman spectroscopic study of ilmenite-type MgTiO\textsubscript{3} and MgGeO\textsubscript{3}

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[Introduction]
Ilmenite-type MgSiO\textsubscript{3} is a high pressure polymorph of enstatite, and characterized by a relatively narrow stability field in the 20-24 GPa, 1100-2000 degrees C range. Since MgSiO\textsubscript{3}-ilmenite is stable at low temperature, it is considered to be candidate component in 600-700 km of subducting slabs. It is important for earth science to understand its crystal structure on the basis of lattice vibrations at high pressure and temperature. High-pressure and high-temperature Raman spectra of ilmenite-type MgSiO\textsubscript{3} have already been collected up to 7 GPa and 1030 K, respectively (Reynard and Rubie (1996) Am. Mineral.). In this study, we conducted a high-temperature Raman spectroscopic study of ilmenite-type MgTiO\textsubscript{3} and MgGeO\textsubscript{3} that have different pressure stability fields from MgSiO\textsubscript{3}. From the point of elasticity and bonding energy, we investigate the behavior of MgTiO\textsubscript{3} and MgGeO\textsubscript{3} at high temperature and compare structures of ilmenite that has different compositions.

[Experimental methods]
High-temperature experiments were performed using a Pt-electric resistant heater. Temperature was monitored with chromel-alamel thermocouples. Raman spectra were obtained using a NRS2100 triple microspectrometer equipped with Ar ion laser (operating at 514.5 nm and 80 mW (for MgTiO\textsubscript{3}), 70 mW (for MgGeO\textsubscript{3})). Raman spectra were collected with an exposure time of 5 sec (for MgTiO\textsubscript{3}), 30 sec (for MgGeO\textsubscript{3}) every 100 degrees C from room temperature to 500 degrees C.

[Results and discussion]
At ambient conditions, we observed nine (for MgTiO\textsubscript{3}) and eight (for MgGeO\textsubscript{3}) Raman bands, respectively. With increasing temperature, each band shifted to lower wavenumber. These phenomena can interpret that bonding energies between atoms become weaker and bonding distances become longer with increasing temperature. As a result, MgTiO\textsubscript{3} and MgGeO\textsubscript{3} expanded. With decreasing temperature from 500 degrees C, each band shifted to higher wavenumber. Thus, no hysteresis was observed. Raman bands of MgGeO\textsubscript{3} shifted more than those of MgTiO\textsubscript{3}, that is, MgGeO\textsubscript{3} expanded much at the same temperature. This is because a mass number of Ge is larger than that of Ti.

From room temperature to 500 degrees C, we observed no softmodes and no dramatically structural change of ilmenite-type MgTiO\textsubscript{3} and MgGeO\textsubscript{3}. Thus, their stabilities are maintained.