INTRODUCTION

Ilmenite and its related compounds have attracted material scientists and crystal chemists because of their practical applications. A²⁺B⁴⁺O₃ ilmenite compounds are composed of a relatively large A cation (A: Mg, Fe, Mn, Co, Zn) and a small B cation (B: Si, Ge, Sn, Ti). However, compounds with a large ion radii ratio \( R_A/R_B \), such as CaTiO₃ and BaTiO₃, do not form ilmenite structures but have the perovskite structure at ambient pressure. Many ilmenites transform to perovskite at high pressure because oxygen is more compressible than the cations and thus the \( R_A^{-}\)-\( R_O^{-} \)/\( R_B^{-}\)-\( R_O^{-} \) ratio increases with pressure. The \( P^{-}\)-\( T \) regions where these ilmenites are stable vary systematically with the cation radius ratios.

The MgSiO₃ ilmenite phase is one of the high-pressure polymorphs of orthoenstatite. It has been much studied because it is one of the essential phases in the upper mantle, in spite of the fact that its stable region of pressure and temperature is relatively limited, being \( 20 \sim 24 \) GPa and \( 1100 \sim 2000 \) °C (Ito and Yamada 1982; Ito and Navrotsky 1985; Sawamoto 1987). (Mg,Fe)SiO₃ ilmenite was found in the shock vein of meteorite and was named akimotoite (Tomioka and Fujino 1997). MgTiO₃ geikielite is found as an accessory mineral in many igneous and metamorphic rocks (Deer and Zussman 1962) and can be synthesized at ambient pressure.

The crystal structure of MgSiO₃ ilmenite was analyzed by single crystal X-ray diffraction study at ambient conditions (Horiuchi et al. 1982) and by Rietveld profile fitting under high pressure (Reynard and Rubie 1996). Molecular dynamics simulation of MgSiO₃ ilmenite has been carried out (Matsui et al. 1987; Karki et al. 2000) and a Raman spectroscopic study has been made (Reynard et al. 1996). MgGeO₃ shows the same polymorphic transitions as MgSiO₃, but their transition pressures are much lower than the corresponding pressures of the MgSiO₃ polymorphs (Ross and Navrotsky 1988).

The Structures of corundum (\( R₃c \)), ilmenite (\( R₃ \)), and LiNbO₃ (\( R₃ \)) are crystallographically closely related and are characterized by different ordering of A and B cations. It has been reported that some LiNbO₂-type structures were found as metastable phases on release of pressure from perovskite stable region. However, there is no clear evidence that the LiNbO₂-type phases are really metastable. Under decompression after forming perovskite, MgGeO₃, MgTiO₃, MnTiO₃, MnSnO₃, and FeTiO₃ ilmenites did not show a reversible transformation to ilmenite but they transformed to the LiNbO₂ or disordered ilmenite structure (Ko and Prewitt 1988; Ross and Leinenweber 1990; Ross et al. 1997, 1999; Lipton et al. 1997, 1999; Leinenweber et al. 1991, 1994). These transformations are monotropic. LiNbO₃ undergoes a transformation to perovskite under high pressure and the transition is enantiotropic and reversible (Mukaida et al. 2003). No