

# Ilmenite-perovskite transformation in germanates and thermodynamic properties of the high-pressure polymorphs

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Some germanates transform from ilmenite to perovskite at high pressures. Comparing with silicates, however, the ilmenite-perovskite phase relations of germanates have not yet been examined in detail. In this study, we have examined the phase equilibrium relations of  $\text{MgGeO}_3$ ,  $\text{ZnGeO}_3$  and  $\text{MnGeO}_3$  at high pressures and high temperatures. We have also calculated enthalpies of ilmenite-perovskite transition for the three germanates from the transition boundaries, and have discussed on relationship between the transition enthalpies and radii of cations.

A multianvil apparatus was used for high pressure experiments, using starting materials of  $\text{MgGeO}_3$  pyroxene,  $\text{ZnGeO}_3$  ilmenite, and  $\text{MnGeO}_3$  ilmenite. The sample was kept at 10-27 GPa and 1200-1800C for 1 hour. The quenched samples were examined by microfocus and powder X-ray diffractometers. In some runs, reverse runs were made using recovered  $\text{LiNbO}_3$ -structured phases as the starting materials.

$\text{MgGeO}_3$  ilmenite transformed to a high-pressure phase which was recovered as the  $\text{LiNbO}_3$ -type phase at ambient conditions. It was interpreted that the recovered phase was perovskite at high pressure (Leinenweber et al., 1994). The  $\text{MgGeO}_3$  ilmenite-perovskite transition boundary was determined as  $P(\text{GPa}) = 36.2 - 0.008T(\text{C})$ . At 21 GPa,  $\text{ZnGeO}_3$  ilmenite transformed to a high pressure phase which was recovered as the  $\text{LiNbO}_3$ -type phase. We judged that the recovered phase was originally perovskite at high pressure like  $\text{MgGeO}_3$ . The  $\text{ZnGeO}_3$  ilmenite-perovskite transition boundary was determined as  $P(\text{GPa}) = 26.4 - 0.003T(\text{C})$ . At 15 GPa and 1200C,  $\text{MnGeO}_3$  ilmenite transformed to perovskite that was quenched at ambient conditions. The negative slope boundaries of the three germanates suggest that high entropies of the perovskites result from high vibrational entropies which occur due to incorporation of the relatively small divalent cations in large 8-12 fold sites of perovskite structure.

From thermodynamic calculation of the three ilmenite-perovskite boundaries, transition enthalpies were estimated as 44.3, 38.8 and 32 kJ/mol for  $\text{MgGeO}_3$ ,  $\text{ZnGeO}_3$  and  $\text{MnGeO}_3$ , respectively. Combining with transition enthalpy (34.3 kJ/mol) of  $\text{CdGeO}_3$  (Akaogi and Navrotsky, 1987), it appears that the ilmenite-perovskite transition enthalpy decreases with difference of ionic radii between  $\text{A}^{2+}$  and  $\text{B}^{4+}$ . This is consistent with decrease of transition pressure with increasing the ionic radius difference.