

Effective potential for Ca-O bonds in CaGeO₃ perovskite.

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Introduction

High-pressure modification of silicate minerals such as perovskite- and garnet-type MgSiO₃ could be the dominant phases in the Earth's mantle, so detailed knowledge of their structures and thermal properties is of great importance for understanding the state of the deep mantle. It is known that phase boundary between perovskite- and garnet-type phases has the negative Clausius-Clapeyron's curve, which has great meaning geophysically. Metagermanates are useful as structural analogues of silicate minerals at high pressures because of thermal stability of high pressure phases. CaGeO₃ perovskite and garnet structures are isotypic with MgSiO₃ perovskite and garnet, respectively. In this study, we have determined the precise local structure around Ca in perovskite- and garnet-type CaGeO₃ polymorphs. The analysis of temperature-dependent Debye-Waller factor allows us to evaluate the interatomic force constants. Unique thermal vibration in perovskite-type phase has been introduced.

Experimental

The perovskite- and garnet-type CaGeO₃ crystals were synthesized in a cubic anvil type high-pressure apparatus under 10GPa 1250K and 3GPa 1300K, respectively. Single-crystal X-ray diffraction measurements were carried out with a four-circle diffractometer at the BL-10A beam line of the Photon Factory, Tsukuba, Japan, using monochromatized synchrotron X-ray ($\lambda = 0.70006 \text{ \AA}$) radiation. Structure refinements were performed using full matrix least squares program RFIN2 (Table 1).

Results and Discussion

Figure 1 shows the temperature dependence of Debye-Waller factor (mean square displacement), u , for atoms in perovskite- and garnet-type CaGeO₃. The Debye-Waller factor u includes the effects of static and dynamic disorders. The static disorder is the configuration disorder, while the dynamic disorder arises from the thermal vibration of atoms. The contribution of the thermal vibration can be estimated under the assumption of classical statistical dynamics by the temperature dependence. A steep slope in the figures represents a weak bonding. The magnitude of MSD for

Ca atom in perovskite-type phase is extraordinary larger than those for other atoms in perovskite and garnet phases: the one particle potential for Ca in perovskite is significantly broader than those for other atoms. The potential coefficients the Ca-O bond in CaGeO₃ perovskite are 4.6 eV/Å² and -4.4 eV/Å³, respectively. The effective pair potential for Ca-O bond in perovskite is broader than those in other CaGeO₃ polymorphs. This is one reason for the Clausius-Clapeyron's curve for perovskite-garnet phase boundary having a negative slope. In the expression, $dP/dT = \Delta S / \Delta V$, the dS becomes negative because denser high pressure phase perovskite has larger thermal vibration amplitude.

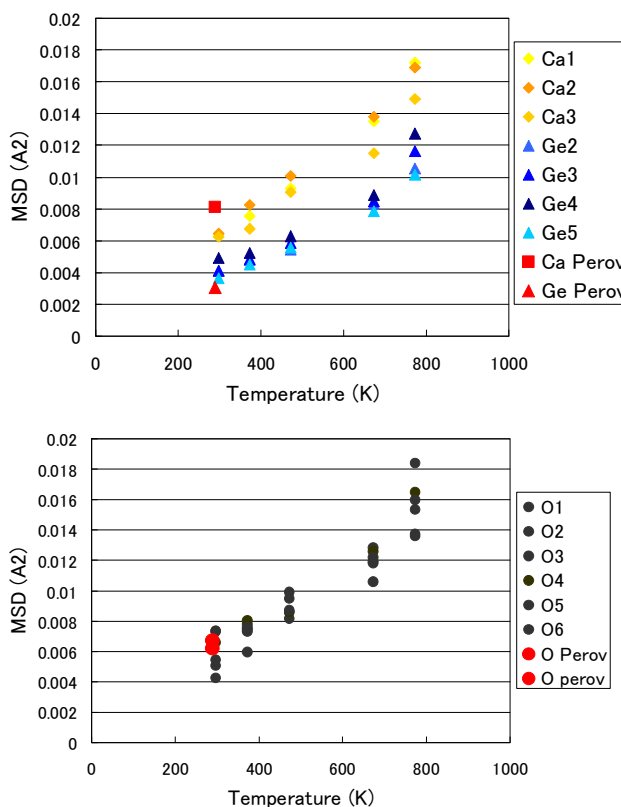


Fig.1. Mean square displacement (MSD) for CaGeO₃ garnet and perovskite.

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