American Mineralogist, Volume 100, pages 1190–1202, 2015

Temperature dependence of crystal structure of $CaGeO_3$ high-pressure perovskite phase and experimental determination of its Debye temperatures studied by low- and high-temperature single-crystal X-ray diffraction

AKIHIKO NAKATSUKA[1,]*, SHOICHI KURIBAYASHI[1], NORIAKI NAKAYAMA[1], HIROSHI FUKUI[2], HIROSHI ARIMA[3], AKIRA YONEDA[4] AND AKIRA YOSHIASA[5]

[1]Graduate School of Science and Engineering, Yamaguchi University, Ube 755-8611, Japan
[2]Graduate School of Material Science, University of Hyogo, Ako 678-1297, Japan
[3]Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[4]Institute for Study of the Earth's Interior, Okayama University, Misasa 682-0193, Japan
[5]Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

ABSTRACT

Single-crystal X-ray diffraction study of $CaGeO_3$ perovskite has been conducted over the temperature range of 98 to 1048 K. The crystal begins to deteriorate at a temperature above about 900 K and completely amorphizes by 980 K. The diffraction-intensity distribution and the structure refinements indicate that the *Pbnm* structure is kept until the occurrence of amorphization. The obtained unit-cell parameters, unit-cell volumes, bond lengths, and displacement parameters increase monotonously with increasing temperature. Thus, no evidence for the existence of the *Cmcm* high-temperature phase, previously suggested above 520 K, is observed. The Ge-O bond lengths show much smaller thermal expansions than the Ca-O bond lengths; the former ranges between $0.42(2) \times 10^{-5}$ K^{-1} and $0.57(2) \times 10^{-5}$ K^{-1}, and the latter between $1.58(4) \times 10^{-5}$ K^{-1} and $3.96(6) \times 10^{-5}$ K^{-1}. The Debye temperatures and static disorder components for each constituent atom were determined by applying the Debye model to the temperature dependence of mean square displacements (MSDs) of the atoms. Consequently, no significant static disorder components can be detected in each atom. The Debye temperatures averaged over all directions, obtained from the Debye model fitting to U_{eq}, yield the harmonic one particle potential coefficients of 4.76(2) eV$Å^{-2}$ for Ca, 11.0(1) eV$Å^{-2}$ for Ge, 5.02(2) eV$Å^{-2}$ for O1, and 5.33(5) eV$Å^{-2}$ for O2. These values become larger in order of $Ca < O1 < O2 << Ge$, which shows that the one particle potential of Ge is much narrower than that of Ca. This relationship between Ca and Ge is consistent reasonably with bonding stiffness expected from the thermal expansion coefficients of the bond lengths. The anisotropies of MSDs are remarkable in O1 and O2 atoms as a consequence of the strong interaction with adjacent Ge atoms, forming the rigid bonds with these O atoms.

In comparison of the three *Pbnm* orthorhombic perovskites of $CaGeO_3$, $CaTiO_3$, and $MgSiO_3$, all of these have the BO_6 octahedra more rigid than the AO_{12} polyhedra (A = Ca or Mg; B = Ge, Ti, or Si) and the tilt angles of BO_6 octahedra are the largest in $MgSiO_3$ perovskite. These observations indicate that if $MgSiO_3$ perovskite under high pressures undergoes the same sequence of the high-temperature phase transitions as $CaTiO_3$ perovskite, the phase boundaries have positive Clapeyron slopes and the phase transition temperatures should become further much higher than those (1512 K for the *Pbnm* to *I*4/*mcm* transition and 1635 K for the *I*4/*mcm* to $Pm\overline{3}m$ transition) observed in $CaTiO_3$ perovskite at ambient pressure. This leads to the conclusion that the high-temperature phase transition to a perovskite phase with different symmetry under high pressures previously suggested in $MgSiO_3$ perovskite is unlikely.

Keywords: $CaGeO_3$, perovskite, single-crystal X-ray diffraction, phase transition, thermal expansion, Debye temperature, one particle potential