
XRD and XAFS Debye-Waller factors in high-pressure perovskite-type compounds

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Abstract

The perovskite-type ABO₃ compounds are the analogues of lower mantle minerals. Single crystals of perovskite-type compounds, MgSiO₃, CaGeO₃, PbTiO₃ etc, were synthesized in a cubic anvil type apparatus under high pressures and temperatures [1]. High temperature single crystal XRD and XAFS measurements were carried out at temperature up to 900 K, leading to the analysis on dynamic and static parts in Debye-Waller factors. Mean-square displacement (MSD) and mean-square relative displacement (MSRD) can be determined by XRD and XAFS methods, respectively. The MSD and MSRD for the A site atom is uniquely large, which is one reason for the Clapeyron's curve (dT/dP) of phase boundary to perovskite-type structure having a negative slope. The potential coefficient, α in $V(u) = \alpha u^2/2 + \beta u^3/3!$, for the A atoms are significantly smaller than those for the framework vibration. The MSRD contains the contribution from the MSD of both X-ray absorbing (a) and backscattering (b) atoms and the displacement correlation function (DCF). The ratios of $2DCF / (MSDa + MSDb)$ for Ca-O and Ge-O in CaGeO₃ are about 0.57 and 0.77, respectively. These values are normal in comparison with various compounds. Weak contributions of DCF to MSD in Ca-O bond indicate the increase in ionic character in the perovskite-type structure. The estimated values of Debye temperature Θ_D for Pb and Ti are 154 and 467 K in tetragonal PbTiO₃ phase and decrease 22% for the high temperature phase. The deviation from the linear temperature dependence in Debye-Waller factors in several ferroelectric tetragonal phases can be interpreted as a precursor phenomenon of the corresponding phase transition. Disturbance of Debye-Waller factor for O is observed at the vicinity of transition point. The O site in PbTiO₃ and Ti site in BaTiO₃ include the clear configurational disorder in the cubic phase [2]. It was observed in several high-temperature perovskite-type phases that the atom for B or O sites occupies on the off-center position in each site. The polar local positional distortions are regarded as the cause of the para-electricity. It could be suggested that statistical distributions of atoms do not occur in A site, but the A atoms have uniquely large thermal vibration amplitudes.

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