

Effective pair potentials in BaTiO₃, PbTiO₃, and related perovskite-type compounds

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Introduction

The ideal perovskite-type structure is cubic symmetry such as SrTiO₃. Many perovskite type compounds have distorted variants with lower symmetry. Detailed knowledge of local structure and thermal properties for each atom in perovskite-type compounds is of great importance for understanding the mechanisms of favorable physical properties.

The analysis of temperature-dependent EXAFS Debye-Waller factor allows us to evaluate the anharmonicity of effective pair potentials and interatomic force constants for neighboring atoms [1,2]. We succeeded in the precise local structure analysis around Ca, Ti and Ge in CaTiO₃, SrTiO₃ and CaGeO₃ perovskite-type compounds [3]. Significant anharmonicity in thermal vibration for each bond was revealed in these compounds. On the other hand, Sicron et al. [4] reported that no anharmonicity for Ti-O bonds in perovskite-type PbTiO₃ ferroelectrics was detected in their EXAFS analysis.

In order to study if the anharmonic thermal vibration for each atom in BaTiO₃, PbTiO₃ and related perovskite-type compounds is dominant, we have determined the temperature variation of the local structure parameters up to 1200 K.

Experimental and analysis

The crystals of BaTiO₃, PbTiO₃, SrTiO₃ and CaTiO₃ perovskite were identified by X-ray diffraction. The measurements of Ca, Ti and Sr K-edge and Ba and Pb L3-edge EXAFS spectra were carried out in the transmission mode at beam line BL-9A of the Photon Factory. X-ray absorption measurements were made in the temperature range from 80 to 1200 K. Mirrors was used to eliminate higher harmonics. Details of the measurement and analysis were given in reference [1,3].

The EXAFS interference function was extracted from the measured absorption spectra and was normalized MacMaster coefficients according to the EXAFS workshop report. In quantitative analyses, we carried out the Fourier-filtering technique and a nonlinear least squares fitting method by comparing the observed and calculated EXAFS interference function. We used the EXAFS formula in the single scattering theory with the cumulant expansion up to the fourth order term.

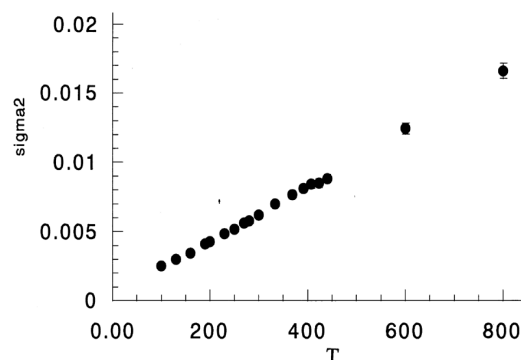


Fig. 1. Temperature (K) dependence of σ_2 for the Ba-O bond in BaTiO₃.

Results and Discussion

Figure 1 shows the temperature dependence of σ_2 for Ba-O bond in BaTiO₃. The Debye-Waller type factor σ_2 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, σ_{thermal} , can be estimated under the assumption of classical statistical dynamics by the temperature dependence of σ_2 [1]. The gradient for the experimental σ_2 is equal to k_B/α , if we evaluate the anharmonic effective pair potential $V(u) = \alpha u^2/2 + \beta u^3/3!$ from the contribution to the thermal vibration, where k_B is the Boltzmann constant, α and β are the potential coefficients and u is the deviation of the bond distance from the location of the potential minimum. β is calculated from the values of σ_2 and σ_3 . The potential coefficient α for the Ca-O bonds in CaTiO₃ is 4.3 eV/Å². The potential coefficient α for the Ba-O bond in BaTiO₃ is 4.1 eV/Å². The magnitude of σ_2 of Ti-O bonds at higher temperature is greater than 0.01 Å². It was revealed that the Ti-O bonds in PbTiO₃ at higher temperature have significant anharmonic contributions.

References

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