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EXAFS Study on the Anharmonic Effective Pair Potential in Rutile Type, α -Quartz Type and Vitreous GeO_2

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Abstract. The pair potentials of Ge-O bonds in rutile type, α -quartz type and vitreous GeO_2 have been investigated by the EXAFS technique from 10 K to 1000 K. An anharmonic effective pair potential for Ge-O bond has been determined by the numerical integration of EXAFS function with assuming the classical Boltzmann distribution. The radial distributions of Ge-O in α -quartz type obtained from EXAFS and our molecular dynamics (MD) simulation agree well with each other. The pair potential of Ge-O bond is not noticeably changed with structural transformation, except for the four coplanar Ge-O bonds in the rutile type structure.

1. INTRODUCTION

In the rutile type structure of GeO_2 , Ge is octahedrally coordinated by oxygen atoms. The four coplanar Ge-O bonds of the octahedron are shorter than the two axial bonds. The rutile type GeO_2 transforms to the α -quartz type at 1306 K. In the α -quartz type structure Ge is tetrahedrally coordinated by the oxygen atoms. It is interesting to know if the effective pair potential changes significantly with structural transformation.

The usefulness of EXAFS as a probe of vibration dynamics have been discussed by many authors [1]. The analysis of temperature-dependent EXAFS spectra with the cumulant expansion method can yield detailed information on the effects of anharmonicity and provide the effective pair potential [2].

In this study, we directly estimate the EXAFS function by the numerical integration in order to determine the precise anharmonic effective pair potential for Ge-O bond without mediating the cumulant terms. The radial distributions of Ge-O bond obtained from molecular dynamics calculation has been compared with that from EXAFS in α -quartz type GeO_2 in order to test the reliability of the interatomic potentials in MD simulations.

2. EXPERIMENT AND ANALYSIS

The rutile type GeO_2 was synthesized under 6.1 GPa at 1273 K. The specimens of rutile type, α -quartz type and vitreous GeO_2 identified by X-ray diffraction. The fine powder samples were pressed with powder of boron nitride into pellets of 10.0 mm in diameter. The Ge K-edge EXAFS has been measured from 10 K to 1000 K at beam line 10B of the Photon Factory in the National Laboratory in High Energy Physics, Tsukuba.

The EXAFS interference function $\chi(k)$ was extracted from the measured absorption data using standard techniques [3], where k is the wave number of a photoelectron given by $k = \{2m(E - E_0)/\hbar^2\}^{1/2}$ with m the mass of the electron. The $\chi(k)$ was normalized using MacMaster coefficients according to the EXAFS workshop report [4].

In order to determine the anharmonic effective pair potential $V(u) = \alpha u^2/2 + \beta u^3/3! + \gamma u^4/4!$... (1) for Ge-O bond, where u is the deviation of the bond length from the location R_0 of the potential minimum, we used an average of EXAFS formula, based on the single-scattering theory and expressed by a distribution function $\rho(u)$ [5,6]:

$$\chi(k) = \text{Im} \left[\sum_b \frac{-1}{k} f_b(k; \pi) \exp(i2\delta_b) \int_{-\infty}^{\infty} \frac{\rho(u)}{(R_0 + u)^2} \exp\left(-\frac{2(R_0 + u)}{\lambda(k)}\right) \exp(i2k(R_0 + u)) du \right] \quad \dots(2)$$

We used the data of high temperature range (1000 K or 900 K). Then we assumed the classical Boltzmann distribution:

$\rho(u) = \exp(-V(u)/k_B T) / \int \exp(-V(u)/k_B T) du$... (3) where k_B is the Boltzmann constant. The EXAFS function $\chi(k)$ is rewritten from above Eqs. (1), (2) and (3) and we carried out a non-linear least-squares parameter fitting by comparing the observed and calculated $\chi(k)$:

$$\chi(k) = \frac{N_b}{k} \left| f_b(k; \pi) \right| \frac{\int_{-\infty}^{\infty} \frac{1}{(R_0 + u)^2} \exp\left(-\frac{1}{k_B T} \left(\frac{\alpha}{2} u^2 + \frac{\beta}{3!} u^3 + \frac{\gamma}{4!} u^4 \right) \right) \exp\left(-\frac{2(R_0 + u)}{\lambda(k)}\right) \sin(2k(R_0 + u) + \delta_{\text{total}}) du}{\int_{-\infty}^{\infty} \exp\left(-\frac{1}{k_B T} \left(\frac{\alpha}{2} u^2 + \frac{\beta}{3!} u^3 + \frac{\gamma}{4!} u^4 \right) \right) du} \quad \dots(4)$$

where the coordination number N_b was fixed at the crystallographic value. Values of the back-scattering amplitude of photoelectrons $|f_b(k; \pi)|$ and the total phase shift between absorbing and scattering atoms δ_{total} were calculated by using FEFF3 program [7]. The mean free path λ of the photoelectron is assumed to depend on the wave number k : $\lambda(k) = k/\eta$ where η is constant. The parameters

we used for the best fitting are R_0 , α , β , γ , η and ΔE_0 : ΔE_0 is the difference between the theoretical and experimental threshold energies [3]. Local structural parameters are given in Table 1. A harmonic two shell fitting is carried out in rutile type GeO_2 .

Table.1 Local structural parameters for the anharmonic potential model.

		α -quartz type		rutile type		vitreous
				2-fold	4-fold	
R_0	($\text{\AA}$)	1.758(5)		1.858(2)	1.904(9)	1.765(5)
α	($10^{-12} \text{ erg/\AA}^2$)	28.7(9)		10.2(0)	32.2(7)	26.0(2)
β	($10^{-12} \text{ erg/\AA}^3$)	-54.(15)		-	-	-
γ	($10^{-12} \text{ erg/\AA}^4$)	0.1(10)		-	-	-
η	($\text{\AA}^{-2}$)	0.26(6)		0.085(7)	0.085(7)	0.57(2)
ΔE_0	(keV)	0.024(3)		0.024(3)	0.024(3)	0.010(3)
R-factor	(%)	4.9		8.7	8.7	0.7

3. RESULTS AND DISCUSSION

The radial distributions of Ge-O in α -quartz type obtained from EXAFS and our best fitting MD simulation agree with each other (Fig.1). Table.2 shows a comparison of the observed values [8,9,10] with the structural values calculated by our best fitting MD simulation.

The pair potential of Ge-O bond is not appreciably changed with structural transformation, except for the four coplanar Ge-O bonds in the rutile type structure. The determined effective pair potentials are shown in Fig.2. The rutile structure consists of chains of GeO_6 octahedra. Each octahedron shares a pair of opposite edges (Fig.3). The shared edges (③-④) are shortening compared with the unshared edges because of the shielding effect and consequent reduction of repulsive force between the Ge atoms (①-②) with the short distance along the c-axis. The neighbor oxygen atoms with the distance of 2.400 $\text{\AA}$ which is short compared with twice of the ionic radius of O exist in the direction parallel to the longer Ge-O bond. Therefore, the effective pair potential for the longer axial Ge-O bond is significantly steeper than the shorter coplanar Ge-O bond. These indicate that effective pair potentials are certainly influenced by atomic arrangements.

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Table.2 Observed and simulated structure of α -quartz type GeO_2

	Calc	Obs
cell lengths		
a ($\text{\AA}$)	4.998	4.987
b ($\text{\AA}$)	4.999	4.987
c ($\text{\AA}$)	5.649	5.652
Ge-O distances ($\text{\AA}$)	1.688	1.737
O-Ge-O bond angle ($^\circ$)	105.5	106.3
bulk modulus		
K_0 (GPa)	27.4	32.8
K'_0 (GPa)	4.3	6.0
Thermal expansiivty (10^{-6} K^{-1})	25.9	24.9

Fig.3 The rutile type GeO_2 structure