present case has a salient feature in that it exhibits a small but significant hump at around $R = 1.3$ Å while that of the MgO case falls into the category of *minimum type* (Sasaki *et al.*, 1980). To determine the EDR, we calculated $dU(R)/dR$ for the region $R = 1.0$–1.6 Å and applied the procedure we used to determine the EDR for the cases of $U(R)$ for the *flat type* (Sasaki *et al.*, 1980). We thus found EDR = 1.28 (1) Å, the error being estimated in terms of the e.s.d.
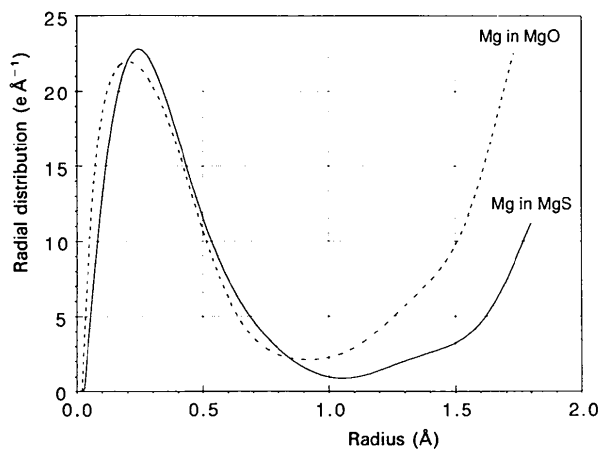
for $C(R)$. This value is significantly larger than any EDR of Mg's in the oxygen-based compounds which we have studied so far; their values range from 0.91 to 0.96 Å with a mean of 0.93 Å.

The number of electrons within a sphere of radius 1.28 Å was thus calculated using *ENAC* (Sasaki *et al.*, 1980) to give a net charge of + 1.50 (1) for the Mg atom. These values are to be compared with those of Mg in MgO: EDR = 0.92 (1) Å and net charge = + 1.847 (2).

Fig. 1. The $U(R)$ curve for Mg in MgS (solid line) as compared to that in MgO (broken line).

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Molecular dynamics study of the TiO₂ (rutile) and TiO₂–ZrO₂ systems.

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Abstract

The molecular dynamics (MD) method is applied to the simulation of the structural and physical properties of the TiO_2 (rutile) and TiO_2–ZrO_2 systems. The interatomic potential model consists of Coulomb and repulsive terms between atoms, and an additional Morse potential term for both titanium–oxygen and oxygen–oxygen interactions. The MD simulations have succeeded in reproducing the structural and physical properties of TiO_2, including the crystal structure and the thermal expansivities. The MD method was further proved successful by its ability to reproduce the observed crystal structure of the TiO_2–ZrO_2 system.

Introduction

In order to investigate the properties of materials, numerical computation is becoming an increasingly important technique. Computer simulations can be applied to a large variety of materials such as fused salts, glasses and proteins. However there are not many studies on inorganic materials owing to the difficulty of construction of practical interatomic potential models. Such constructions are one of the most essential parts of molecular dynamics (MD) methods.

For inorganic materials, Matsui (1988, 1990) has reported that the MD method successfully reproduced the available structural and physical properties of the perovskite $MgSiO_3$, and he has also investigated the structure of three types of TiO_2 (rutile, anatase, brookite) with the object of predicting the high-temperature and high-pressure behavior, where the crystal structures were successfully reproduced, but the thermal expansivities were smaller than the observed values. The potential function in Matsui's work was composed of Coulomb, van der Waals and a Gilbert (1968) type repulsion term.

TiO_2 (rutile) has a high dielectric constant and a low dielectric loss which are valuable properties for microwave dielectric ceramics (Egerton & Thomson, 1971). The physical properties such as dielectric constant and thermal

Table 1. *Energy parameters used for the calculations*

Ion	z	a (Å)	b (Å)	Ion pair	D (Å)	β (Å^{-1})	r* (Å)
Ti	+2.8	1.280	0.125	Ti—O	35.0	1.98	1.70
O	−1.4	2.087	0.190	O—O	6.0	1.90	2.60
Zr	+2.8	1.470	0.125	Zr—O	35.0	1.98	1.70

expansivities vary considerably with the direction of the crystal axis. Thus it is important to examine the mechanism by which dielectric properties are generated by MD simulation by using a proper potential model which is able to reproduce the structural and physical properties, including the anisotropic properties.

In this paper we have tried to adopt a Morse potential instead of the van der Waals term in the MD method in order to reproduce both the crystal structure and the thermal expansivity of TiO_2 (rutile), and we have also applied the model to the TiO_2–ZrO_2 system to test its ability to deal with replacement in the MD calculation.

Methods

MD simulation was carried out using the simulation program, *XDORTO*, developed by Kawamura (1992). The potential energy was approximated by a sum of pairwise interactions between atoms of the form:

$$u_{ij} = z_i z_j e^2/r_{ij} + f_0(b_i + b_j)\exp[(a_i + a_j - r_{ij})/(b_i + b_j)]$$
$$+ f_0 D_{ij}\{\exp[-2\beta_{ij}(r_{ij} - r_{ij}^*)] - 2\exp[-\beta_{ij}(r_{ij} - r_{ij}^*)]\},$$

where the terms represent a Coulomb potential, a repulsive potential, and an additional Morse potential, respectively. Here, z_i is the charge number of the ion i, e the unit charge, r_{ij} the distance between ions i and j, f_0 a force constant of 4.184 kJ mol^{-1} Å^{-1}, and a_i and b_i are the crystal constant and compressibility of atom i, respectively. The coefficients D_{ij}, β_{ij} and r_{ij}^* are the energy parameters between atoms i and j. We determined the potential parameters empirically as shown in Table 1.

A rectangular parallelepiped basic cell and periodic boundary conditions were adopted and no space-group symmetry constraints were imposed on the atomic positions in the basic cell for the present MD calculations. The starting configurations used to initialize the MD simulations were taken from the observed structures reported by Abrahams & Bernstein (1971). We take a basic cell composed of 96 ($4a \times 4b \times 6c$) unit cells which contains 576 (192 Ti and 384 O) ions for TiO_2. For the TiO_2–ZrO_2 system, we magnify the unit cell of TiO_2 by eight ($2a \times 2b \times 2c$), and a basic cell composed of 12 ($2a \times 2b \times 3c$) enlarged unit cells which contains 576 ions in all is used. In each unit cell one or two Ti ions of the 16 are replaced with Zr ions (the amount of replacement is 6.25 and 12.5%, respectively) in order to compare the experimental results of $Ti_{1-x}Zr_xO_2$ ($x = 0.05$, 0.10) with the calculated values. The basic cell size is chosen so that the structural and energetic results are not dependent on the cell size.

The electrostatic interactions are handled by the Ewald method and the equations of motion are solved by the Verlet algorithm with a time increment of 2.5 fs. In each MD run, a sufficiently long period of 'aging' (~5000 steps) is performed to establish an equilibrium for the system under the desired temperature and pressure conditions.

Table 2. *Summary of the structural and physical properties of* TiO_2

	Measured* at ambient conditions	Simulated 300 K 0.1 MPa	400 K 0.1 MPa
Lattice parameters			
a (Å)	4.594	4.585	4.588
c (Å)	2.959	2.964	2.967
V (Å^3)	62.4	62.3	62.5
a/c	1.552	1.546	1.546
Fractional coordinates			
x(Ti)	0.0000	0.0000	0.0000
y(Ti)	0.0000	0.0000	0.0000
z(Ti)	0.0000	0.0002	0.0000
x(O)	0.3048	0.3022	0.3024
y(O)	0.3048	0.3022	0.3023
z(O)	0.0000	0.0000	0.0003
Thermal expansivities at 400 K, $(1/p)\delta p/\delta T$ (10^6 K^{-1})			
a	7.55	–	7.18
c	9.38	–	9.31
V	24.48	–	23.67

* Observed values from Abrahams & Bernstein (1971) for the lattice parameters and the fractional coordinates, and from Rao *et al.* (1970) for the thermal expansivities.

Results

Table 2 lists the simulated structural properties of TiO_2 at 300 K and 0.1 MPa, and 400 K and 0.1 MPa, together with the measured values for comparison. The standard deviations for the simulated lattice parameters at 300 K are 0.0005 and 0.0004 for the a and c axis, respectively. The simulated structure at 300 K and 0.1 MPa agrees quite closely with the observed structure (Abrahams & Bernstein, 1971) under ambient conditions. Indeed, the calculated unit-cell dimensions agree with the experimental result to within 0.2%. Matsui (1990) has reported simulation results of TiO_2 using a different potential model, and obtained calculated lattice parameters of 4.51 and 3.02 Å for the a and c axis, respectively. Our simulated coordinates differ from the observed values by less than 0.02 Å. Rao, Naidu & Iyengar (1970) first measured the thermal expansivity of TiO_2 (rutile) using a high-temperature powder camera and their results for the a and c axis at 400 K are 7.55 and 9.38 p.p.m. K^{-1}, respectively. Our simulated thermal expansivities agree with the observed values to within 5%.

The potential model of TiO_2 obtained here was then tested for its ability to reproduce the observed structure of the TiO_2–ZrO_2 system. The Ti ions in TiO_2 can be replaced experimentally with Zr ions up to about 15 mol% (Brown & Duwez, 1954). Table 3 shows the unit-cell dimensions of our experimental results for $Ti_{1-x}Zr_xO_2$ ($x = 0.05$, 0.1), together with the calculated values ($x = 0.0625$, 0.125) for comparison. The unit-cell dimensions agree comparatively well with the simulated result and the fact that the degree of expansion for the c axis is about twice as large as that for the a axis is also in agreement with the simulation.

For TiO_2 the dielectric constant along the c axis is known to be about twice as large as that along the a axis (Galasso, 1970). The reason may be that the ions can move more easily along the c axis than along the a axis.

Table 3. *Comparison of the observed and simulated lattice parameters for the* $Ti_{1-x}Zr_xO_2$ *system*

Values in parentheses are the degress of expansion (%).

			Amount of replacement, x		
	0	0.05	0.0625	0.10	0.125
Observed					
a (Å)	4.594	4.605 (0.24)	–	4.619 (0.53)	–
c (Å)	2.959	2.974 (0.55)	–	2.991 (1.09)	–
Simulated					
a (Å)	4.585	–	4.596 (0.26)	–	4.608 (0.53)
c (Å)	2.964	–	2.982 (0.59)	–	2.999 (1.17)

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Refinement of atomic positions in bixbyite oxides using perturbed angular correlation spectroscopy. Erratum.

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Abstract

The name of R. W. G. Wyckoff is incorrectly given as Wyckhoff on pages 165 and 169 of the paper by Bartos, Lieb, Uhrmacher & Wiarda [*Acta Cryst.* (1993), B49, 165–169].

All relevant information is given in the *Abstract*.