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Journal of Alloys and Compounds 387 (2005) 9–14

Journal of ALLOYS AND COMPOUNDS

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Molecular dynamics studies of neptunium dioxide

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Received 22 March 2004; received in revised form 9 June 2004; accepted 14 June 2004

Abstract

The molecular dynamics (MD) calculation has been performed for neptunium dioxide (NpO_2) in the temperature range from 300 to 2500 K to evaluate the thermophysical properties viz., the lattice parameter, thermal expansion coefficient, compressibility, heat capacity, and thermal conductivity. The Morse-type potential function added to the Busing-Ida type potential was employed for the ionic interactions. The interatomic potential parameters were determined by fitting to the experimental values of the lattice parameters of NpO_2. The thermal expansion coefficient and compressibility were calculated from the temperature and pressure dependences of the lattice parameter, evaluated from the fixed pressure MD calculation. The heat capacity at constant volume (C_V) was calculated from the variation of the internal energy of the system, evaluated from the fixed volume MD calculation. The lattice dilation contribution to the heat capacity (C_d) was evaluated from the calculated thermal expansion coefficient and compressibility. The thermal conductivity was calculated by using a Green-Kubo relation.

Keywords: Molecular dynamics; Neptunium dioxide; Heat capacity; Thermal conductivity

1. Introduction

The minor actinide (MA: Np, Am, and Cm) oxides are produced in irradiated oxide nuclear fuels, and they affect the thermophysical properties of the fuel. In addition, the MA containing mixed oxide fuel, $(U,Pu,MA)O_2$ is candidate for advanced nuclear fuels for fast breeder reactors and/or transmutation reactors [1,2]. Therefore, it is important to evaluate the properties of the MA oxides. However, there is only a little information on these properties for the MA oxides, due to the difficulties associated with the high radiation fields. These studies are limited to a few properties, or a small temperature range. Because the recycled fuel will be widely used in the future, it is necessary to develop a new technique to evaluate the thermophysical properties of the MA oxides. Molecular dynamics (MD) calculations can be one useful technique, and provide information to understand the properties of the compounds.

In recent years with the advance of computer simulation techniques, we have performed extensive MD studies on uranium and plutonium oxides and/or nitrides to understand their thermophysical properties [3–6]. However, in the case of the MA oxides, there are no studies on the MD calculations. In the present study, the MD calculation for NpO_2 is performed to evaluate the thermophysical properties such as the heat capacity and thermal conductivity.

2. Calculation procedure

The MD calculations for NpO_2 were performed for a system of 324 ions (108 cations and 216 anions) initially arranged in a CaF_2 type crystal structure. In our previous studies, the MD simulations were performed for UO_2 and

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doi:10.1016/j.jallcom.2004.06.037

PuO_2 under the same cell size conditions (324 atoms), and we have succeeded in reproducing several thermal properties of the actinide dioxides [4–6]. Therefore, the box size with 324 atoms is enough to perform MD simulations for NpO_2. In the present study, the calculations were performed by a molecular dynamics program based on MXDRTO [7]. The standard constant pressure–temperature (NPT) and constant volume–temperature (NVT) MD calculations at the thermodynamic equilibrium were performed. A quantum effect [8] was taken into account in the present calculation. The lattice, containing a fixed number of atoms, was assumed to repeat periodically throughout the material, and there was no edge or surface effect. The long-range coulomb interaction was treated with Ewald's summation [9]. The equations of motion were integrated using Verlet's algorithm [10] with on integration time step of 2.0×10^{-15} s. At the start of the calculation, the initial velocity of each atom was assumed to take random velocities, which was about 0.01 Å fs^{-1}.

The calculations were made in the temperature range from 300 to 2500 K, and in the pressure range from 0.1 MPa to 1.5 GPa. The temperature and pressure of the system were controlled independently with a combination of the methods proposed by Andersen [11] and Nose [12]. A 10,000-step equilibrium run was made at the desired temperature and pressure. Although the number of steps was small, equilibrium was achieved as judged from the changes in the temperature (±3%), pressure (±9%), density (±0.02%), and internal energy (±0.04%). At 300 K, the mean square displacement of oxygen ions in the MD cell was within 0.02 $Å^2$, which is close to the magnitude of thermal vibrations at that temperature.

We employed the semi-empirical two-body potential function proposed by Ida [13] for cation–anion interactions. In this potential, the f-electrons and relativistic effects are accounted for implicitly, but the three-body effect is not accounted for. It would be desirable to use the three-body (or beyond) potential. For the present study, however, the two-body potential is sufficient, because the system (fluorite structure) is relatively simple. The potential is a partially ionic model including a covalent contribution:

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij}\{\exp[-2\beta_{ij}(r_{ij} - r_{ij}^*)] - 2\exp[-\beta_{ij}(r_{ij} - r_{ij}^*)]\}, \quad (1)$$

where f_0 equals 4.186, Z_i and Z_j are the effective partial electronic charges on the ith and jth ions, r is the atom distance, r_{ij}^* is the bond length of the cation–anion pair in vacuum, and a, b, and c are the characteristic parameters depending on the ion species. In this potential function, D_{ij} and β_{ij} describe the depth and shape of this potential, respectively. The first term is the coulomb interaction, the second term denotes the core repulsion, and the third term, which is called Morse-type [14] potential, corresponds to the covalent contribution.

Table 1
Values of the interatomic potential function parameters for NpO_2

Ion	z	a	b	c	D_{ij}	β_{ij}	r_{ij}^*
O	−1.2	1.926	0.160	20			
Np	2.4	1.190	0.080	0	10.5[a]	3.27[a]	2.339[a]

[a] For Np–O pairs.

The parameters (a, b, and c) for oxygen ions given by Kawamura [15] were used in the present study. These parameters have been used in the studies of other oxides such as SiO_2, $MgSiO_4$, Al_2O_3, and $NaAlSiO_4$ [15]. The parameters of neptunium ion were determined by trial and error using the experimental values of the changes in the lattice

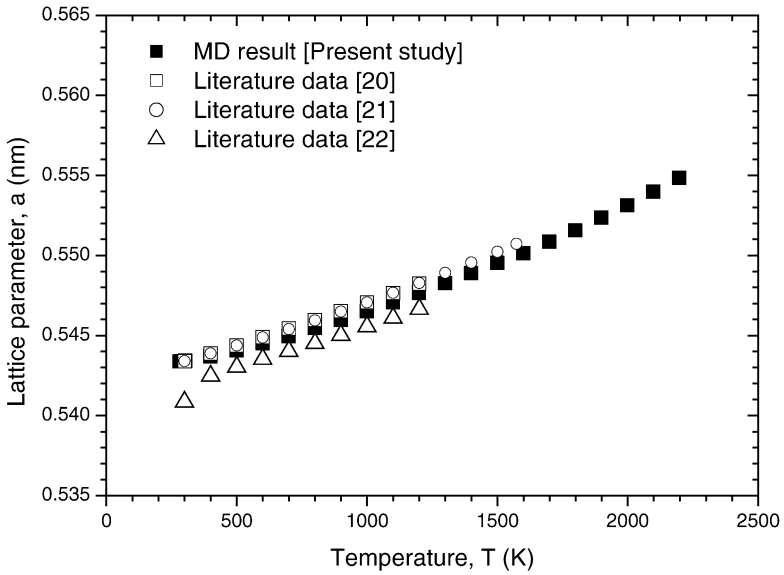

Fig. 1. Temperature dependence of the lattice parameter of NpO_2, together with the experimental data [20–22].