4.4 Molecular Dynamics Studies of Actinide Nitrides

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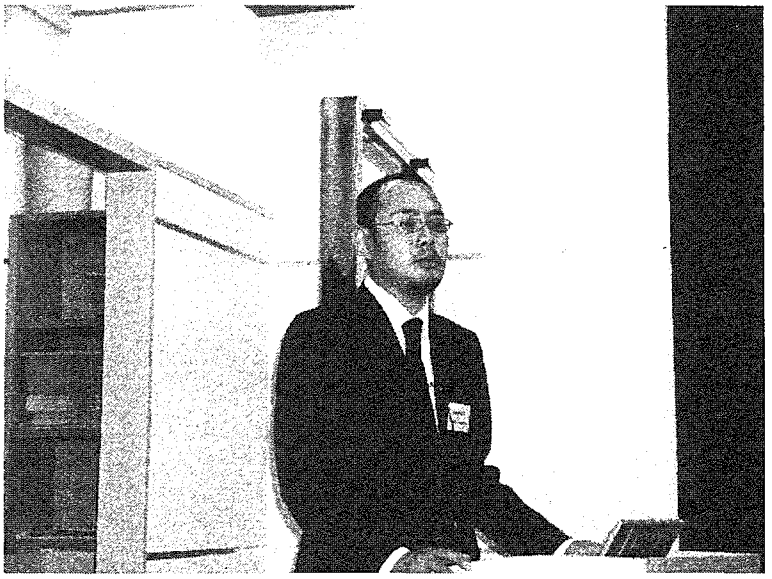

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Molecular Dynamics Studies of Actinide Nitrides

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Abstract

The molecular dynamics (MD) calculation was performed for actinide nitrides (UN, NpN, and PuN) in the temperature range from 300 to 2800 K to evaluate the physical properties viz., the lattice parameter, thermal expansion coefficient, compressibility, and heat capacity. 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 data of the lattice parameter. The usefulness and applicability of the MD method to evaluate the physical properties of actinide nitrides were studied.

1. Introduction

In order to develop the technologies for nuclear fuel cycle based on nitride fuel and pyrochemical reprocessing, it is very important to understand the physical properties of actinide nitrides. In Osaka University, we have carried out the molecular dynamics simulation to evaluate the properties of oxide fuel, such as UO_2, PuO_2, and MOX [1-3]. In the present study, the molecular dynamics (MD) calculation is performed for actinide nitrides (UN, NpN, and PuN), and their thermal and mechanical properties are evaluated.

2. Calculation

The MD calculations for AnN (An: U, Np, Pu) were performed for a system of 512 ions (cation: 256, anion: 256) initially arranged in the NaCl type crystal structure. In the present study, the calculations were performed by a molecular dynamics program based on MXDORTO [4]. 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 through a simple

velocity scaling method. However, in calculating the thermal conductivity, a combination of the methods proposed by Andersen [5] and Nose [6] was used to control the pressure and temperature.

We employed the semi-empirical two-body potential function proposed by Ida [7] for cation-anion interactions. The potential is a partially ionic model including a covalent contribution [8]:

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

where f_0 equals 4.186, z_i and z_j are the effective partial electronic charges on the ith and jth ions, r_{ij} is the interatomic 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 potential parameters were determined by trial and error using the experimental values of the lattice parameters. Using the parameters so obtained, the linear thermal expansion coefficient (α_{lin}), compressibility (β), and heat capacity (C_P) were evaluated.

The values of the interatomic potential parameters used in the present study are summarized in Table 1.

Table 1 Values of the interatomic potential function parameters for UN, NpN, and PuN

Ions	z	a	b	c	D_{ij}	β_{ij}	r_{ij}^*
N	-1.450	1.797	0.080	20			
					(for U-N pairs)		
U	1.450	1.228	0.080	0	7.00	1.25	2.364
					(for Np-N pairs)		
Np	1.450	1.248	0.080	1	9.56	1.25	2.364
					(for Pu-N pairs)		
Pu	1.450	1.196	0.080	0	0.10	0.80	2.453

3. Results and discussion

The temperature dependence of the lattice parameter of UN, NpN, and PuN obtained by the MD calculation controlled at 0.1 MPa is shown in Fig. 1, together with literature data [9-11]. The calculation was performed in the temperature range between 300 K and 3000 K. Although the temperature range of the experimental data is limited for NpN and PuN, the high temperature data are obtained from the MD calculation. The calculated results well agree with literature data.

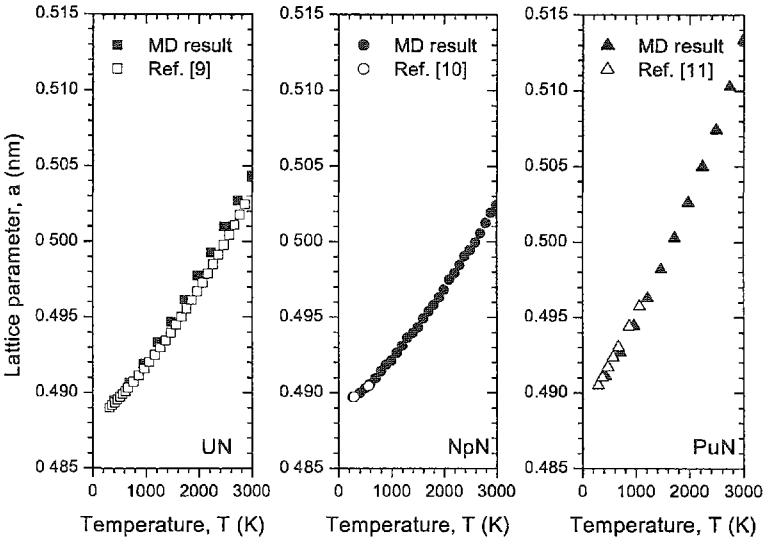

Fig. 1. Temperature dependence of the lattice parameter of UN, NpN, and PuN.

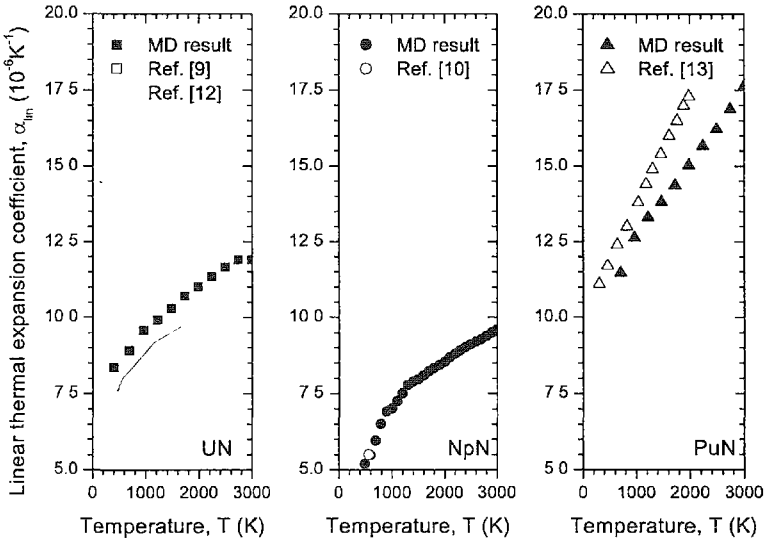

Fig. 2. Temperature dependence of the linear thermal expansion coefficient of UN, NpN, and PuN.

The linear thermal expansion coefficient (α_{lin}) and compressibility (β) of UN, NpN, and PuN can be evaluated from the variation of the lattice parameter with temperature. In case of NpN and PuN, the experimental data for linear thermal expansion coefficient and compressibility are scarcely reported.

The results are shown in Figs. 2 and 3, together with literature data [9,10,12-14]. It is confirmed that the calculated results almost agree with literature data.

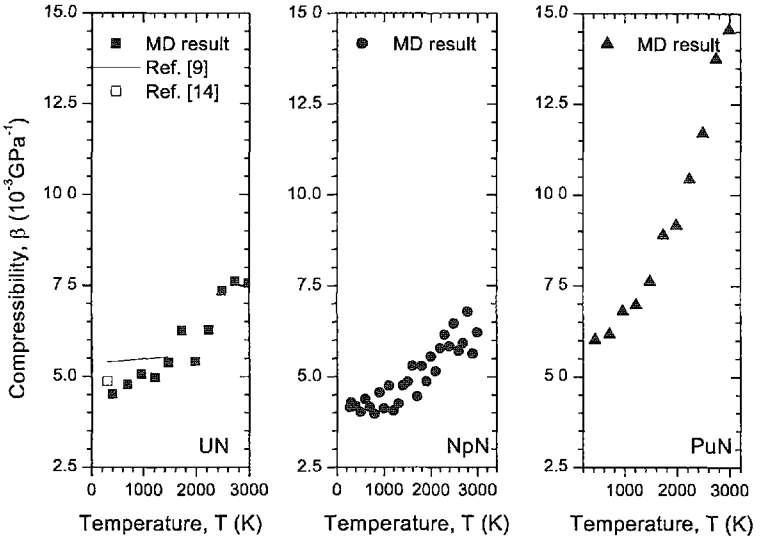

Fig. 3. Temperature dependence of the compressibility of UN, NpN, and PuN.

Although there are electronic contributions in actinide nitride system, we can evaluate only the lattice contribution to the heat capacity by the MD calculation. In the temperature range from 300 K to 3000 K, the heat capacity at constant pressure (C_P) was evaluated as sum of the heat capacity at constant volume (C_V) and lattice dilation team (C_d). The C_V was evaluated from the variation of the internal energy of the system with temperature calculated by the NVT MD simulation. The C_d was evaluated from the following relationship:

$$C_d = \frac{(3\alpha_{lin})^2 VT}{\beta} \qquad (2)$$

where V is the molar volume, α_{lin} is the linear thermal expansion coefficient, β is the compressibility, and T is the absolute temperature. The C_d was evaluated by using the calculated values of α_{lin}, V, and β obtained from the NPT MD simulation. The temperature dependence of the calculated C_V+C_d of UN, NpN, and PuN is shown in Fig. 3, together with literature data [15-19]. The calculated values of CV+Cd are slightly lower than the experimental results. This may be caused by the electronic contributions.

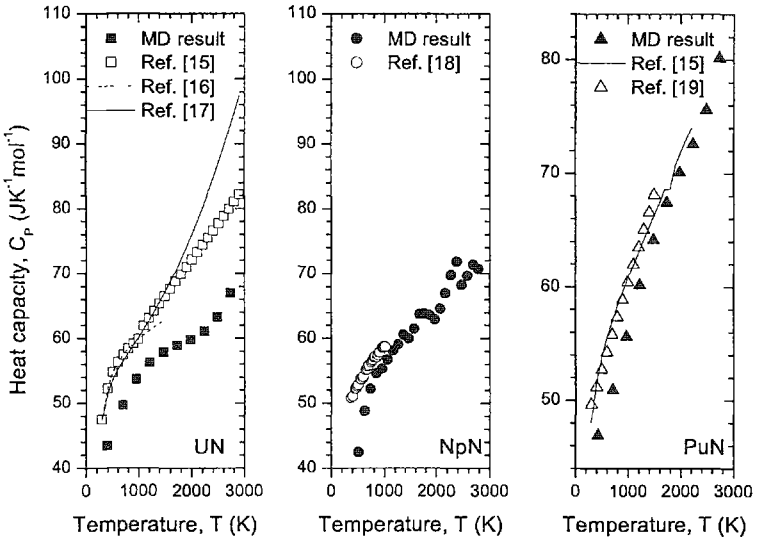

Fig. 4. Temperature dependence of the heat capacity of UN, NpN, and PuN.

4. Conclusion

The lattice parameter, linear thermal expansion coefficient, compressibility, and heat capacity of UN, NpN, and PuN were evaluated with the MD simulation. The interatomic potential parameters were determined from the variation of the lattice parameter with temperature. The calculated results are almost identical with the experimental data. The present study shows that the MD method can be usefully applied to determine the physical properties of actinide nitrides.

Acknowledgements

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