Thermophysical Properties of α-Pu2O3: A New Potential Model

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Abstract. α-Pu_2O_3 is an important material among plutonium based materials in nuclear industry. Pure plutonium surfaces quickly oxidizes into α-Pu_2O_3 and PuO_2 which are in the form of layers one on another [1]. Here we have investigated thermal properties of α-Pu_2O_3 by molecular dynamics simulation by using a partially ionic semi-empirical rigid ion potential. Mechanical properties, thermal expansion, and heat capacity are calculated. Results were compared with available experimental data and quantum calculation [2]. Due to the experimental limitations such as toxicity and radiation effects, studying the physical properties of such materials from molecular dynamics simulations have vital importance.

Keywords: α-Pu_2O_3 , molecular dynamics simulation, β-Pu_2O_3, lattice constant, elastic modulus, bulk modulus, coordiantion number
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INTRODUCTION

Thermodynamics and physical properties of plutonium oxides are interesting for the uses in nuclear facilities. It is also hard to store pure plutonium. When plutonium surface contact with the dry air, it turns into PuO_2 . By time, PuO_2 layer changes into a thin layer of Pu_2O_3. This may be either plutonium sesquioxide (β-Pu_2O_3) which has a hexagonal structure or cubic plutonium sesquioxide (α- Pu_2O_3) which has a cubic cell with 32 Plutonium and 48 Oxygen atoms [3]. In this study we developed new potential parameters for α- Pu_2O_3 in order to understand physical properties better. By this way we could also avoid the experimental limitations, like toxicity and radiation effects.

MOLECULAR DYNAMICS SIMULATION

In this study, we have used Born-Mayer-Huggins potential with Coulomb potential which is given in equation 1.

$$\phi_{ij}(r) = \frac{z_i z_j e^2}{r} - \frac{A}{r^6} + B\exp(-Cr). \quad (1)$$

Here the first term is the Coulomb interaction where zi,j are the charges, r is the distance between ions. Second term is the dipole-dipole contribution. Third term models the repulsion between the ions. A,B and C are the potential parameters which are given in Table 1.

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TABLE 1. Potential parameters for BMH potential

		Z	A (eV*A^6)	B (eV)	C (A^{-1})
Pu	Pu	3.0	0.0	0.0	1.0
Pu	O		13.50	1150.745	2.67
O	O	-2.0	70.39	9547.96	4.56

Molecular dynamics simulation of α- Pu_2O_3 with 864 Pu+3 ions and 1296 O-2 ions was performed at different temperatures up to 900K. α- Pu_2O_3 has Mn_2O_3-type bcc structure which can be obtained by 2x2x2 supercell of PuO_2. Here 25% of oxygen ions were removed from the supercell that is constructed of 3x3x3 simulation box[4]. The molecular dynamics program, MOLDY is used to carry out the calculations. We have used the Beeman's algorithm with the system time step Δt =0.001ps and the total simulation step is 50000. The calculations were performed with the NPT ensemble.

RESULTS AND DISCUSSIONS

In Table 2 calculated results of lattice parameter, bulk modulus, and elastic constants of α- Pu_2O_3 are compared with the available experimental and quantum calculations. In order to test the range of applicability of potential we also calculated the mentioned properties for the beta phase with the same potential. Unfortunately α- Pu_2O_3 has not been studied much because of its complex structure. In the Table 2, calculated parameters are obtained by fitting Birch-Murnaghan equation of state. Here obtained parameters are in good agreement with experimental data.

TABLE 2. Properties of both α-Pu_2O_3 and β-Pu_2O_3 compared with experimental and ab-initio data[1,2,5].

	Exp. (α-Pu_2O_3)	Ab Initio (α- Pu_2O_3)	This Study (α- Pu_2O_3)	Exp. (β-Pu_2O_3)	This Study (β- Pu_2O_3)
a (A)	11.04	10.91-11.20	10.93	3.840	3.83
c (A)				5.957	6.20
Bulk Modulus (GPa)		119-133	138.23	140	141.68
C11 (GPa)			209.99		259.04
C12 (GPa)			102.61		159.60
C44 (GPa)			80.29		76.07

Figure 1 shows the change of lattice parameter versus temperature up to 900K where pressure of the system close to zero. Experimental results show that structure of α- Pu_2O_3 is only stable below 573K [4]. The behavior of the lattice displays a sudden drop at 500K which is close to the experimental value. Previous MD study [1] shows a good agreement with the experimental lattice parameter at 300K but predicted linear change of lattice parameter up to 1500K which physically not reasonable because of this transition.

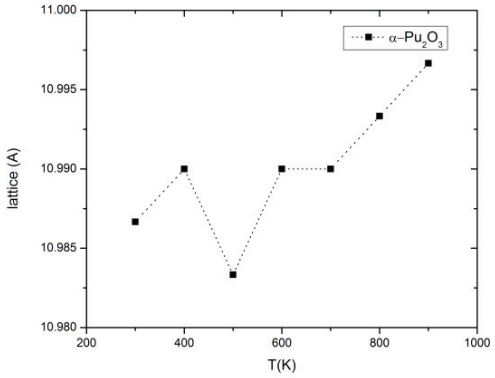

FIGURE 1. Lattice change vs. temperature

In Figure 2 and Figure 3 radial distribution functions of alpha and beta phase of Pu_2O_3 are displayed at 300K. First nearest neighbor distances of Pu-O, O-O and Pu-Pu are 2.33 Å, 3.02 Å and 3.64 Å for α- Pu_2O_3 also 2.35 Å, 3.00 Å and 3.68 Å for β- Pu_2O_3, respectively. Experimental values for Pu-O distance for α- Pu_2O_3 change between 2.342-2.383 and for β- Pu_2O_3 , 2.353-2.623[3].

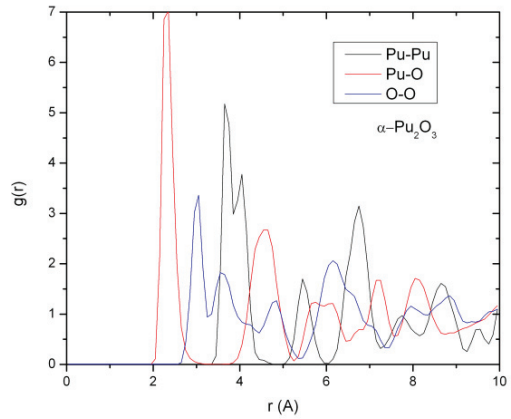

FIGURE 2. Radial distribution function of α-Pu_2O_3 at 300K.

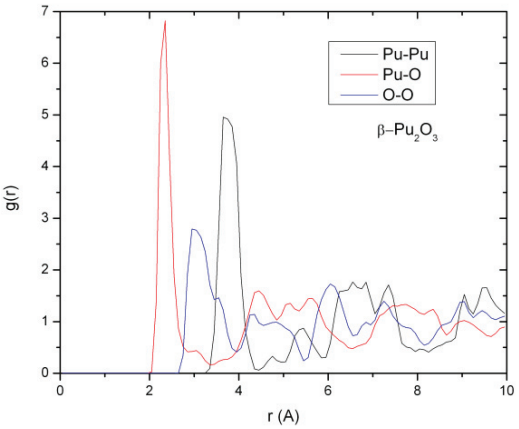

FIGURE 3. Radial distribution function of β- Pu_2O_3 at 300K.

PuO_2 and α- Pu_2O_3 have similar cubic structures. PuO_2 has fluorite type crystal structure but when 25% of oxygen atoms are removed, the structure turns into α-Pu_2O_3. As a result coordination number of Pu-O also decreases from 8 to 6. In order to compare results from simulation, coordination number is calculated,

$$\left\langle n_{ij}\Delta r = 4\pi r^2 \Delta r \rho_j g_{ij}(r) \right\rangle. \quad (2)$$

Here $n_{ij}(r)\Delta r$ denotes the number of j particles around i particles between r and $r+\Delta r$. ρ_j is the mean number of density of j type particles in the box [6]. $g_{ij}(r)$ is the radial distribution function. Here obtained the coordination number of α- Pu_2O_3 which is 6, in agreement with experimental value.

Heat capacity Cp is found by the change of internal energy with temperature at constant pressure.

$$C_p(T) = \left(\frac{\partial E}{\partial T}\right)_p. \quad (3)$$

Values are compared with the experimental, ab-initio and MD results.

TABLE 3. Heat capacity of . α-Pu_2O_3 are compared with MD, ab- initio and experimental results.[1,5]

	Exp	**Ab initio**	**MD**	**This study**
Cp ($JK^{-1}T^{-1}$)	120.35	107	117	130

CONCLUSION

In this study a new potential is proposed in order to obtain physical properties and model the system better. Lattice parameter, bulk modulus, elastic constants, coordination number and heat capacity are reproduced within a reasonable agreement. Experimental data of temperature dependence of physical properties are needed to understand and to model Pu_2O_3 material better.

REFERENCES

1. M. Chu, D. Meng, S. Xiao, W.Wang, Q. Chen*, J. Alloys Compd*. **539,** 7-11 (2012).
2. H. Shi, P. Zhang, *Journal of Nuclear Materials* **420,** 159-163 (2012).
3. L. R. Morss, N. M. Edelstein, *The Chemistry of the Actinide and transactinide elements,* 4 th edition, Netherlands, Springer.
4. *IAEA technical reports series*, No. 79, 1967.
5. Y. Lu, Y. Yang, F. Zheng and P. Zhang, arxiv:1208.3746v1, (2012).
6. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquid*, London, Academic Press, 1986.