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Evaluation of thermal properties of PuO_2 and α-Pu_2O_3 by atomic simulation

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ABSTRACT

Some important thermal properties of both PuO_2 and α-Pu_2O_3 have been investigated by atomic simulation between 298 K and 1500 K using BMH empirical potential and shell potential, including thermal expansion coefficient, entropy, heat capacity and enthalpy. The BMH empirical potential of Pu–O bond in α-Pu_2O_3 was fitted by GULP program. The calculated values are in good agreement with the experimental data for PuO_2, shows that the parameters we selected are appropriate. But especially for α-Pu_2O_3, these thermal properties were too difficult to be truly measured in experiments because of its radio-toxicity and the high chemical activity. So we could not evaluate our calculated results accurately.

1. Introduction

PuO_2, and α-Pu_2O_3 are two kinds of important oxides of plutonium. Extensive investigation of the plutonium–oxygen system shows that binary oxides formed at room temperature are the well known stable PuO_2 and α-Pu_2O_3 [1]. The plutonium with clean surface can be easily oxidized to cubic α-Pu_2O_3 even in O_2 partial pressure of 10^{-7} Pa. α-Pu_2O_3 is a silver-gray and lustrous compound with high chemical activity, consistent with the reports that Pu_2O_3 is pyrophoric [2,3]. In the air pressure of 10^{-4} Pa at room temperature, partial α-Pu_2O_3 can be further oxidized to PuO_2 easily, forming the sandwich structure with α-Pu_2O_3 steadily exists between plutonium and PuO_2. Because PuO_2 can be reduced by plutonium with the increasing temperature or in high vacuum, the fraction of α-Pu_2O_3 in oxidation film increases sharply [4]. The evaluation of thermal properties of PuO_2 and α-Pu_2O_3 is necessary in researching the long storage of plutonium.

The experimental studies of Pu and its compounds have been limited because of the international rules, radio-toxicity of Pu, and so on. Moreover, α-Pu_2O_3 is so active in atmosphere that it is too difficult to be detected. However, the atomic simulation by using computational techniques is free from these limitations for such materials. Atomic simulation is comprised of the molecular statics (MS) and molecular dynamics (MDs) methods, with empirical interatomic potential between atoms. The empirical potential functions, essential part of the atomic simulation, were studied systematically by Lewis and Catlow [5,6] about ionic oxides related to nuclear fuel materials. And the useful potential parameters of Born–Mayer–Huggins (BMH) type with or without the shell model were presented. Recently, for some thermal properties of UN, PuN, UO_2 and PuO_2 such as thermal expansion, ionic diffusion and heat capacity, the MD simulation was extensively carried out by Yamada and Kurosaki [7–10]. Terentyev [11] studied the thermal properties and oxygen transportation of mixed-oxide fuels with the BMH potential of partially ionic model.

The evaluation of properties of α-Pu_2O_3 is also very important, from which we can estimate its thermal stability, chemical activity and catalytic property in Pu + H_2 and Pu + O_2 and/or N_2 reactions. However, it seems that there are no reports about the simulation of α-Pu_2O_3 by MS or MD.

In this paper, we studied entropy and enthalpy of PuO_2 and α-Pu_2O_3 as well as their heat capacity and thermal expansion by MS and MD simulations. Our calculated results were in good agreement with experimental data.

2. Simulational details

2.1. Crystal structure

The fcc (CaF_2-type) crystal structure of PuO_2 is shown in Fig. 1a (with a_0 = 5.3960 Å). Its space group is *Fm3m*. α-Pu_2O_3 is considered to be formed at low temperature by facile movement of anions in the preexisting fcc metal lattice of δ Pu or δ *Pu–Ga* alloy. Fig. 1b shows the unit cell of α-Pu_2O_3 optimized by MS, consist of 16 plutonium atoms and 24 oxygen atoms. Its space group is *Ia3*. The bcc (Mn_2O_3-type) structure with a_0 = 11.04 Å shows that, α-Pu_2O_3 seems to come from ordered removal of oxygen atoms from a fourth of the anion sites in the cell of PuO_2 [1,12]. The fractional coordinates of cations and anions in α-Pu_2O_3 cell are not

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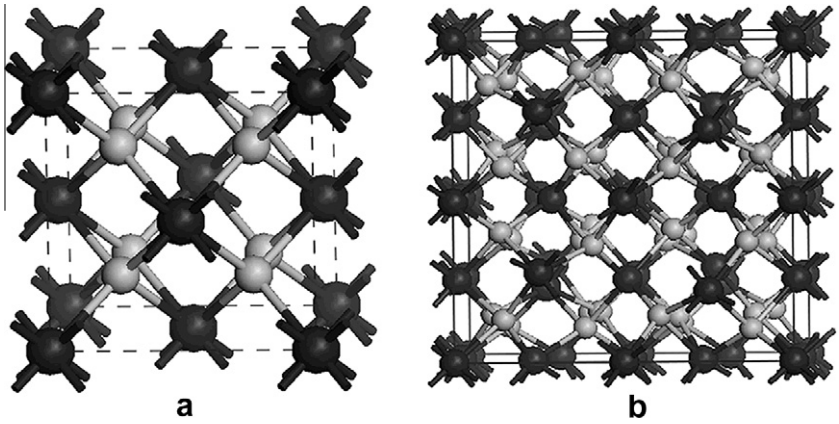

Fig. 1. The unit cell of PuO_2 (a) and α-Pu_2O_3 (b) optimized by MS (large black atom: Pu, small gray atom: O).

fully consistent with those in Mn_2O_3, because its cell structure is very complex and the interaction of Pu–O is different from that of Mn–O.

2.2. Interatomic potential function

The GULP program [13–16], including MS and MD methods, was used to simulate PuO_2 and α-Pu_2O_3 structures. All calculations have been performed by using the BMH pair interatomic potential and shell model potential with the fully ionic model for the Pu–O system.

The BMH potential function is given by:

$$\Phi_{ij}(r) = \frac{Z_i Z_j e^2}{r_{ij}} + A\exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6} \quad (1)$$

where r_{ij} is the distance between ions of types i and j, z_i is the charge of type i. Potential parameters, A_{ij}, ρ_{ij} and C_{ij}, for O–O pairs are obtained from Ref. [16]. And the ones for Pu–O pairs in PuO_2 are obtained from Ref. [10]. The first term on the right side of Eq. (1) stands for the long-range Coulomb interaction. In order to avoid the divergence of the calculation concerning the long-range term, Ewald summation algorithm was introduced into the GULP program. Other terms stand for short-range interactions: the second one is the repulsive potential between ionic cores, and the third one is originated from van der Waals interaction. But the Potential parameters for Pu–O pairs in α-Pu_2O_3 structure are determined by the try-and-error method here, in order to reproduce the experimental cell parameters, density and space group at room temperature.

Another shell model potential function proposed by Dick and Overhauser is taking the polarization of ions into account quantificationally [15]. In this model, ions are consist of a core (including the atomic nucleus shielded by the inner electrons) and a shell (corresponding nominally to the valence electrons). For an ion i, the interaction between the core and the massless shell, on which all pair potentials act, is described by the potential of a harmonic oscillator:

$$U = 1/2K_{2i}\,R_i^2 \quad (2)$$

where R_i is the distance between the core and the shell, and K_{2i} is the elastic coefficient. This type of potential has been fitted for the oxygen ion of PuO_2 by Gale [16]. There only the polarization of oxygen ion has been considered. The charges of O_{core} and O_{shell} are 0.86 and −2.86 respectively. And the cations are represented by formal charges Pu^{4+} and Pu^{3+}. These obtained potential parameters are given in Table 1.

2.3. Procedure of atomic simulation

Recently, different thermal properties of PuO_2 and α-Pu_2O_3 were studied separately by MS and MD simulation. The atomic simulations were carried out as following steps.

According to the potential parameters in Table 1, the simulations were performed in $5 \times 5 \times 5$ unit cells for PuO_2 ($Pu_{500}O_{1000}$, with total 2512 particles), while in $3 \times 3 \times 3$ unit cells for α-Pu_2O_3 ($Pu_{864}O_{1296}$, with total 3456 particles). The MS optimization criterion is that energy tolerance of every atom in last optimization step is less than 0.00001 eV, and the last gradient norm tolerance of calculated system is less than 0.001 eV.

For MD simulation, in order to avoid the transition state of the system, the so-called 'initial relaxation' calculation was done under the desired temperature and pressure. It took 3×10^4 steps (a time step is 0.5 fs) to relax the system. Then the MD simulation with 6×10^4 steps was performed to deduce the relevant results under the same desired temperature and pressure, using NPT ensemble.

3. Results and discussion

3.1. Some properties in standard condition

In order to obtain the reliable results from the atomic simulation, it needs to know whether the selected interatomic potential parameters are reasonable first. We tried to simulate the properties of PuO_2 and α-Pu_2O_3 at 298 K in 1 atm, because in this condition there are more experimental data in the literature that can be used to evaluate the calculated results. Comparisons between the calculated and experimental parameters of PuO_2 and α-Pu_2O_3 are given in Table 2. The agreement with the experimental values is fairly satisfactory. So we suggest that the optimized potential parameters of Pu–O pairs in α-Pu_2O_3 in this paper and selected other parameters are appropriate.

3.2. Thermal expansion

Fig. 2 shows the lattice constants for PuO_2 and α-Pu_2O_3 estimated by MD simulation as a function of temperature between 298 K and 1500 K. As shown in Fig. 2a, the calculated lattice constants for PuO_2 are in good agreement with the experimental data. Though it is determined by the balance of forces among particles in the simulated cell, the predicted results cannot be thermally expanded as much as experimental data. Because the Coulomb force between ions depressed, especially between plutonium and oxygen, which leads to relatively large thermal expansion at high temperature.