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First-principles investigation of the physical properties of cubic and orthorhombic phase Na_3UO_4

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ABSTRACT

The anisotropic elastic properties, Vickers hardness, Debye temperature and the minimum thermal conductivity of *c*-Na_3UO_4 and *o*-Na_3UO_4 have been investigated by means of the first principles calculations. The lattice parameters are in good agreement with the available experimental data and the theoretical results. The elastic constants satisfy the mechanical stability criteria show that both of them are mechanically stable. The value of *B*/*G* and Cauchy pressure reveal that the *c*-Na_3UO_4 holds a ductile behavior while the *o*-Na_3UO_4 behaves a brittle manner. The elastic anisotropy of *c*-Na_3UO_4 is less weak than that of *o*-Na_3UO_4. The hardness shows that both of them can be classified as "soft materials". Finally, the Debye temperature is 452.6 K and 388.4 K, and the minimum thermal conductivities k_{min} is 0.883 W m^{-1} K^{-1} and 0.753 W m^{-1} K^{-1} of *c*-Na_3UO_4 and *o*-Na_3UO_4, respectively. Due to relatively lower thermal conductivity, and thereby they are suitable to be used as thermal insulating materials.

1. Introduction

Looking around the world, rapid development of the national economy has given rise to energy shortages, and the reliance on fossil fuels has led to much environmental pollution. The nuclear power is possibly the key to resolving energy shortage problem quickly, while the storage or disposal of high-level radioactive waste is a subject of primary concern not only for public security, but also for the nuclear industry development. One effective way is to transmute the long-lived and highly radiotoxic of actinide elements (^{237}Np, ^{241}Pu and ^{241}Am) in spent nuclear fuel into less radioactive elements or isotopes with shorter half lives [1,2]. Sodium-cooled fast reactors (SFR) are considered to be a promising option for management of the actinides. The metallic sodium come in and react with the $(U,Pu)O_2$ fuel, the main reaction products are $Na_3U_{1-x}Pu_xO_4$ with much lower density and thermal conductivity relative to the $(U,Pu)O_2$ fuel [3–7]. For this reason, many researches had been carried out on the Na-U-O system in order to study the crystal structures and thermodynamic properties of the potential reaction products [8–18].

According to Scholder and Gläser's reported [19], Na_3UO_4 exhibits a face-centered-cubic (*fcc*) structure with a = 4.77–4.79 Å in which the Na and U atoms are randomly distributed throughout the cationic sites at room temperature (this phase is known as α-phase, in this work we called *c*-phase). Bartram et al. [20] discovered a second *fcc* structure at high temperature (> 1273 K) with space group *Fd3-m* and a cell parameter of 9.56 Å (known as β-phase). O'hare [13] investigated the enthalpy of formations of α-Na_3UO_4 is -477.7 ± 0.9 kcal mol^{-1}. Fredrickson et al. [14] measured the enthalpy of Na_3UO_4 using high-precision drop-calorimetric system in the temperature range 298–1200 K. Lorenzelli et al. [4] observed a reversible phase transition between the α and β forms around 1348 ± 25 K. Hofman et al. [15] discussed thermal conductivity and thermal expansion of Na_3UO_4. The results show that compositional differences in the samples have a pronounced effect on thermal expansion and on thermal conductivity below 773 K. Persson [21] predicted an orthorhombic structure with space group *cmmm* and a = 5.81 Å, c = 3.499 Å and γ = 107.827° (in this work we called *o*-phase). Up to now, to the authors' knowledge, there have not been detailed studies for the elastic properties, hardness, Debye temperature and the minimum thermal conductivity of Na_3UO_4. In view of these circumstances, we calculated the elastic and anisotropy properties of Na_3UO_4 by using the first-principles. We have also analyzed the hardness, Debye temperature and the minimum thermal conductivity of Na_3UO_4 in order to understand their physical properties.

2. Calculation methods

In this work, the calculations were performed using the density functional theory (DFT) within the ultrasoft pseudo-potential plane-

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Table 1
Calculated equilibrium lattice parameters a and c along with the experimental data and theoretical results.

Materials	Phase	Space group	a (Å)		c (Å)		γ (°)	
			Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
c-Na_3UO_4	cubic	Fm-3m	4.755	4.770	-/-	-/-	-/-	-/-
o-Na_3UO_4	orthorhombic	$cmmm$	5.747	5.810*	3.496	3.499*	109.692	107.827*

* Data come from Ref. [21].

wave (UPPW) method as implemented in the CASTEP code [22]. For the exchange and correlation terms, the Perdew-Burke-Ernzerhof for solids (PBEsol) [23] function was used within the generalized gradient approximation (GGA). Using the UPPW, the $2s^22p^4$ of O, $2s^22p^63s^1$ of Na and $5f^36s^26p^66d^17s^1$ of U were treated explicitly as valence electrons. Plane-wave cutoff energy is 800 eV and an 8 × 8 × 8 Monkhorst-Pack k-point ensures convergence in energy to within 1 meV.

3. Results and discussions

3.1. Structural properties

To investigate ground-state properties, the optimized lattice constants of Na_3UO_4 were computed first. In the present work, the optimized lattice constants were calculated by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme [24–27]. The calculated results are summarized in Table 1, along with the available experimental data and theoretical results for comparison. For the c-Na_3UO_4, the optimized lattice constant a = 4.755 Å is somewhat underestimated from experimental data (4.77 Å) [13,19]. The difference between our result and experimental data is less than 0.32%. For the o-Na_3UO_4, our calculated value a = 5.747 Å, c = 3.496 Å and γ = 109.692°, which are smaller than that of Persson's reported (a = 5.81 Å, c = 3.499 Å and γ = 107.827°) [21]. The difference between our results and reported data are less than 2%. These results confirm that the methods used in the present work are reliable, and thereby the optimized lattice constants can be used for future calculations of elastic and thermodynamic properties.

3.2. Mechanical properties of polycrystalline aggregates

The elastic constants, an important property of solid which is closely related to various fundamental physical properties, are calculated by using the stress-strain method. The three elastic constants (C_{11}, C_{44} and C_{12}) for c-Na_3UO_4 and nine elastic constants (C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13} and C_{23}) for o-Na_3UO_4 at zero pressure are given in Table 2. For the o-Na_3UO_4 the C_{33} is bigger than C_{11} and C_{22}, which means that the resistance against deformation along the [001] are higher than that of the [100] and [010] direction.

A given crystal structure cannot exist in a stable phase unless its elastic constants obey certain relationship. For the cubic crystals, as is known, the mechanical stability criteria are given by [28]:

$$\begin{Bmatrix} C_{11} > 0;\ C_{44} > 0 \\ C_{11} - C_{12} > 0 \\ C_{11} + 2C_{12} > 0 \end{Bmatrix} \tag{1}$$

Table 2
Calculated elastic constants C_{ij} (GPa) of Na_3UO_4.

Materials	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
c-Na_3UO_4	184.8	-/-	-/-	69.4	-/-	-/-	87.4	-/-	-/-
o-Na_3UO_4	104.3	98.3	203.6	28.6	57.4	47.2	34.2	29.8	29.1

whereas, for the orthorhombic crystal, the criteria are [29]:

$$\begin{Bmatrix} C_{ii} > 0,\ i = 1\sim6 \\ C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0 \\ C_{11} + C_{22} - 2C_{12} > 0 \\ C_{11} + C_{33} - 2C_{13} > 0 \\ C_{22} + C_{33} - 2C_{23} > 0 \end{Bmatrix} \tag{2}$$

From the Table 2, all of elastic constants are satisfying the mechanical stability criteria, meaning that both of them are mechanically stable.

The bulk modulus B and shear modulus G are two important mechanical quantities for technology and engineering applications. The B and G were determined using the Voigt-Reuss-Hill approximation [30].

$$X = \frac{1}{2}(X_V + X_R),\ (X = B,\ G) \tag{3}$$

where $X_{V,R}$ are Voigt's and Reuss's modulus corresponding to the upper and lower bound of G and B values, respectively. For the cubic phase, the Voigt's and Reuss's modulus are [31]:

$$\begin{Bmatrix} G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \\ B_V = B_R = \frac{1}{3}(C_{11} + 2C_{12}) \\ G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \end{Bmatrix} \tag{4}$$

For orthorhombic phase, they are [31]:

$$\begin{Bmatrix} G_V = \frac{1}{15}[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})] \\ G_R = 15\{4[C_{11}(C_{22} + C_{33} + C_{23}) + C_{22}(C_{33} + C_{13}) + C_{33}C_{12} \\ \quad - C_{12}(C_{23} + C_{12}) \\ -C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} + C_{23})]/\Delta + 3(\frac{1}{C_{44}} + \frac{1}{C_{55}} + \frac{1}{C_{66}})\}^{-1} \\ B_V = \frac{1}{9}[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] \\ B_R = \Delta[C_{11}(C_{22} + C_{33} - 2C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{33}C_{12} \\ \quad + C_{12}(2C_{23} - C_{12}) \\ +C_{13}(2C_{12} - C_{13}) + C_{23}(2C_{13} - C_{23})]^{-1} \\ \Delta = C_{13}(C_{12}C_{23} - C_{13}C_{22}) + C_{23}(C_{12}C_{13} - C_{23}C_{11}) + C_{33}(C_{11}C_{22} - C_{12}^2) \end{Bmatrix} \tag{5}$$

Through the B and G, the Young modulus E and Poisson's ratio σ can be computed: $E = 9BG/(3B + G)$ and $\sigma = (3B - 2G)/(6B + 2G)$[32]. The obtained values of the above-mentioned macroscopic elastic parameters are illustrated in Table 3. The B denotes the resistance against volume change under hydrostatic pressure, while the G reflects the resistance against shape change caused by a shearing force. The calculated B for c-Na_3UO_4 (119.9 GPa) is higher than o-Na_3UO_4 (63.3 GPa), indicating that c-Na_3UO_4 in lower compressibility than o-Na_3UO_4. The c-Na_3UO_4 can withstand higher shear stress than o-Na_3UO_4 due to its higher shear modulus value. Moreover, the ratio of B/G can be utilized for predicting brittle or ductile behavior of polycrystalline materials. According to Pugh criterion, if $B/G > 1.75$ the material behaves in a ductile manner, otherwise, it behaves a brittle