



States of the Schottky defect in uranium dioxide and other fluorite type crystals: Molecular dynamics study



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ABSTRACT

Mass transfer processes in fluorite-type systems are determined by the diffusion of cations via vacancies from Schottky defects. To predict diffusion coefficients of cations and other parameters based on it the Lidiard and Matzke approximation of the point defects model, namely the assumption of isolated vacancies, is widely used. States of the Schottky defect were studied with the high-speed molecular dynamics method in a wide temperature range, with six different interaction potentials. Schottky vacancies were dynamically detected during the simulation. It is shown that contrary to the Lidiard and Matzke model, the Schottky cation vacancy is always associated with anion vacancies.

The degree of the Schottky defect association depends on the temperature, at high temperatures near the cation vacancy two or more anion vacancies are located. It is shown that the calculated formation energy of Schottky defects in the form of the trivacancy (5.8–7.4) eV for all potentials are close to the experimental value (6–7) eV, in contrast to the formation energy of Schottky defects in the form of isolated vacancies that exceeds 10 eV.

Point defects model of the simulated system in the presence of an artificially created Schottky defect was constructed and compared with calculation results. According to our study the point defects model is applicable only at low temperatures less than half of the melting temperature.

It is shown that the presence of anion vacancies near the cation vacancy reduces the migration energy of cations. However, for systems with several Schottky defects the vacancy clusterization and the formation of voids are observed. This leads to an increase of the diffusion activation energy due to the contribution of the energy that needs to separate the single cation vacancy from the void.

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1. Introduction

The task of the prediction of the behavior and properties of crystalline systems with the fluorite structure, typical examples of which are the uranium dioxide and substitution solid solutions such as uranium–plutonium oxide, is one of the most important problems in materials science. The specificity of the fluorite-type structure is a very high stability (a low mobility) of the cation sublattice in comparison with the anion sublattice. At high temperatures the anion sublattice exists in a superionic state and the mobility of anions are close to the mobility of ions in melts [1,2]. The diffusion of cations in the crystal lattice of the specified type occurs by the vacancy mechanism via Schottky vacancies [3–5]. Mass transfer processes in the cation sublattice limit the crystal

stability, creep, cracks growth and similar parameters that are crucial for the long term exploitation of materials in heavy-load conditions, such as uranium dioxide in nuclear reactors and solid solutions based on the cerium dioxide in solid oxide fuel cells.

The diffusion of cations via the vacancy mechanism with Schottky defects is determined by the defect formation energy and its migration energy. In principle, these parameters are easily calculated by the lattice statics method with semi-empirical interaction potentials, or by ab initio methods. But despite successes of these methods, the analysis of the published data shows that calculated formation energies of a Schottky defect with different interaction potentials for uranium dioxide (8–15) eV [6,7], as well as ab initio calculations (7.6–10.6) eV [8,9] systematically overestimate experimental values of the formation energy equal to (6–7) eV [3]. Calculated migration energies of cations systematically overestimate experimental values as well.

Calculations of the Schottky defect formation energy are based on the assumption that the defect consists of the isolated cation vacancy and two anion vacancies, ideally separated to the infinity

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distance from each other. It is in fact assumes that the temperature is sufficiently high to “scatter” vacancies through the crystal and the concentration of Schottky defects is sufficiently low. In a commonly used approximation of Lidiard and Matzke (see for example [4]) in the model of point defects it is postulated that cation and anion vacancies in a Schottky defect are isolated and do not form any complexes. However, it is known that the point defect model is not able to describe, for example, superionic transition, which was studied well experimentally [1,2] and by the molecular dynamics (MD) method for systems with the fluorite structure. This model is also poorly applicable in general to systems with a high defect concentration and with the strong interaction between defects. Therefore it is interesting to find out, using the molecular dynamics method, states of cation vacancies (isolated or associated with anion vacancies) at different temperatures, as well as to clarify limits of the applicability of the standard thermodynamic model of point defects.

There are no published studies in the literature in which vacancies had been determined dynamically during the MD simulation. Instead, indirect methods such as analysis of the radial distribution function of anions around cations [10] or the determination of the number of ions in a certain region (calculation of the number of nearest neighbors) with following freezing and visual observations [7] are used. In fact, in the latter case authors concluded that at high temperatures one anion vacancy is located near the cation vacancy in the uranium dioxide.

It is interesting to determine anion and cation vacancies dynamically during the MD simulation, which will make possible to derive the spatial distribution of anion vacancies around the cation vacancy and to calculate the corresponding temperature dependences. This will give an opportunity to examine the state of the Schottky defect in a wide range of temperatures, and to carry out a direct comparison with experimental data. The calculation of the migration energy of cations in the presence of anion vacancies nearby, both by the method of lattice statics and by the MD method at high temperatures, as well as the study of the interaction of cation vacancies, can also clarify the mass transport properties in fluorite-type crystals.

To eliminate the influence of a specific interaction potential set on general results of MD simulations, all calculations in this study were carried out with six sets of pair interaction potentials for four crystals with the fluorite-type structure.

2. MD details

2.1. MD simulation technique and interaction potentials

In this paper we used the home-made program, which realize the classical MD method using graphics processors to accelerate calculations, and was described in detail in [11,12]. Simulations were performed in the approximation of pair interaction potentials and rigid ions (without the shell model). In this study crystals with the fluorite lattice type (space group $Fm\bar{3}m$), namely stoichiometric uranium dioxide, cerium dioxide, barium fluoride and pseudo-crystal of MOX-fuel ($U_{0.8}Pu_{0.2}O_2$) [13], were investigated.

For the uranium dioxide three sets of interaction potentials, namely MOX-07 [14,15], Arima-05 [16] and Yakub-09 [17], were used. All these potentials are semi empirical with non-integer charge, and are fitted to different thermophysical properties of the uranium dioxide. MOX-07 and Arima-05 potentials have the form of Buckingham–Morse form and the Yakub-09 potentials set has the Buckingham–Morse form. According to comparative reviews [6,15,18], where the quality of interaction potentials was estimated based on the reproducibility of experimental parameters

of the uranium dioxide, MOX-07 and Yakub-09 potentials are most appropriate for MD simulations.

Barium fluoride crystals were simulated using the Catlow-77 potential set [19], which was derived in 1977. For the simulation of the cerium dioxide the recently created Cui-11 potentials set [10] was chosen. It was derived from first principles and was fitted to pair interaction potential with a formal charge and Morse form. In general it should be noted, that, despite the successes of ab initio methods, they lead to significantly overestimated values of the lattice parameter and melting temperature in comparison with the experimental data. For the investigation of the mixed uranium–plutonium fuel authors in [13] proposed an approach where U and Pu cations are replaced by some pseudo-cation X, and the system of XO_2 with the fluorite-type structure is simulated. Potentials for this binary system are fitted to experimental data of the ($U_{0.8}Pu_{0.2}$) O_2 system. This potential set will be denoted as Basak-12 below in the text.

With all of these potentials the time step of 3.5 fs in the MD integrator was used, and it does not give any noticeable integration errors. Simulations were performed under periodic and isolated boundary conditions. Simulation technique with periodic boundary conditions (PBC) is widely used and it is de-facto the standard for calculations by the MD method. In this study we generally used the cubic supercell of 4116 ions under PBC (7 unit cells in one dimension), and applied the Berendsen barostat [20] with a relaxation time of 1 ps. Nanocrystals of a finite size in a vacuum were simulated under isolated boundary conditions (IBC), and this approach is relevant in connection with modern tendencies of nanoscale objects creation. One of the advantages of this approach is the presence of a free surface, where Schottky defects, actually investigated in the present work, are formed. This surface in the equilibrium has a complicated Wulff shape [21]. For simulations nanocrystals of 12,000 ions with an equilibrium shape of the octahedron with truncated corners [22] were used.

2.2. Vacancy detection

Anion vacancies are extremely mobile, especially at high temperatures. And it is also desirable to somehow exclude short-living anti-Frenkel anion vacancies. The algorithm we used to detect anion vacancies was as follows. The average period of anion oscillations is approximately 50 MD steps (175 fs) and weakly depends on temperature. The average period and amplitude of ion oscillations were derived by the registration of local extremums of ion coordinates separately along X, Y and Z axis. The extremum was registered at N MD step if the ion coordinate $x(N)$ was more (or less) than $x(N-1)$ and $x(N+1)$. The positions of knots in the ideal anion sublattice were derived and updated through cation positions every 10,000 MD steps, and every 50 MD steps coordinates of anions were averaged over this period. If near the knot at a distance less than $a\sqrt{3}/8$ (half the distance between the knot and interstitial in the anion sublattice) no one anion with averaged coordinates was detected, then the knot was considered as vacant. Knots, that have not been marked as vacant at least two periods in succession, were considered as occupied – thus we excluded very short-living anti-Frenkel (exchange) vacancies and situations where the anion was migrating from one knot to another. Occupation number of each anion sublattice knot was calculated every 500 MD steps, and was defined as the number of periods in which the knot was marked as vacant, divided by 10 – the overall number of calculation periods.

The mobility of cations is substantially lower than that of anions, thus to detect the cation vacancy it is sufficient to check the absence of cations in the knot every 500 steps MD, averaging cation coordinates during this period. Cation vacancies should be

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