Molecular dynamics study of irradiation damage in $LaPO_4$ and $YbPO_4$

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Abstract. *The radiation resistance of the monazite $LaPO_4$ and the compound $YbPO_4$ (zircon structure type) has been investigated using the computer simulation. The number of Frenkel pairs, which are formed in the structure of these minerals after the passage of a primary knock-on thorium atom with an energy of 30 keV, has been calculated by the molecular dynamics method. The formation of Frenkel pairs and their recombination in the motion of recoil nuclei in the structure of the studied minerals have been discussed. It has been shown that the probability of the "survival" of Frenkel pairs in the $LaPO_4$ monazite is significantly lower than in the $YbPO_4$ compound. The tendency of these minerals toward amorphization under radiation damage has been described numerically. The obtained results have demonstrated that one of the main factors determining the radiation resistance of orthophosphates $LnPO_4$ is the type of crystal structure, and the compounds with the monazite structure are more radiation resistant than the compounds with the zircon structure.*

Keywords

Radiation resistance of minerals, semiempirical interatomic potential method, grid-calculations, computer simulation, method of molecular dynamics

1 Introduction

Over recent decades, in a number of countries there has been traced a tendency to increase the use of electricity generated by nuclear power plants. In particular, according to the International Atomic Energy Agency (IAEA) data, in 2012 the share of electricity generated by nuclear power plants is 75% in France, 46% in Ukraine, 19% in the United States, and 18% in the Russian Federation [1]. On the other hand, the prospects for the development of nuclear power engineering are associated with the effective management of nuclear waste.

The development of nuclear power engineering raises a number of problems relating to the disposal of long-lived radioactive waste and plutonium. One of the main problems in this respect is the choice of radiation resistant matrices, which, in contact with long-lived high-level radioactive waste, for a long time will not change their physical and chemical properties. At present, aluminophosphate or borosilicate glasses have been used as matrices for spent fuel. However, high-level radioactive waste can be stored in these matrices for a time of no longer than 30–40 years. This is the reason that the search for matrices with efficient performance characteristics has been actively continued. It has been found that crystalline ceramic materials are significantly better suited for the utilization of high-level radioactive waste. To date, a number of ceramic materials have been developed for the disposal of high-level radioactive waste and plutonium. Extensive studies have been performed on materials such as zircon $ZrSiO_4$, pyrochlores $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$, monazites $(La,Ce,Nd)PO_4$, zirconolite $CaZrTi_2O_7$, perovskite $CaTiO_3$, and other complex oxides, as well as rutile TiO_2 and baddeleyite ZrO_2.

Many researchers have considered zircon as a promising matrix for the disposal of nuclear fuel and weapon-grade plutonium [2–5]. However, over geological time, the alpha decay of uranium and thorium atoms leads to the damage of the structure of zircon and its transition from the crystalline state to the X-ray amorphous (metamict) state. Each act of alpha decay results in the formation of an alpha particle and a heavy recoil atom [5]. Alpha particles with an energy of 4.2–5.5 MeV, as was noted in [4], displace approximately 100 atoms in the end of the path with a length of 10–20 μm, whereas heavy recoil atoms with an energy of 70–90 keV displace several thousand atoms within an interval of 20 nm.

A promising alternative for zircon can be natural orthophosphates $LnPO_4$ (Ln is a lanthanide) with the structures of zircon and monazite, as well as their artificial analogues. In contrast to zircon, these compounds are very rare in the

metamict state despite the significant amount of uranium and thorium atoms [6]. The orthophosphates containing heavy rare-earth elements (Tb, Tm, Yb, Lu) crystallize in the tetragonal zircon structure ($I4_1/amd$) [7]. The monazites containing lighter and larger rare-earth elements (from La to Dy) are characterized by the monoclinic monazite structure ($P2_1/n$) [8]. Earlier, the radiation resistance of these compounds was experimentally investigated by Meldrum et al. [6, 9]. The results of these studies showed that orthophosphates with the monazite structure have a higher radiation resistance than the orthophosphate containing heavy rare-earth elements. In particular, the critical temperature of amorphization (the temperature above which the material does not transform into an amorphous state under irradiation with a beam of heavy particles) is $T_c \sim 1000$ K for zircon [9], 570 K for the $YbPO_4$ compound with the zircon structure, and 333 K for the $LaPO_4$ monazite [6]. The processes of forming and annealing a damaged region, resulting from the alpha decay, usually occur for a few tens of picoseconds. Therefore, in order to investigate the damage of minerals due to the alpha decay, in addition to experimental studies it is extremely useful to carry out computer simulation experiments.

The purpose of this work was to perform a computer simulation for investigating the mechanisms of formation of a displacement cascade and the subsequent relaxation processes in the structure of the $LaPO_4$ monazite and in the $YbPO_4$ compound with the zircon structure as a result of the alpha decay due to the recoil of the nucleus.

2 Simulation technique

The molecular dynamics (MD) method consists in calculating trajectories of the motion of all atoms involved in a system on the basis of Newton's second law. The initial data are taken as the initial coordinates and velocities of all the atoms and the interatomic interaction potentials. In addition to the Coulomb interactions of all electrostatic charges between themselves, the interatomic interaction potential takes into account the repulsion of electron shells of the atoms and the dipole–dipole interaction between the atoms in terms of the short-range interaction Buckingham potential:

$$V(r) = A \cdot \exp(-r/\rho) - C \cdot r^{-6}, \quad (1)$$

where r is the distance between two atoms (Å), A is the pre-exponential factor for the term characterizing the repulsion (eV), ρ is the stiffness parameter (Å), and C is the force parameter of the van der Waals interaction (eV·Å^6).

Parameters specified in (1) were taken from work [10]. Optimization of these structures was made using experimental values of unit-cell parameters, atom coordinates, elastic constants, and thermodynamic properties.

In the structure of the monazite, we chose a fragment containing approximately 5 million atoms. One of the lanthanum atoms was replaced by a thorium atom. At small interatomic distances (less than 1 Å), we used the internuclear repulsion potential ZBL, which was introduced to correctly take into account the strong internuclear repulsion [11]. The simulation time step was 0.5 fs.

As a result of critical consideration of various programs, we dwelt on the DL_POLY program complex [12], elaborated for simulation of structural fragments of minerals, macromolecules, polymers, and ion systems. This program complex gives an opportunity to of radiation mineralogy (investigation of structures due to alpha decay of actinides), study of processes in minerals, study of forming migrations of point defects in these minerals. For realization of calculations the web-sites of uagrid.org.ua and grid.inpracom.kiev.ua were used. All calculations were executed in the virtual organization «GEOPARD», organized by Glushkov Institute of Cybernetic of NAS of Ukraine, M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of NAS of Ukraine and S.I. Subbotin Institute of Geophysics of NAS of Ukraine.

3 Results and discussion

The motion of a primary knock-on atom leads to its collision with other atoms of the system. These atoms are displaced from their equilibrium positions, begin to move, and, in turn, displace other atoms. This stage can be referred to as ballistic. This process results in the creation of an amorphous zone surrounded by relatively undistorted regions (point defects). A substantial fraction of displaced atoms returns to their original positions during a period of several picoseconds. Other atoms form a displacement cascade (Fig. 1).

For a more detailed investigation of the processes occurring in a cascade of displaced atoms, we examined the differences in the kinetics of accumulation and recombination of defects for the two minerals.

The estimated probability of the "survival" of Frenkel pairs of the oxygen atoms (FP(O)) for the studied structures depends on the displacement of the oxygen atoms: with an increase in the distance between the vacancy and the displaced atom (d_{V-I}), the probability of the recombination of Frenkel pairs decreases (Fig. 2). These data also indicate

that the probability of the "survival" of Frenkel pairs is significantly lower in the structure of the $LaPO_4$ monazite than in the $YbPO_4$ compound.

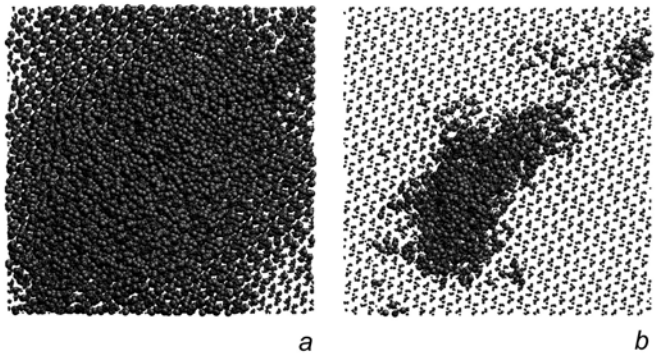

Figure 1. Radiation damage, produced by 30 keV Th recoil in monazite at the peak of the damage (*a*) and after structure relaxation (*b*).

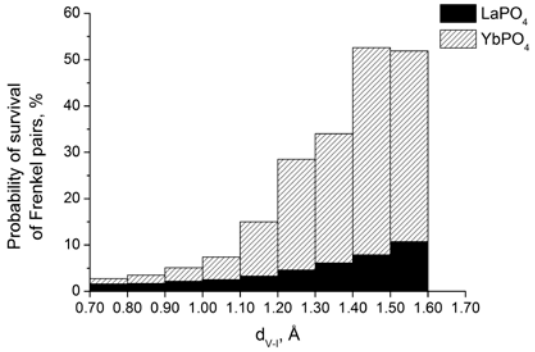

Figure 2. Relative number of *FP*(O) on the distance between the vacancy and the displaced atom for $LaPO_4$ and $YbPO_4$.

In [13], we proposed the parameter δ, which reflects the tendency of minerals toward amorphization under radiation damage. This parameter characterizes a part of the energy of a knock-on atom, which is consumed for the formation of Frenkel pairs in a cascade of displaced atoms, and can be calculated according to the formula

$$\delta = \frac{1}{E_{PKA}}(E_{FP}(\mathrm{Ln}) \cdot N_f(\mathrm{Ln}) + E_{FP}(\mathrm{P}) \cdot N_f(\mathrm{P}) + E_{FP}(\mathrm{O}) \cdot N_f(\mathrm{O})), \quad (2)$$

where E_{FP}(Ln), E_{FP}(P), and E_{FP}(O) are the energies of Frenkel pairs of the atoms Ln, P, and O, respectively; N_f(Ln), N_f(P), and N_f(O) are the numbers of Frenkel pairs of the atoms Ln, P, and O, respectively, at the end of the simulation; and E_{PKA} is the energy of the knock-on atom.

The calculations have demonstrated that the parameter δ is equal to 0.39 for the $LaPO_4$ monazite, whereas for the $YbPO_4$ orthophosphate, it is approximately equal to unity. These values are consistent with the experimental data: the critical temperature of amorphization is equal to 570 K for the $YbPO_4$ compound and 333 K for the $LaPO_4$ monazite [6].

4 Conclusions

The mechanisms of radiation-induced damages in the $LaPO_4$ monazite and in the $YbPO_4$ compound with the zircon structure as a result of the alpha decay due to the recoil of the nucleus have been investigated using the molecular dynamics computer simulation. The kinetics of accumulation and recombination of Frenkel pairs in the cascade of displaced atoms after the passage of the primary knock-on thorium atom with an energy of 30 keV in the monazite structure were calculated.

We introduced a parameter that reflects the tendency toward amorphization of the minerals under radiation damage. This parameter characterizes a part of the energy of a knock-on atom, which is consumed for forming Frenkel pairs in a cascade of displaced atoms. The results have shown that this parameter for the $LaPO_4$ monazite is equal to 0.39, and for the $YbPO_4$ orthophosphate, it is approximately equal to unity. This is in agreement with the experimental data.

The obtained results have also demonstrated that one of the main factors determining the radiation resistance of the orthophosphates $LnPO_4$ is the type of structure. Compounds with the monazite structure are more radiation resistant than compounds with the zircon structure. The higher radiation resistance of the $LaPO_4$ monazite as compared to the $YbPO_4$ compound is most likely also associated with the longer relaxation of the monazite structure.

The results of this investigation can be used to solve the fundamental and applied problems associated with the isolation and disposal of high-level radioactive waste and, in particular, to evaluate the radiation resistance of orthophosphate matrices proposed for waste disposal. The computer simulation performed in this work can be helpful in analyzing and predicting the behavior of matrices under radiation effects. The obtained results can also be useful in saving time and financial resources and, eventually, in choosing the most suitable matrices.

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