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Material fast transport in nano-crystals of (AB_{n-x})-type ionic compounds

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The effectiveness of material transport by the mechanism of single-file diffusion in comparison with the conventional mechanism of the classical diffusion of atoms is discussed. The conditions under which the single-file diffusion can provide fast mass transport are considered. The analysis and assessment made indicate that the diffusion of atoms along one-dimensional vacancy clusters formed in the (AB_{n-x})-type ion nano-crystals, may have a much faster mass transport compared to transport by the classical diffusion mechanism of atoms, which is defining for massive crystals.

Keywords: single-file diffusion, one-dimensional vacancy clusters, (AB_{n-x})-type ion nano-crystals.

Обговорюється ефективність транспорту речовини механізмом однофайлової дифузії у порівнянні з механізмом звичайної класичної дифузії атомів. Розглянуто умови, за яких однофайлова дифузія може забезпечити прискорений масоперенос. Проведений аналіз та оцінка свідчать про те, що дифузія атомів вздовж одномірних вакансійних кластерів, що формуються в іонних нано-кристалах типу AB_{n-x}, може характеризуватися значно швидшим перенесенням речовини порівняно з перенесенням звичайним класичним механізмом дифузії, який є визначальним для масивних кристалів.

Ключові слова: однофайлова дифузія, одномірні вакансійні кластери, іонні нано-кристали типу AB_{n-x}.

Обсуждается эффективность транспорта вещества механизмом однофайловой (одноканальной) диффузии по сравнению с механизмом обычной классической диффузии атомов. Рассмотрены условия, при которых однофайловая диффузия может обеспечить ускоренный массоперенос. Проведенный анализ и сделанная оценка свидетельствуют о том, что диффузия атомов вдоль одномерных вакансионных кластеров, формирующихся в ионных нано-кристаллах типа AB_{n-x}, может характеризоваться значительно более быстрым переносом вещества по сравнению с переносом обычным классическим механизмом диффузии, который является определяющим для массивных кристаллов.

Ключевые слова: однофайловая диффузия, одномерные вакансионные кластеры, ионные нано-кристаллы типа AB_{n-x}.

Introduction

Nano-crystals – are the crystals with the linear size of $\leq 1-10$ nm. As the experimental and theoretical studies demonstrated the nano-crystals physical properties are radically different from those of usual size scale crystals [1−3].

The special properties of nano-crystals are caused by the fact that in comparison with bulk crystals the very important changes occurs in the nano-crystals structure and in its electron energy spectrum. The main reason for these changes is the fact that the surface atoms of crystal and the atoms of subsurface layer by thickness of $\delta \approx 3a$ (a – the lattice parameter) have the number of nearest neighbors (the number of particles of the first and of the subsequent coordination spheres) reduced in comparison with those in bulk of crystal. An elementary estimate shows that if the crystal size is $d \approx 10\delta \approx 10$ nm, the number of atoms that are "feeling" the absence of half of the space is $\approx 50\%$ of the total atoms number.

The natural consequence of change in the number of surrounding atoms (the coordination number change) is that the "surface" and "near-surface" atoms are have to displace to new positions. This changes their oscillations parameters, charge state, polarization and thus changes the nature of their interaction. In (AB_{n-x})-type ionic crystals due to changes in the valence of ions and due to additional polarization in the surface layers of nano-crystals the specific transitional structures or so-called layered lattices are formed [4]. These structures are characterized by the appearance of a covalent component of the chemical bond between the layers of ions. Herewith very important is the fact that the rearrangement of the crystal lattices is accompanied by the crystal stoichiometry violation.

So formation of a layered crystal structure entails a change in valence of the ions. This in turn results to appearance of the excess (non-stoichiometric) vacancies in the corresponding sub-lattice due to the necessity to satisfy the condition of electrical neutrality of the crystal as a whole. Conglomerations of the stoichiometric vacancies form one-dimensional channels (clusters), which in the

case of nano-sized crystals can penetrate through them. A typical example of ionic crystals in which by decrease their linear size to the value of ≤ 10 nm were experimentally observed all the above mentioned changes in the structure, are the crystals of cerium oxide CeO_2 [5, 6].

One-dimensional vacancy clusters penetrating nano-crystal cause the possibility of an unconventional material transport mechanism – the mechanism of so-called single-file diffusion [7, 8].

In this work, we assessed the efficiency of material transport by the mechanism of single-file diffusion in comparison with the conventional mechanism of the classical diffusion of atoms, which is determining for the massive crystals. The conditions under which the single-file diffusion can provide fast mass transport are considered.

Classical and single-file diffusion of atoms in crystals

It is known that the basis of description of the traditional (classical) mechanism of atoms diffusion in crystals is the model of random walks. According to this model, atoms jumps during their thermal migration occur independently from each other, i. e. there is no correlation between them: next jump of the atom does not depend on what was the previous jump. All directions of the subsequent jump are equiprobable [9]. In this model, the radius-vector of the average displacement of a large number of atoms equal to zero: $\langle X(t) \rangle = 0$, and their mean square displacement is not zero: $\langle X^2(t) \rangle \neq 0$. For one-dimensional diffusion of atoms in crystals in the framework of the classical model the Einstein – Smoluchowski ratio is valid:

$$\langle X^2(t) \rangle = 2Dt. \qquad (1)$$

Here D – diffusion coefficient of atoms characterizing the material transport efficiency, t – time of diffusion.

It should be noted that if one compares the distance of the atom diffusion displacement from an initial position

$$L_d = \sqrt{2Dt} \qquad (1a)$$

with a total length L, which it passes during the same time, it appears that $L_d \ll L$. This inequality indicates the low efficiency of random walks (of chaotic motion) by diffusion mass transferring mechanism and explains why so small the penetration depth of the diffusing material is even after long diffusion annealing.

In the case of the single-file diffusion unlike the above-described mechanism, thermal chaotic migration of atoms is limited to "one-dimensional" channel in which an atom can move in one direction only and diffusing particles can not bypass each other. The mean square displacement for this diffusion mechanism is described by the following formula [6]:

$$\langle X^2(t) \rangle = 2Ft^{1/2}, \qquad (2)$$

where F – mobility – parameter characterizing the movement of atoms in the single-file diffusion. By itself, the parameter F can't be used to characterize the effectiveness

of the mass transport. However, if we use the random walk model applied to a single particle that is moving in one direction and that is not experiencing any interaction with other particles (an analogue of the single-channel or single-file diffusion), the mean square displacement can be described by the following equation [10]:

$$\langle X^2(t) \rangle = \lambda \langle X(t) \rangle. \qquad (3)$$

$\langle X(t) \rangle$ – the average displacement of atom in one dimensional channel, λ – the average distance between neighboring diffusing atoms. Considering that in the case of single-file diffusion: $\langle X(t) \rangle = \sqrt{2D_{sf}t}$ (similarly to the relation (1a)), and using (2) we have:

$$D_{sf} = 2F^2/\lambda^2. \qquad (4)$$

D_{sf} parameter has the dimension of the diffusion coefficient and can be used to characterize the effectiveness of the atoms transport by the single-file diffusion mechanism.

Comparative evaluation of effectiveness of the considered above two diffusion mechanisms of atoms in crystals

For a quantitative estimation of the effectiveness of mass transport by the classical diffusion mechanism and by the single-file diffusion mechanism let's consider the dimensionless ratio:

$$\chi = D_{sf}/D = 2F^2/\lambda^2 D. \qquad (5)$$

Substituting in the equation (5) reasonable values of quantities: $\lambda \approx 0{,}5$ nm, $D \approx 10^{-12}$ m^2/s (for ionic crystals at the premelting temperatures [9]), as well as the experimentally found value of the mobility factor: $F \approx 10^{-12}$ m^2/s$^{1/2}$ [6], we have: $\chi \approx 10^7$.

Conclusions

The analysis and assessment made indicate that the diffusion of atoms along one-dimensional vacancy clusters formed in the (AB_{n-x})-type ion nano-crystals, may have the much faster mass transport compared to the transport by the classical diffusion mechanism of atoms, which is defining for massive crystals.

In fact, this result suggests that in the case of single-file diffusion the length of the diffusion path of atom along the vacancy cluster L_d approaches the value of its total path L, i. e. $L_d \approx L$. As it already was mentioned, for the classical diffusion of atoms based on the random walk model the inequality $L_d \ll L$ takes place.

The described effect of accelerated material transport in the ionic nano-crystals, in the structure of which there are vacancy clusters, must occur in the greater extent, the smaller is the homologous temperature, i.e. the smaller is the value of D; also the more the density of diffusing ions is in cluster, i.e. the smaller is the value of λ (see Relation (5)).

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