

Ion transport in salts orientationally disordered in anionic sublattice

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ABSTRACT

A short review of transport properties of orientationally disordered phases (ODP) of alkali nitrates and perchlorates is presented. Analysis of the data shows that the conductivity, the activation energy and the pre-exponential factor do not change trivially with the increase of the cation size. It may be explained by two mechanisms: a classic one and a cooperative mechanism involving reorientation of anions, the latter becomes dominant in systems with a large free volume. Among nitrates ODP RbNO₃-III is the most conducting and its stability range may be controlled via cationic and anionic substitutions. The mechanism of the ionic transport in RbNO₃ seems to be different from those in perchlorates. According to the results of MD simulation conductivity is limited by the defect formation rather than the cation migration which proceeds via vacancy mechanism. Correlation times for the anion reorientation process correlate with ionic conductivity values thus suggesting that the cation diffusion and anion reorientation are closely interrelated.

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1. Introduction

Among known disorder phenomena in solids one can distinguish an orientation disorder which is characteristic of high-temperature polymorphs of organic molecular crystals [1,2]. In the literature such orientationally disordered phases (ODP) are classified as plastic or rotator phases [1,2]. In the crystal structure of these phases molecules or single molecular groups can be oriented in several directions corresponding to energetically equivalent states. If the potential barrier separating these states is low then the molecules can easily change their orientation. The reorientation process can affect both the mechanism and the rate of the chemical reactions and could be used for practical application in chemical synthesis or even for the development of molecular motors [2]. High-temperature ODP are known also for inorganic salts like cyanides, nitrites, nitrates, carbonates, (hydro)sulfates, (hydro)phosphates, etc. [1], both polyatomic anions and cations (for example, salts of pure or substituted ammonia) may be orientationally disordered. Reorientation processes in inorganic ODP have been studied much less in comparison with organic compounds. Nevertheless, the anion reorientation is known to facilitate the cationic transport. For instance, high-temperature ODP of alkali sulfates [3–5] and orthophosphates [6–8] possess high ionic conductivity. Rather high ionic conductivity was observed in hybrid organic–inorganic salts: substituted ammonia salts [9] or other systems [10,11]. Orientation disorder is characteristic of superprotonic phases of cesium hydrosulfates and hydrophosphates [12].

In these conductors the proton transfer occurs through a Grotthuss mechanism and is limited by proton hops between anions. The anion reorientation reduces the hopping distance and thus enables fast proton diffusion. For explanation of high ionic conductivity in a high-temperature ODP of lithium sulfate a “paddle wheel” mechanism has been proposed [3] which consists in a simultaneous proceeding of the cation hop and the anion rotation. Such cooperative mechanism is characterized by low cation migration energies, high diffusion coefficients of lithium cations and fast heterodiffusion of bivalent cations in this phase [3]. Similar mechanism of cation transport was experimentally shown to take place in ODP of sodium orthophosphate [13,14].

In the present work transport properties of ODP are reviewed on the example of alkali perchlorates and nitrates. Transport properties of high-temperature phases of these salts have been studied by us earlier [15,16] and are discussed in the following sections. The correlations between parameters of the crystal structure, such as the ionic radius, the conductivity bottleneck size and the free volume of a crystal lattice, and the transport properties of ODP are analyzed. Atomic mechanisms of the ionic transport in the rubidium nitrate investigated using a molecular dynamics (MD) computer simulation are discussed.

2. Alkali perchlorates

A series of ODP based on alkali perchlorates MeClO₄ (Me = Na, K, Rb, Cs) represents a convenient model system for investigation of correlations between the cation size and transport characteristics: their high-temperature ODP have similar structure with the cubic elementary lattice of the symmetry type Fm3m. It was supposed

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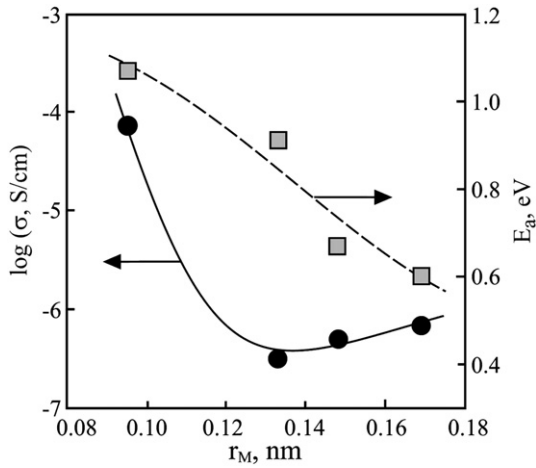


Fig. 1. Variation of the conductivity at 350 °C (σ) and the activation energy (E_a) with the cation radius in alkali perchlorates.

[15,16] that owing to easy reorientation of the anions the alkali cations are displaced to the adjacent interstitial positions with formation of high concentration of Frenkel defects. In that case the activation energy of conductivity is limited by the cation migration energy. To investigate the influence of crystallochemical factors on transport properties of perchlorates the dependence of conductivity on the cation radius was analyzed (Fig. 1). It turned that conductivity (σ) changes non-monotonically with increase in cation radius (r_M): at small r_M (for $M = Na, K$) the conductivity sharply decreases, however on further increase in r_M (at $M = Rb, Cs$) there is a clear tendency of the increase in σ . This effect can be caused by a mutual influence of the two opposite factors: the change of the relative size of the conductivity bottleneck and the variation of the relative free volume. The size of the conductivity bottleneck is determined by a width Δ of the narrowest gap between anions, separating cation positions and can be estimated from the structural data. The ion migration probability is determined by a relative value of the bottleneck size Δ/r_M . As seen from Fig. 2, at transition from $NaClO_4$ to $CsClO_4$ the

relative bottleneck size monotonically decreases. It leads to the decrease in the cation mobility by classic mechanism when anions are rigid and not able to rotate. In parallel the relative free volume of the crystal lattice, $v_f = (V - V_0)/V_0$ increases; here V is the total volume occupied by ions in the elementary cell and V_0 is the geometric volume of the cell. The increase in the free volume facilitates the anion reorientation that, in turn, promotes the cation migration via the “paddle wheel” mechanism [3]. According to this mechanism, elementary acts of cation migration and anion reorientation should be coupled and the cation migration is defined by a probability of simultaneous occurrence of two events: attempts of cations to overcome potential barrier and the reorientation of surrounding anions. Increase in the free volume results in the intensifying of the reorientation dynamics of the anions and generation of the fluctuations in the potential barrier height for the cationic migration. In this case the enhanced ionic motion (EIM) model [17] can be applied for the interpretation of the experimental data. Accordingly, in disordered systems the activation energy has a Gaussian distribution with a characteristic width p which is constant for a series of isostructural compounds. It leads to the following expression for the ionic conductivity

$$\sigma T = A^0 \cdot \exp\left(-\frac{E_a^0 - \frac{p^2}{4kT}}{kT}\right) \quad (1)$$

where A^0 and E_a^0 are the pre-exponential factor and the activation energy for an ordered system. It has been demonstrated [18] that within a narrow temperature range centered at a mean value T_0 the expression (1) can be represented in the approximate form

$$\sigma T \approx A^0 \cdot \exp\left(-\frac{p^2}{4k^2T_0^2}\right) \exp\left[-\left(E_a^0 - \frac{p^2}{2kT_0}\right) \frac{1}{kT}\right] \quad (2)$$

and leads to a compensation law, i.e. a linear dependence between the pre-exponential factor $A^0 \cdot \exp\left(-\frac{p^2}{4k^2T_0^2}\right)$ and the activation energy for conductivity $\left(E_a^0 - \frac{p^2}{2kT_0}\right)$. It may be supposed that in a series of ODP of

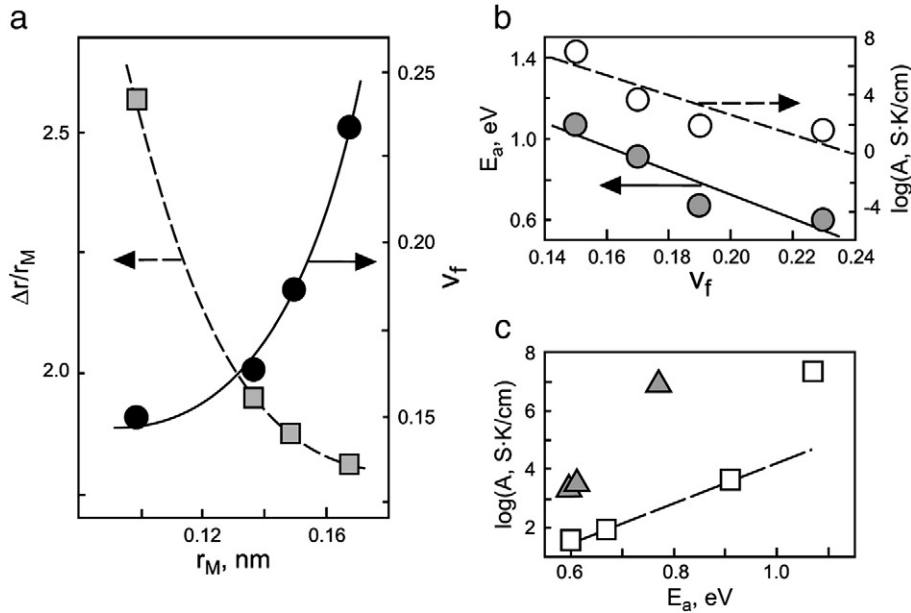


Fig. 2. (a) Dependences of relative bottleneck size (Δ/r_M) and the free volume (v_f) on the cation radius in a series of alkali perchlorates; the shape of the perchlorate anion was assumed to be a sphere with the radius of 0.246 nm. (b) The dependence of the activation energy (E_a) and the pre-exponential factor, $\log(A)$, for conductivity on the free volume in a series of perchlorates. (c) The interrelation between the pre-exponential factor, $\log(A)$, and the activation energy (E_a) in perchlorates (white squares) and phases III, II and I of $RbNO_3$ (grey triangles).

alkali perchlorates p^2 increases proportionally to the free volume leading to linear dependences

$$E_a \approx E_a^0 - \frac{\alpha}{2kT_0} \cdot v_f \quad (3)$$

$$\log(A) \approx \log(A^0) - \frac{\alpha}{4 \cdot 2.303 \cdot k^2 T_0^2} \cdot v_f \quad (4)$$

where α is a constant and T_0 is the mean temperature of the conductivity measurement range. As seen from Fig. 2(b), such dependences are indeed experimentally observed. Fig 2(c) shows the interrelation between $\log(A)$ and E_a . The line corresponds to the values of E_a and A calculated at $\alpha = 0.177$ and $T_0 = 350$ K. One sees that the experimental value of the pre-exponential factor $\log(A, \text{S/cm}) \sim 7.4$ for NaClO_4 strongly deviates from the linear dependence obtained from Eqs. (3) and (4). It suggests that the mechanism of cationic migration in NaClO_4 differs from that in KClO_4 , RbClO_4 and CsClO_4 .

3. Alkali nitrates: rubidium nitrate

High-temperature ODP exist in all alkali nitrates, except for LiNO_3 . In a series of the nitrates RbNO_3 exhibits minimal values of the enthalpy and entropy of melting, that indirectly indicates to the highest degree of the orientational disorder in this compound. Thermodynamic data fairly correlate with the ionic conductivity data: rubidium nitrate has the highest conductivity among alkali nitrates [19], therefore this compound is the most interesting both for theoretical studies and for practical applications. At room temperature the trigonal phase RbNO_3 -IV (space symmetry group P31 or P32, $Z=9$) is stable; in its structure nitrate anions are ordered [20–22]. On heating RbNO_3 undergoes 4 phase transitions: $\text{IV} \leftrightarrow \text{IV}'$, $\text{IV}' \leftrightarrow \text{III}$ (a cubic lattice, structural type of CsCl , $\text{Pm}3\text{m}$, $Z=1$), $\text{III} \leftrightarrow \text{II}$ (rhombohedral, $\text{R}3\text{m}$, $Z=1$) and $\text{II} \leftrightarrow \text{I}$ (cubic lattice, structure of the NaCl type, $\text{Fm}3\text{m}$, $Z=4$) at 73, 164, 219 and 286 °C, respectively [22,23]. The transition at 73 °C found recently [23] comprises a weak distortion of structure of the phase IV without the change of symmetry. The last three transitions are characterized by greater changes of the entropy and enthalpy [1]. The crystal structure of a phase IV can be obtained by a weak distortion and contraction of a cubic lattice of the phase III with small volume change (5%) and differ by ordering of anions. The phase transition to the RbNO_3 -III phase is accompanied by high enthalpy and entropy changes due to the anionic reorientation and formation of ODP [20,21]. In parallel the ionic conductivity increases by three orders of magnitude reaching values of $\sim 1 \times 10^{-3} \text{ S/cm}$ at 200 °C [19,24–27], that is comparable with the rubidium ionic conductivity a superionic conductor Rb^+ - β -alumina [28]. It would be assumed that ODP existing at higher temperatures should be more orientationally disordered and have higher ionic conductivity. However, it is not the case: at phase transition from phase III to phase II conductivity of rubidium nitrate decreases by more than order of magnitude and weakly raises at phase transition $\text{II} \rightarrow \text{I}$ (Fig. 3). Temperatures of phase transitions can be varied using cationic or anionic substitutions. For example, it was shown, that at introduction even small concentration of nitrite anions into a matrix of rubidium nitrate leads to a decrease in the temperatures of $\text{IV} \leftrightarrow \text{III}$ and $\text{III} \leftrightarrow \text{II}$ phase transitions, i.e. highly-conducting ODP RbNO_3 -III can be stabilized at low temperatures [29]. A possible reason of the stabilization of this phase could be an introduction into anionic sublattice the nitrite anions with smaller size and other symmetry that creates local free volume and favors to the anionic disordering. Thus, the presence of the orientational disorder favors high ionic conductivity.

In Fig. 2(c) pre-exponential factors and activation energies for conductivity of the phases III, II and I of RbNO_3 (triangles) are compared with the corresponding parameters of perchlorates (squares). It is seen that the data for all phases of RbNO_3 strongly deviate from

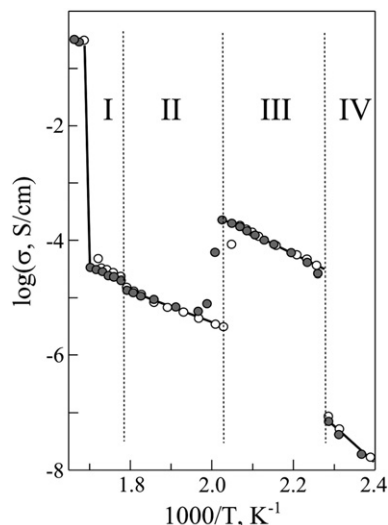


Fig. 3. Arrhenius dependence of conductivity of RbNO_3 . Black and white symbols correspond to the values obtained on heating and cooling, respectively.

linear dependence obtained for a series of perchlorates. Therefore, despite of anionic disorder, the cation migration mechanism in ODP of RbNO_3 may be different from those in perchlorates. To reveal the atomic mechanism of ionic transport in ODP and its interrelation with the anionic reorientation effects MD simulation of rubidium nitrate was carried out, the results are presented later.

4. Molecular dynamics simulation

4.1. The description of the model. The modeling of the crystal structure

For MD simulations of RbNO_3 a Buckingham potential $U(r)$ was used with a Van der Waals attraction term $\sim r^{-6}$ and the exponential function as a repulsion term. Coulomb electrostatic interaction between ions was also taken into account. The positive charge has been localized on rubidium ions and negative charge was uniformly distributed over oxygen atoms of NO_3^- anion. For acceleration of calculation and increase in the particle number of the simulated ensemble polarization effects were neglected. MD simulation was performed using MD calculation program packages GROMACS4 [30] and DL_POLY 2.20 [31]. They support parallel calculations, are capable to work effectively with large ensembles and are widely applied to model ionic systems. GROMACS package offers also various useful utilities for the analysis of models. On the first stage appropriate parameters of the interionic potential were chosen in order to reproduce the structure of all experimentally observed phases of rubidium nitrate. As a result, the optimal potentials were found at which the simulated parameters of crystal lattices appear close to experimental ones. Moreover, change of temperature leads to observable experimentally sequence of phase transitions. Small shift of phase transition temperatures to higher temperatures is characteristic for the model. Thus, it was demonstrated that, at least qualitatively MD simulation gives an adequate description of the system under study.

4.2. An estimation of the defect formation energies

According to the results of MD simulation, despite of rather high ionic conductivity in a phase RbNO_3 -III, no spontaneous formation of defects was observed even in a case when system was artificially heated to higher temperatures. (Using a DL_POLY package one can forbid the model box to be reconstructed even in high-temperatures condition.) Taking into account that for a 30 ns interval no defect was observed in an ensemble of 216 particles, the estimated fraction of

defects did not exceed $n/N_0 < 1/216 = 4.6 \cdot 10^{-3}$. Therefore, in order to study the evolution of defects we created point defects artificially. To create Frenkel defect, a pair of interstitial cation and cation vacancy was generated and the defects were placed on the maximal distance within the limits of the model box with periodic boundary conditions. The Schottky defect was generated by a simple removal of a pair of cation and anion followed by the separation of the formed cationic and anionic vacancies to the maximal distance. The formation energy of the Frenkel defect, E_F , was calculated from a difference between the time-averaged total potential energy of the system containing the defect $\langle U_{\text{def}} \rangle$ and the energy of pure matrix without defect, $\langle U_{\text{ideal}} \rangle$ obtained after the recombination of the interstitial cation–cation vacancy pair (Fig. 4). The formation energy of the Schottky defect, E_S , was determined using an expression:

$$E_s = \langle U_{\text{def}} \rangle - \langle U_{\text{ideal}} \rangle + \langle U_{\text{ideal}} \rangle / N_0 \quad (5)$$

where the last term is included to compensate the energy needed for a removal of a ion pair from the system. The obtained values of the defect formation energies are presented in Table 1.

4.3. Cation diffusion and orientation dynamics of anions

MD technique is known to be a powerful tool to study local atomic arrangements and mechanisms of diffusion. It turned that in phases IV, III and II the interstitial rubidium cations form strongly bound complexes with anion and do not show any detectable diffusion mobility. The detailed description of these complexes is out of the scope of this paper and shall be given in our further publications. The most mobile defects in all phases of rubidium nitrate are cationic vacancies which enable a rather fast ion mobility. Due to the diffusion of cation vacancies during a time interval of nearly 100 ps the recombination of the Frenkel pair takes place (see Fig. 4). The defect recombination lifetimes in phases IV and II were 5 and 4 times greater than in phase III. Therefore the cationic diffusion in phases IV and II proceeds more slowly than in the phase RbNO₃-III, however the cationic diffusion remains the prevailing mechanism of ion transport.

To investigate the influence of anionic subsystem upon the cation diffusion the orientational dynamics of anions in phases IV–II was analyzed. In planar triangle NO₃⁻ anion three oxygen atoms surround the central atom of nitrogen. The orientation of such anion is defined by two vectors, corresponding to the symmetry axis of the anion: a vector **N** directed from the nitrogen atom to the oxygen atom, and a vector **n**, directed from the N atom in perpendicular to the anion plane. The MD model allows to calculate autocorrelation functions for these vectors at different temperatures by means of the standard

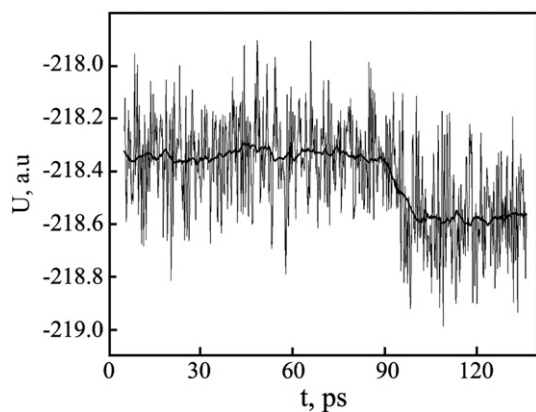


Fig. 4. The evolution of the total potential energy of the system after the introduction of the Frenkel defect (a pair of interstitial cation and cationic vacancy, separated on the maximal distance). At the time of nearly 100 ps the defects recombination takes place which is accompanied by the decrease in energy.

Table 1

Values of the formation energy for Frenkel defect (E_F) and Schottky defect (E_S) in phases IV–II of rubidium nitrate obtained from MD simulation. For comparison the average value of total energy per mole of the nitrate is shown.

Phase of RbNO ₃	E_F , kJ/mol	E_S , kJ/mol	$\langle U \rangle / N$, kJ/mol
IV	240	157	642
III	75	60	628
II	245	205	635

expression $A(t) = \langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle$, representing an average cosine value of the angle between an initial direction of a vector and its direction after time t . The decay rate of the function $A(t)$ is defined by a correlation time t which characterizes a time interval when the system loses memory on the initial direction of a given vector. As rotations are caused by random disturbances, the time t may be regarded as a measure of the anion reorientation rate which changes as $1/t$. Fig. 5 represents temperature dependences of correlation time t , calculated by MD technique for vectors **N** and **n**. Analysis shows that on average the anion rotation rate increases with heating. However rotation of vectors **N** and **n** occurs differently. The autocorrelation function of vector **n** is characterized by rather small values of t , i.e. there is an intensive in-plane rotation of the anion around of the 3-fold axis perpendicular to the anion planes. The rate of such rotation monotonically increases with temperature. The vector **N** is characterized by a longer correlation time t , i.e. flips of anion around 2-fold axis of NO₃⁻ anion occur much slower than its in-plane rotation. It should be noted that in the phase RbNO₃-III the values of the correlation time for such movements are smaller than in phases IV and II, i.e. the reorientation mobility is higher than in other phases. As temperature dependences of correlation time for anion reorientation and ionic conductivity are very similar, it may be suggested that the reorientation processes and the cation diffusion are strongly correlated in agreement with the “paddle wheel” mechanism [3]. However, as shown earlier, the orientational disordering not only influences on the migration mechanism, but also leads to an essential decrease in the defect formation energy. This effect is unexpected and needs further detailed investigation and analysis.

5. Conclusion

Transport properties of high-temperature ODP of alkali perchlorates and nitrates were reviewed. It was found that in a series of perchlorates with isostructural high-temperature ODP the increase in the cation radius causes the change of the mechanism of cationic diffusion gradually from the classic one (via migration through rigid conductivity bottlenecks) to a cooperative mechanism involving

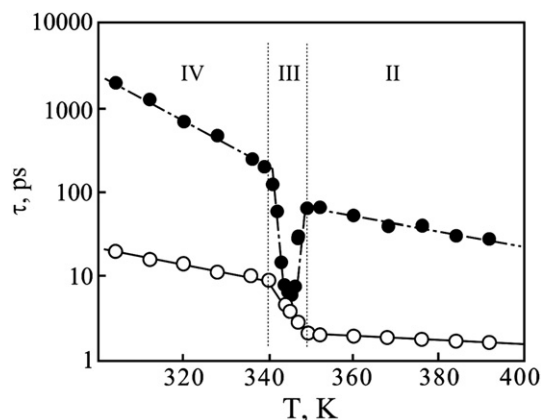


Fig. 5. The temperature dependences of correlation times for anion reorientation in rubidium nitrate. Black and white symbols correspond to vector **n** and **N**, respectively.

reorientation of anions. The latter becomes dominant in systems with a large free volume, such as KClO_4 , RbClO_4 and CsClO_4 and can be approximately described in terms of EIM model where the free volume determines a dispersion of the Gaussian distribution of the activation energies. Experimental data on ionic conductivity of rubidium nitrate were analyzed and it was shown that conductivity parameters of RbNO_3 strongly differ from those of perchlorates. Results of the MD simulation of phases IV–II of RbNO_3 show that the formation energy of Frenkel and Schottky defects in these phases are high and the concentration of the defects is low. The Schottky defects are preferable and the cation migration occurs by vacancy mechanism. Correlation times for the anion reorientation process correlate with ionic conductivity values thus suggesting that the cation diffusion and anion reorientation are closely interrelated. Thus, unlike to perchlorates, RbNO_3 is strongly ordered in cationic sublattice and its conductivity is limited by the defect formation energy rather than cationic migration process. More thorough investigations of the atomic mechanism of the cation diffusion in rubidium nitrate are underway.

Acknowledgements

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