Ionic Transfer in Solids

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Abstract

A short review of research of the transfer mechanism in crystals conducted at the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences over the last 40 years is presented.

Key words: ammonium perchlorate, proton conductivity, superionic conductors, compositional solid electrolytes, dimensional effects

INTRODUCTION

It is known that the phenomena of the electron and ion transfer play a huge part in implementing chemical reactions in the solid phase: redox reactions are performed due to the electron transfer, and without diffusion of atoms and ions, the mass transfer, formation of embryos and growth of products of solid phase reactions are impossible. In this regard, the direction associated with the study of the mechanism transfer in crystals has always been priority for the laboratory of the Institute of Solid State Chemistry and Mechanochemistry (ISSCM), Siberian Branch, Russian Academy of Sciences (Novosibirsk) headed by V. V. Boldyrev.

TRANSFER PHENOMENA AND THE REACTIVITY OF SOLID SUBSTANCES

Historically, the first works of the group were devoted to the investigation of the interconnection between the ionic conductivity of ammonium perchlorate and its reactivity in the thermolysis reactions. Ammonium perchlorate, a traditional object of solid state chemistry was studied relatively intensively, however, the mechanism of its thermal decomposition remained unclear [1]. Three hypotheses in relation to the limiting stage of the process were expressed: 1) electron transfer from the cation to the anion; 2) oxygen–chlorine bond cleavage; 3) proton transfer from the anion to the cation. Based on large volumes of experimental data, including the measurements results of the conductivity of pure and doped crystals, coulometry, dielectric measurements and effects of the composition of the gas phase on the conductivity the following was conclusively shown [2]:

– ammonium perchlorate is a proton conductor, in which connection, the formation of defects, carriers of protons is implemented due to the proton transfer from the cation to the anion:

$$NH_4^+ + ClO_4^- \rightarrow NH_3 + HClO_4 \qquad (1)$$

– resultant particle $HClO_4$ is reoriented and the proton is transferred at the neighboring anion;

– doping of protons by donors, additives HSO_4^- leads to the increase of the extrinsic

conductivity and appearance of the dipole relaxation, what confirms the proposed above mechanism of the formation of proton defects and mechanism of their transfer.

A new mechanism of the low temperature thermal decomposition of ammonium perchlorate consisting in the further accumulation and decomposition of the particle $HClO_4$ was proposed. This decomposition occurs on active sections of the crystal and is catalyzed by impurities of particles-traps of protons (*e. g*, anions ClO_3^- that can be obtained by irradiating, for example).

SUPERIONIC CONDUCTORS: SEARCH STRATEGIES

In the world in the 1970s, an interest to the study of superionic conductors − a new class of chemical compounds possessing high ion conductivity, comparable with the electron conductivity of ion melts or aqueous solutions, significantly increased. The availability fact itself of high ion conductivity in such compounds as silver iodide, lead fluoride or zirconium dioxide doped with various oxides was known for a long time ago. Nevertheless, systematic studies of superionic conductors started only in 1960s with the discovery of high cation conductivity of compounds $Na_2O \cdot 11Al_2O_3$ with the layered structure of beta alumina [3]. It was suggested that these solid electrolytes could be used for the development of sodium-sulphur accumulators. It became clear by the mid-1970s that the major distinctive feature of superionic conductors was a structural disordering of one from the crystal sublattices that could be considered as an analogue of the melted state of the sublattice. Phase transitions and the disordered superionic state is usually accompanied by sharp conductivity drops, though in some cases (*e. g*. in compounds with the fluorite structure), transition into the superionic phase has the diffuse nature and "stretched" on dozens and hundreds of degrees.

Solid electrolytes with the structure of beta alumina were studied by us in a close collaboration with N. P. Tomilov [4]. It was shown that the introduction of an additional amount of Na_2O into the structure of the base compound $Na_2O \cdot 11Al_2O_3$ led to not only an increase of the sodium conductivity, but and to a notice-

able increase of the contribution of oxygen ionic conductivity. This is explained by the fact that in the plane of conductivity of beta alumina, there is a sufficient number of vacant places, convenient for the placement of cations Na^+ and anions O^{2-}. A partial substitution of aluminum by iron leads to an increase of ionic conductivity and significant increase of the contribution of electronic conductivity [5].

New approaches were proposed to solve the tasks of the targeted search for new solid electrolytes. Thus, in normal ordered crystals, there is only one transition into the disordered state − melting. It was shown by us [6, 7] that in a wide row of simple substances and chemical compounds, there was a correlation between the enthalpy formation of the point defect (h_0) and melting enthalpy (H_m):

$$h_0 N_A = \beta H_m \tag{2}$$

moreover, coefficient β, equal to 8.0−9.2, and virtually equal for metals, molecular crystals and binary ionic compounds, *i. e.* the correlation (2) is of the generic universal nature and does not depend on the crystal structure and specific kind of the potential of the interatomic interaction. Correlation (2) can be interpreted on the basis of the quasicrystallic model of melt, herewith, the proportionality coefficient is determined by the relative defect concentration in the melt ($x_L = 1/\beta$) that amounts to 11−12.5 mol. % [7]. Based on this correlation, one can assess the defect formation volume according to the value of the relative volume change of the substance when melting. Knowing the value of the melting entropy one can calculate the entropy of the defect formation and concentration of defects in the crystal at the melting point. It was discovered that there was a linear correlation between the activation energy of self-diffusion and melting enthalpy in a row of isostructural compounds (*e. g.* in alkaline-haloid crystals or metals) [8]. In a row of alkaline-haloid crystals, the compensational effect, *i. e.* the existence of linear correlations between enthalpy and entropy [9] of the defects formation and their migration was discovered. The compensational effect will be observed only in a row of compounds with comparable melting points. Therefore, for example, in metals the compensational effect for self-diffusion is not observed.

Thus, thermodynamic parameters of melting of normal ordered compounds depend on parameters of point defects determining transport properties of crystals. In particular, decreasing entropy and enthalpy of melting is conditioned by increasing the defects concentration and a sharp growth of the ionic conductivity. Substances possessing a high disorder degree, for example, superionic compounds are characterized by low values of the melting enthalpy or entropy. The same compounds possess by a phase transition into the superionic state. The ratio between the values of melting entropy and entropy of phase transition can serve as a quantitative measure of the disorder degree of the substance in the high temperature phase and, thus, be a criterion of the search for new solid electrolytes with a high ionic conductivity.For example, in a row of alkaline metals nitrates, rubidium nitrate possesses the highest conductivity, is characterized by the least value of melting enthalpy and entropy [10].

High-temperature phases of nitrates, like of many other salts with complex anions or cations, refer to a class of orientationally disordered crystals. In these systems, the orientational disordering is implemented that can be considered as a particular case of the positional disordering, when a complex ion or group can occupy several energetically equipollent positions, different only by the ion orientation or group relatively to the crystal symmetry axes.In the process of the group reorientation, a potential barrier for the counter-ion migration can significantly decrease, which will lead to its accelerated diffusion. According to the data of computer modelling, the migration energy of rubidium cations in $RbNO_3$ is anomalously low ($0.1-0.2$ eV). This is conditioned by the cooperative mechanism that includes simultaneously a cation transition and the reorientation of neighbouring anions [11]. It turned out that the conductivity of rubidium nitrate was predominantly limited by not the cation migration, and the processes of the formation of point defects. It was shown that the Schottky defects were characterized by the lowest energy of formation [12].

In a row of alkaline metals perchlorates, with a growth of a cation radius, conductivity goes through the minimum, which is explained by a gradual change of the conductivity mechanism [13].

On the one hand, at migration the cation is forced to proceed through a narrow channel of conductivity and in this case increasing the cation size should lead to the increase of the energy of migration and conductivity decrease. On the other hand, with a rise of the cation size, a free volume is increased, which facilitates the process of the anion reorientation and promotes the cation transfer according to the cooperative mechanism. Reducing the energy of activation and sharp decreasing the preexponential conductivity multiplier with an increase of the cation radius points out at the availability of such a mechanism [14].

When defreezing the reorientation movement the mechanism of the Grotthuss proton transfer is significantly facilitated. For example, in acidic salts, such as hydrosulphates and hydrophosphates, the superprotonic conductivity arises in this case. Conductivity studies of alkaline metals hydrosulphates conducted by Heinowski *et al.* [15] showed that when increasing the cation size the conductivity increase is observed. Herewith, the high-temperature phase of cesium hydrosulphate possesses by the highest conductivity. This is associated with defrosting the reorientational mobility of anions HSO_4^-, facilitation of the protons transfer between neighboring anions by the mechanism of tunneling [16] and with the formation of a dynamically disordered grid of hydrogen bonds. A similar effect is observed and for cesium dihydrophosphate. In the subsequent years, the group under the supervision of V. G. Ponomareva conducted systematic studies of the composites conductivity based on cesium hydrosulphate and dihydrophosphate, the results of which are discussed below.

CONCENTRATION ASSESSMENT OF CURRENT CARRIERS

From the very beginning of the study of superionic conductors, and then and amorphous solid electrolytes, there were held discussions in the literature, what the real concentration of current carriers in these systems was. Two major hypotheses were declared: model of weak electrolytes prevailing when describing the ion conductivity of glasses and theory of strong electrolytes that was mainly attracted for in-

terpreting the experimental data in solid electrolytes. However, convincing evidences for the both models were absent. Usual methods of separating contributions of the mobility and concentration into the total conductivity based on the method of doping of the substance with heterovalent additives are unacceptable in this case, since for a significant change the conductivity of superionic or amorphous electrolytes, it is necessary to introduce a very large amount of admixture into their matrix.

To solve this task Khairetdinov proposed the model of non-Debye migration relaxation [17]. It quantitatively describes regularities empirically found by that time, such as Jonsher's [18] "universal dielectric response", universal ratios of Barton − Namikawa − Nakajima [19], Namikawa [20] and power dependence of conductivity (σ) from the frequency of alternate field (ω) proposed by D. P. Almond and A. R. West [21]:

$$\sigma(\omega) = \sigma_{DC}[1 + (\omega/\omega_0)^{\alpha}] \qquad (3)$$

In particular, it was shown that the frequency (ω_0) was the frequency of ion transfer; degree index is changed α within the limits $0 < \alpha < 1$. This fact allows dividing the contributions of mobility and concentration into the value of ion conductivity (σ_{DC}) and assessing the concentration of current carriers by frequency dependence of conductivity. The analysis of the frequency dependence of the glasses conduction [22, 23], super-ion conductor $CsHSO_4$ [24] and solid electrolytes with the conduction on fluorine anions [25, 26] showed that the concentration of current carriers (n) in these systems was high ($n \sim 10^{21}-10^{22}$ cm^{-3}), consequently, models of strong electrolytes can be applied in this case. Calculated values of the concentration of current carriers in monocrystals NaCl are low ($n < 10^{18}$ cm^{-3}) [27], i. e. these systems are weak electrolytes. Thus, the approach proposed by Khairetdinov turned up very efficient. It was convincingly shown that super-ion compounds and glasses fundamentally differed from ordered crystals by the availability in their structure of a sufficiently large number of defects − current carriers, the concentration of which was large and depended weakly on the temperature.

COMPOSITIONAL SOLID ELECTROLYTES

Compositional solid electrolytes of the type ionic salt−oxide MX-A (MX − silver and cesium halogenides, alkaline metals nitrates and perchlorates, lithium sulphate, cesium hydrosulphates and dihydrophosphates and systems based on them; A − nanocrystalline and highly-dispersed aluminum, silicon, titanium, magnesium oxides etc.) can be considered as a new class of ion conductors possessing a high ion conductivity. A combination of a high conductivity with the elevated mechanical strength, broad possibilities of the targeted control of the electrolyte properties by varying the type and concentration of the additive make composites promising for the practical use in real electrochemical systems. The conductivity increase when doping with disperse oxides is observed virtually for all composites based on classic (not superionic) ion salts and is a general effect, which requires a scientific explanation and theoretical substantiation.

The effect of the conductivity increase at heterogeneous doping was discovered in 1973 by Liang [28] and successfully explained by Maier in 1985 in the framework of the Frenkel model, proposed earlier to describe a double layer on the ion crystal surface. Maier applied this model for the semiquantitative calculation of the concentration of excessive defects formed in a double layer on the interphase boundary ion crystal/oxide [29]. In the late 1980th for the first time in Russia, systematic studies of compositional solid electrolytes were started by us. As heterogeneous additives, oxides with a high specific surface (100−600 m^2/g) were selected with the purpose to achieve the maximum possible effect of heterogeneous doping. Taking into account the work experience accumulated earlier with superionic compounds for heterogeneous doping, we selected salts, in which there are phase transitions, including those into the superionic state. At the absence of the chemical interaction between phases in the composite, the change for it of the phase transition temperature served a criterion of the change of thermodynamic properties of the substance, and enthalpy change of the phase transition into the super-ion state pointed out

at the increase of the disorder of the substance at low temperatures. The disappearance of the heat effect associated with melting testifies a complete substance amorphization in the composite.

Over the last 20 years, composites and nanocomposites MX−A have been studied by us. Based on the obtained results, several theses were prepared [30−33], a number of reviews [34−39] and monograph [40] were published. As a result of numerous studies, it was shown that properties of compositional solid electrolytes were determined by both own disordering an ionic salt, and the interphase superficial interaction between the composite components. Own disordering of the usual ion crystal includes the stages of the defects formation in the volume and on the surface of the crystal. Superficial disordering is described well by the Stern model, in the framework of which the value of the superficial potential is easily calculated [41]. The same model is applicable to describing the formation mechanism of defects as the basic stage of the interphase superficial interaction that includes the stage of chemical adsorption of ions on the oxide surface. Calculation methods of the electron conductivity of composites MX−A based on the generalized equation of mixing were proposed [42]:

$$\sigma^{\alpha(f)} = (1-\beta f)(1-f)\sigma_{MX}^{\alpha(f)} + 2\beta f(1-f)\sigma_{S}^{\alpha(f)} + f\sigma_{A}^{\alpha(f)} \quad (4)$$

where $\alpha(f)$ and β are parameters depending on the morphology of the composite; σ_i are conductivities of components (MX, A) and superficial layer (S); f is volumetric proportion of the additive. At certain values of these parameters, the dependence $\sigma(f)$ has the view of a curve with a maximum and describes well the experimental data on the ion conductivity and dielectric permittivity of very various composites [43]. Assessment methods of the concentration of the surface phase and thickness of the surface layer were developed [44]. The issues of the thermodynamic stability of nanocomposites, genesis of morphologies of the composite at sintering were considered. The total regularities of changing the properties of ion salts in a wide row of the ion salt−oxide systems and dimensional effects were analyzed [39]. An unusual conductivity dependence on the pores size that has the view of a curve with a maximum, was discovered, *i. e.* for obtaining nanocomposite with the maximum conductivity one should use additives with the optimal pore size [41].

It was discovered that at a sufficiently strong interphase superficial interaction in heterogeneous systems, the effect of self-dispersing of the ion salt was observed that enables to synthesize nanocomposites by the method of liquid-phase or solid-phase spreading [39, 40]. The nanodimensional state of the salt in the systems obtained in such a way is usually amorphous but at the same time thermodynamically stable under the condition of the constancy of the oxide particles size. For the first time, based on the complex investigation of a wide range of nanocomposites MX−A with various ion compounds, it was shown that thermodynamic and structural properties of ion salts were significantly changed. Especially clearly, these changes are manifested for compounds possessing by high-temperature disordered phases. Thus, the transition from micro- to nanodimensional systems is accompanied by strong dimensional effects, due to what one can obtain new materials with unusual properties.

RESULTS AND PROSPECTS

Over the last 40 years, collaborators of the group of transfer phenomena have reached a significant progress in the study of transport properties of ion compounds. The studies cover a wide compounds range, including classic ion crystals, super-ion compounds, orientationally disordered phases, glasses and a broad row of composites based on them. The results obtained turned up useful both for clarifying the mechanism of solid-phase reactions, and for solving tasks of the targeted search for new solid electrolytes. New approaches that allow assessing the frequency of ion transitions and the concentration of current carriers in solid electrolytes were worked out. A wide range of compositional solid electrolytes was studied, basic factors that set conditions high ion conductivity was determined. The effect of stabilizing the amorphous phase in nanocomposites was discovered. New solid electrolytes with high conductivity by protons, alkaline metal ions and silver were developed.

Hereinafter, both the started earlier fundamental studies of the ion transfer mechanism in crystals, and the synthesis and study of properties of systems with a special morphology (heterostructures, nanodomains, nanocomposites with ordered pores, nanocomposites based on organometallic and mesoporous matrixes [46−48] *etc.*) can be continued. Applied studies aimed at the use of the resulting solid electrolytes in electrochemical devices: fuel cells, chemical current sources, supercondensers, gas sensors and electrochromic devices, could become another works direction. Such works have already started [49−52] and will be developed in the future.

Acknowledgements

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