SUPERIONIC CONDUCTORS WITH INTRINSIC AND IMPURITY-INDUCED STRUCTURE DISORDER

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INTRODUCTION

The superionic conductors (SICs) are a special class of solids; one of the most important feature of superionic conductors is their unusualy high ionic conductivity as compared to other solids. The ionic conductivity of SICs is close to the values typical of melts or concentrated solutions of strong electrolytes. For this reason superionic conductors are often called solid electrolytes.

As is known, ionic conductivity of solids is associated with different types of disorder. In ordinary crystals intrinsic ionic conductivity is associated with lattice defects: either Schottky or Frenkel defects are formed; in superionic conductors more complicated structure disorder type is observed. So, the ion transport may be facilitated by the thermally generated point defects or may be provided by some inherent structural disorder.

Proceeding from specific character of the structure and character of ionic conductivity, superionic conductors may be divided into three large groups. The first group includes crystals with the so called intrinsic structure disorder. They are, in particular, classical α-phase of silver iodide and also fluorides of some di- and trivalent metals.

The second group includes crystals with so called impurity-induced structure disorder. In these solids the conductivity is due to a high concentration of impurity ions which promote the disordering of the structure. Various concentrated solid solutions are typical examples of superionic materials of this kind.

Finally, some non- crystalline substances may also be regarded as solid electrolytes. These are, in particular, glasses possessing high ionic conductivity caused by the presence of electroactive impurities, and also supercooled amorphous phases of some compunds.

The present paper deals with physical properties of SICs of two clas-ses-compounds with the intrinsic and with the impurity-induced structu-ral disorder.

These superionic conductors were synthesized and studied at the Ins-titute of Crystallography USSR Acad. Sci. (Moscow). Various stages of the investigations were carried out by Drs. A. B. Bykov, L. N. Demya-nets, P. P. Fedorov, B. A. Maksimov, O. K. Mel'nikov, S. E. Sygaryov, Prof. V. I. Simonov, Prof. B. P. Sobolev, N. I. Sorokin, V. A. Timofeeva, to whom the author expresses his gratitude.

SUPERIONIC CONDUCTORS WITH INTRINSIC STRUCTURE DISORDER

SICs with Na$^+$ cation conductivity

It should be noted that many cation-conducting solid electrolytes have been found among various phosphates, silicates and germanates. We discuss in more detail the results of studies[1-3] of electrical and structural characteristics of rare-earth (R) silicates and germanates in the following series:

$$NaR (Si, Ge) O_4 — Na_3R (Si, Ge)_2 O_7 — Na_5R (Si, Ge)_4 O_{12}$$
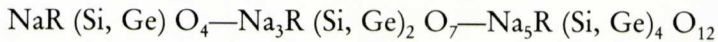
All these compounds can be characterized by a rigid three– dimensio-nal framework. The framework voids are filled with sodium cations. When the sodium concentration increases the rigid framework becomes more complex and these crystals have a more "loose" structure.

Fig. 1 presents the electrical conductivity of sodium –yttrium silica-tes. It can be seen that conductivity changes by several orders of magnitu-de as the chemical composition becomes more complex. An explanation can be made on the basis of the structural features of the compounds.

The most –conductive rare-earth silicates are pentasodium silicates $Na_5RSi_4O_{12}$ (Fig. 2). These compounds have an unusual crystal structure, which was determined by Maksimov.[4] The structure is characterized by twelve–membered meta–silicate rings which together with R octahedra form an infinite skeleton with large number of voids. The 42 sodium ca-tions occupy positions in the channel between the rings and they are sta-tistically distributed over the sites along c axis. Na ions in these channels prove to be weakly bound to the mixed skeleton.

The conductivity was measured on the single crystals oriented along c axes[5,6] and the temperature dependences of conductivity are shown in
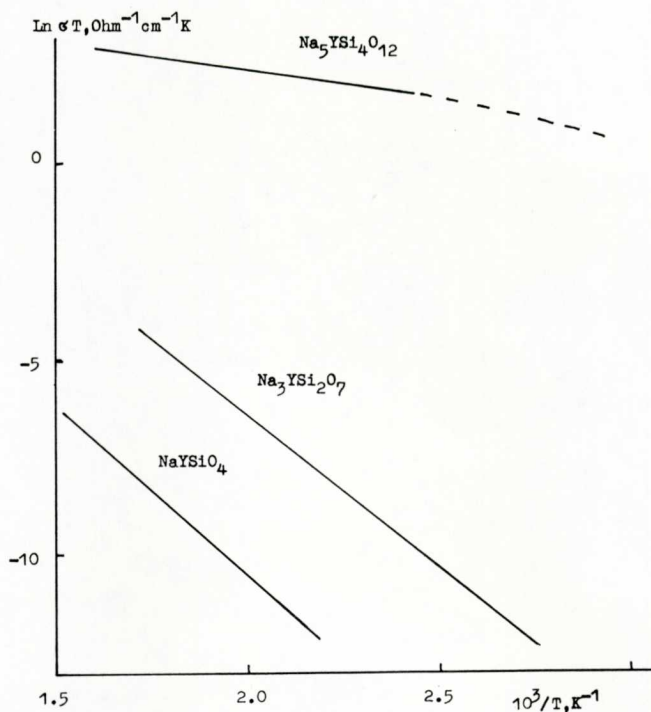
Fig. 1. The temperature dependence of the conductivity for some sodium-yttrium silicates.

Fig. 3. There are anomalies of conductivity at temperatures above 380K: the activation energy is changed. This effect, as well as the presence of additional superlattice reflections at room temperature indicate the existence of a disorder–disorder phase transition. Such conclusion was confirmed by specific heat measurements.[7]

SICs with Li+ cation conductivity

Al present, several dozens of lithium superionic conductors are known. The solid electrolytes of a new class of phosphates – $Li_3M_2(PO_4)_3$, M = Fe, Sc, Cr– are discussed in[8,9]. These compounds may be characterized by a mixed $\{M_2P_3O_{12}\}^{3-}$ skeleton. This means that no M–O–M or P–O–P bonds are present; each M atom is surrounded by six oxygen atoms located at the vertices of six phosphoric tetrahedra and each P atom is surrounded by four oxygen atoms located at the vertices of four octahedra.
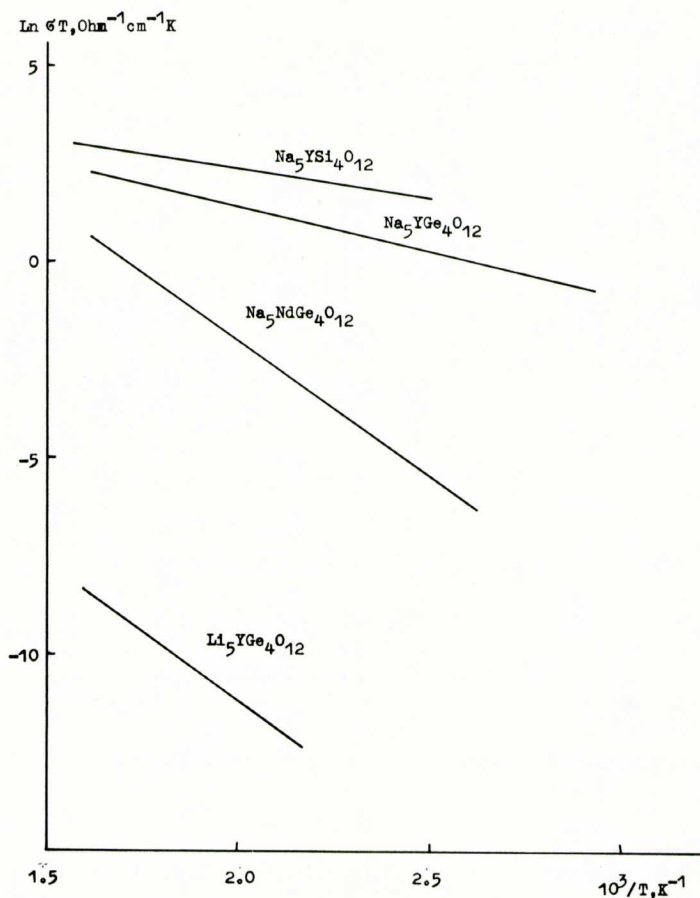
Fig. 2. The temperature dependence of the conductivity for pentasodium (lithium) silicates and germanates.

The specimens were prepared by several methods: solid–phase synthesis, hydrothermal synthesis, crystallization from a solution, from flux, and from melt.

Fig. 4 shows the temperature dependence of the conductivity for lithium phosphate ceramics.[10,11] Only two points will be emphasized here:

1) high ionic coductivity: 10^{-2} Ohm^{-1} cm^{-1} at 600K.

2) phase transitions, one of them being definitely a transition of the crystal to the superionic state.[11,12]

The existence of phase transitions can also be seen on DTA curves.

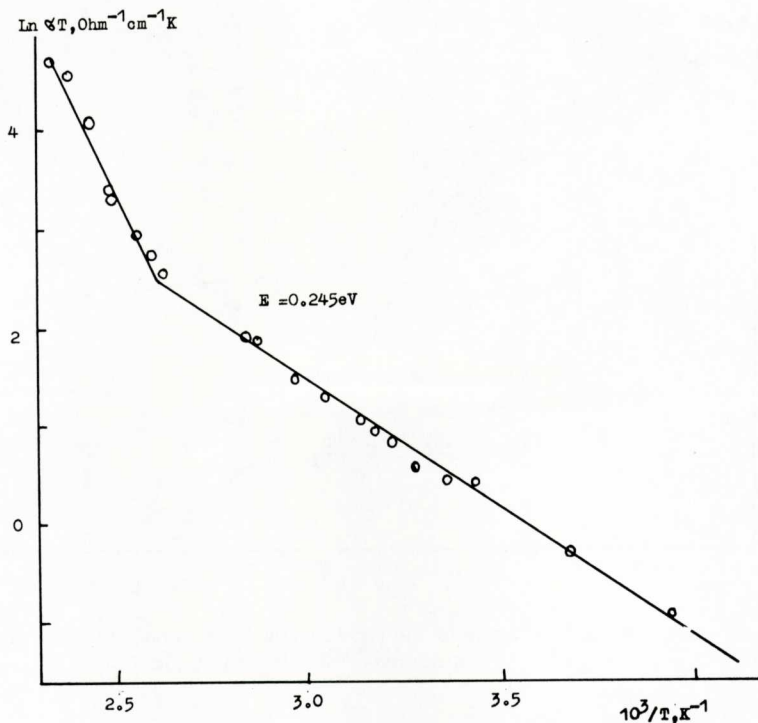The lithium-scandium phosphate is characterized at room temperatu-

Ln σT, Ohm^{-1}cm^{-1}K

$E = 0.245$eV

2.5   3.0   3.5 $10^3/T$, K^{-1}

Fig. 3. The temperature dependence of the conductivity for Na$_5$YSi$_4$O$_{12}$ single crystal.

re by monoclinic symmery (space group P2$_1$/n). At higher temperatures due to the phase transition, the symmetry is risen (Pcan).

All the modifications are based on a three-dimensional network of M octhedra and P tetrahedra sharing oxygen vertices. The void of the mixed framework contains mono-valent lithium ions.

Phase transitions are attended by minor framework distortions but the main structure rearrangements are related to the distribution of lithium ions.

The schematic arrangement of lithium ions in different phases is shown in Fig. 5. In the monoclinic low-temperature modification, 12 lithium cations of the unit cell fully occupy three sets (Li1, Li2, Li3) of the 4-fold crystallographic positions. As a result of phase transition, the space group changes, and the lithium sublattice undergoes drastic rearrangements: the high– temperature superionic modification has three eight-fold sets of positions, that is, 12 Li cations are distributed over 24 sites. Crystal structure studies indicate that only one sort of positions (Li1) is fully oc-
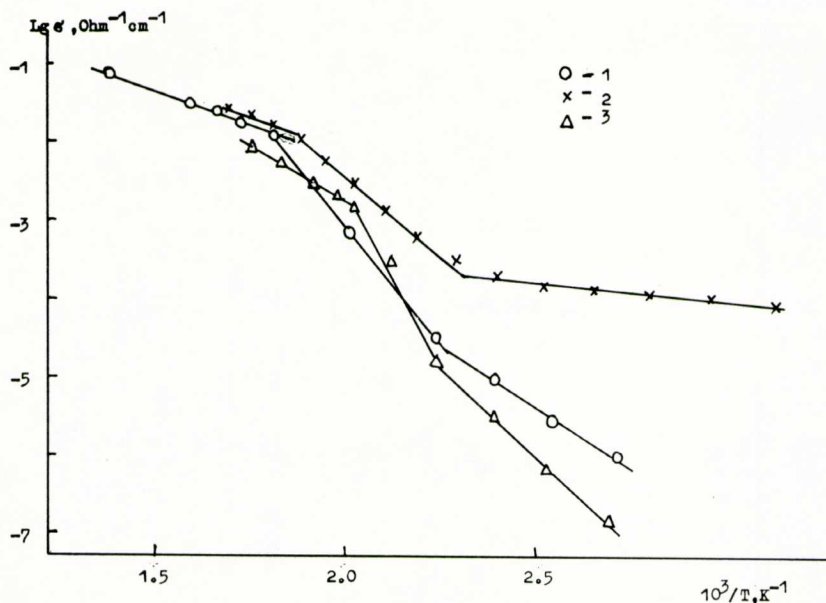
Fig. 4. The temperature dependence of the conductivity for lithium phosphate ceramics: 1– $Li_3Fe_2(PO_4)_3$; 2– $Li_3Fe_2(PO_4)_3$, σ, measured at 500 MHz; 3– $Li_3Sc_2(PO_4)_3$.

cupied, while the remaining 4 lithium ions are statistically distributed over 16 sites (Fig. 5). Thus lithium ions can easily move along these positions within rigid skeleton of the crystal, thus giving rise to a high conductivity.

A detailled analysis of the results permitted us to follow that Li1 ions do not take an active part in ion transport and hat conductivity is due to Li2 and Li3 ions forming conducting channels in the [001] direction (c-axis).

In order to check this hypothesis, the resistance of single crystals was measured.

The temperature dependence of conductivity of $Li_3Sc_2(PO_4)_3$ single crystal is shown in Fig. 6. Two facts should be emphasized here. Firstly, the transition to the superionic state is accompanied by a sharp jump in σ and, secondly, clearly expressed conductivity anisotropy is observed both prior to and after the superionic phase transition. It can be seen that maximum σ is observed for measurements along c-axis which agrees with the sturctural data. The ion transport along this direction should be favourable, which follows from the analysis of conductivity activation energies for different directions, as shown in Fig. 6.

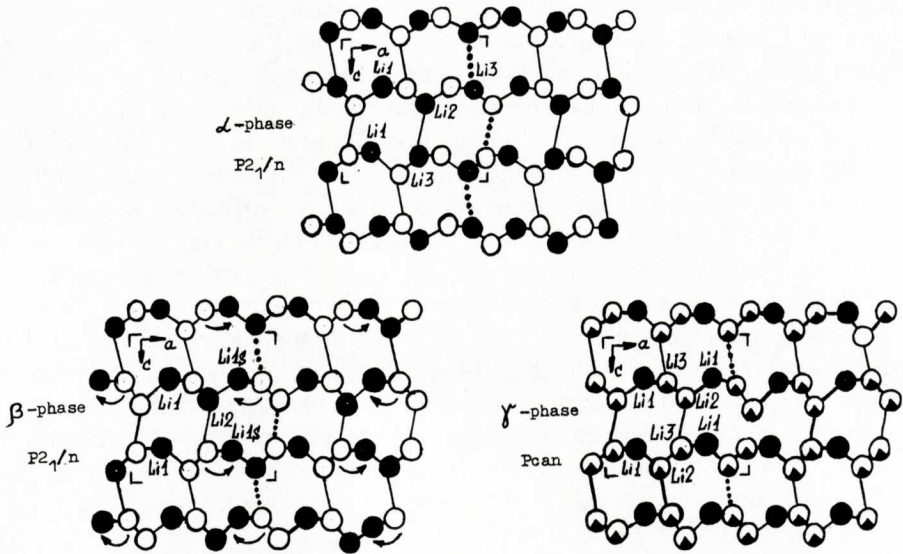The temperature dependence of conductivity for $Li_3Fe_2(PO_4)_3$ is dif-

Fig. 5. Schematic arrangement of lithium ions in different phases.
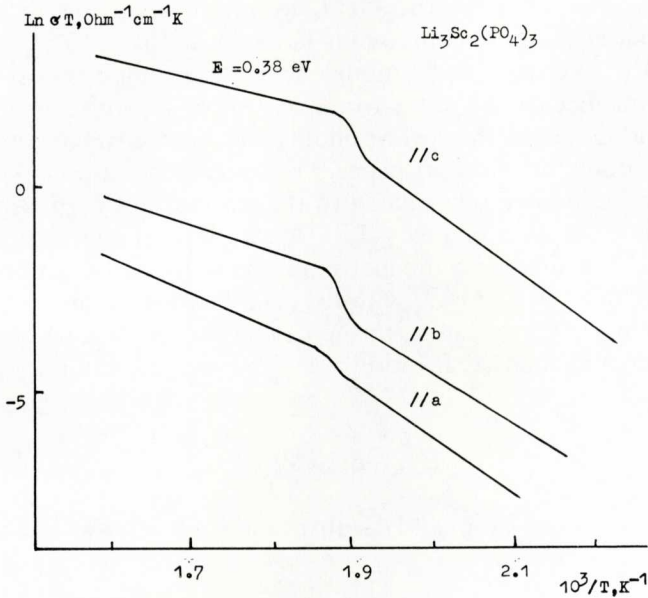

Fig. 6. Ionic conductivity, σ_i, versus reciprocal temperature, $1/T$, for $Li_3Sc_2(PO_4)_3$ single crystal.

ferent. Maximum σ is observed (Fig. 7) for measurements along a and c –
axes, and there is no noticeable jump of conductivity, as was found for
$Li_3Sc_2(PO_4)_3$. It is assumed that such behaviour may be explained by diffe-
rent distribution of lithium ions in the superionic phase.

It should be noted that electronic conductivity of the lithium phos-
phates is much lower than ionic conductivity. Fig. 8 shows the temperature
behaviour of the ionic and electronic conductitivy of scandium and iron
phosphates. It is evident that these compounds behave as good solid elec-
trolytes. The values of electronic conductivity and activation energy (E_{el} =
0.5eV) indicate an extrinsic character of electronic conductivity.

Some variants of heterovalent isomorphism were studied. The results
of measurements of conductivity of a number of synthesized solid solu-
tions are presented in Table 1 and Fig. 9. It can be seen that the con-
ductivity changes are not very large. The slight effect of substitutions
seems to be due to the fact that in the superionic phase the concentration
of mobile ions is independent of the dopant and possible slight structural
distortions have no effect on the potential relief.

Solid electrolytes based on Li_4GeO_4 (lithium orthogermanate).

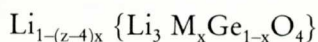Solid solutions based on Li_4GeO_4 are promising materials with high
ionic conductivity. These compounds have about $10^{-3} - 10^{-1}$ Ohm^{-1} cm^{-1}
at 300°C. We have suggested a model,[13] which provides a consistent des-
cription of the mechanism of the formation of phases with high ionic con-
ductivity and describes the corresponding transport characteristics.

As was noted in an earlier paper,[14] the crystal structure of solid solu-
tions under study is closely related to the structure of high-temperature
lithium orhtophosphate phase– γ–Li_3PO_4. We have shown that the intro-
duction of M^{z+} cations into the matrix results in the stabilization of high-
temperature phase of Li_4GeO_4 with the so-called γ-structure.

According to these results, the general chemical formula of solutions
may be written as follows. If cations M^{z+} substitude lithium ions, we ob-
tain

$$Li_{1-(z-1)x} \{Li_{3-x} MGeO_4\}$$
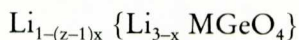
and in the case, when cations M^{z+} substitude Ge ions, we obtain

$$Li_{1-(z-4)x} \{Li_3 M_x Ge_{1-x} O_4\}$$
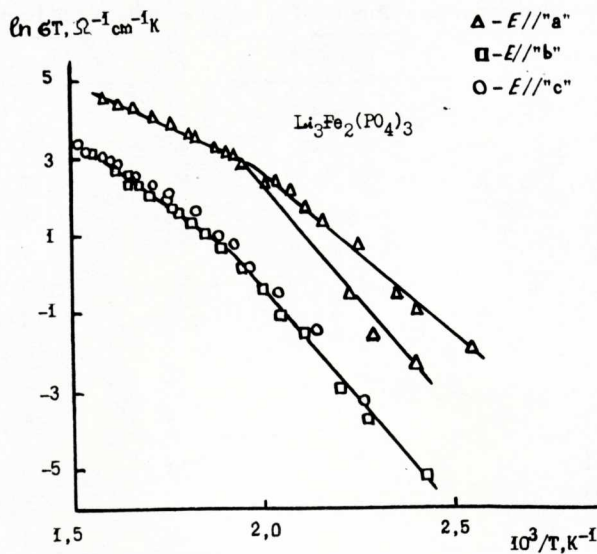
Here there is a pseudo-rigid framework possessing γ-structure. The lit-

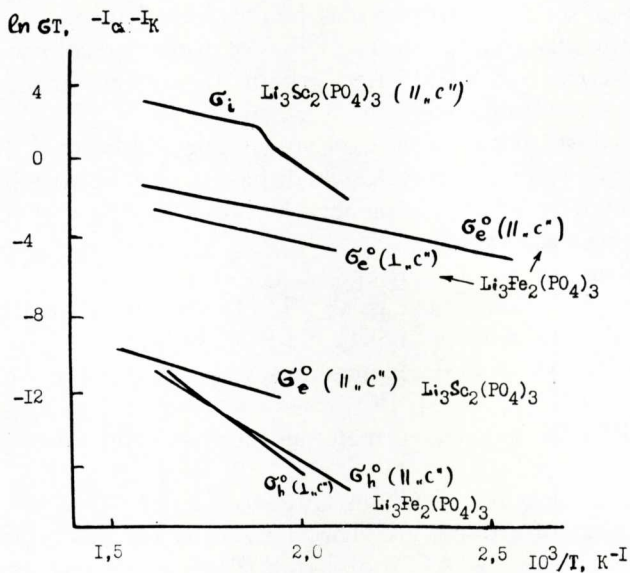Fig. 7. Ionic conductivity, σ_i, versus reciprocal temperature, $1/T$, for $Li_3Fe_2(PO_4)_3$ single crystal.

Fig. 8. Ionic, σ_i, electron, σ_e, and electron-hole, σ_h, conductivities versus reciprocal temperatue, $1/T$, for $Li_3M_2(PO_4)_3$ single crystals.

Table 1. Ionic conductivity some compounds based on scandium and iron phosphates

Composition	T, °C	Conductivity, Ohm^{-1} cm^{-1}
$Li_3 Sc_{1.8} In_{0.2} P_3 O_{12}$	470	$1.78 \cdot 10^{-2}$
$Li_3 Sc_{1.8} Cr_{0.2} P_3 O_{12}$	470	$8.58 \cdot 10^{-2}$
$Li_3 Sc_{2.9} Y_{0.1} P_3 O_{12}$	470	$7.94 \cdot 10^{-2}$
$Li_3 Sc_{1.8} Y_{0.2} P_3 O_{12}$	470	$5.62 \cdot 10^{-2}$
$Li_3 Sc_2 P_3 O_{12} \cdot 0.1 Y_2 O_3$	470	$9.43 \cdot 10^{-2}$
$Li_{2.8} Fe_{1.8} Ti_{0.2} P_3 O_{12}$	470	$5.01 \cdot 10^{-2}$
$Li_{2.9} Sc_{1.7} Zr_{0.2} P_3 O_{12}$	470	$6.58 \cdot 10^{-2}$
$Li_3 Sc_2 P_{2.8} Mo_{0.2} O_{12}$	470	$5.3 \cdot 10^{-4}$
$Li_{3.3} Fe_2 P_{2.7} Si_{0.3} O_{12}$	320	$1.5 \cdot 10^{-2}$
$Li_{3.1} Fe_2 P_{2.9} Si_{0.1} O_{12}$	320	$3.8 \cdot 10^{-2}$
$Li_{2.8} Fe_2 P_{2.9} Si_{0.1} O_{12}$	320	$1.0 \cdot 10^{-2}$
$Li_2 Mg Sc P_2 Mo O_{12}$	450	$1.99 \cdot 10^{-2}$
$Li_3 Sc_{1.8} Zn_{0.2} P_{2.8} Mo_{0.2} O_{12}$	470	$3.2 \cdot 10^{-2}$

hium ions which have not entered the pseudo– framework are distributed over the conduction channels and provide the fast ion transport in the above systems.

So, these solid electrolytes may be considered as materials with "mixed" structure disorder: the introduction of dopants results in the high ionic conductivity, but in this case the high-temperature intrinsic structure disorder phase is stabilized.

The analysis of numerous experimental data indicates[15] that there are few groups of solid electrolytes which have a specific structural feature; namely, they have isolated tetrahedral anions $T^z K_4^{(y-z)}$ (were K is halide or oxygen anion with z valency).

The materials of these group are:

1. Complex oxides, such as $A_{8-z}^+ T^z O_4$, where A is an alkali-ion. For example, solid electrolytes Li_2SO_4, Na_3PO_4, Li_4SiO_4.

2. NASICON and related materials with mixed framework $M_2T_3O_{12}$, such as $Li_3M_2(PO_4)_3$, $Na_3M_2(PO_4)_3$.

3. LISICON and related materials, such as solid solutions based on Li_4GeO_4.

4. Compounds $A_{4-z} T^z Cl_4$, $A_2Cu_2(MoO_4)_3$.

Substances of group 1 are characterized by tetrahedral anions $T^z O_4$, which are connected by AO_n polyhedra. The compounds and solid solutions belonging to NASICON and LISICON groups have a rigid skeleton.
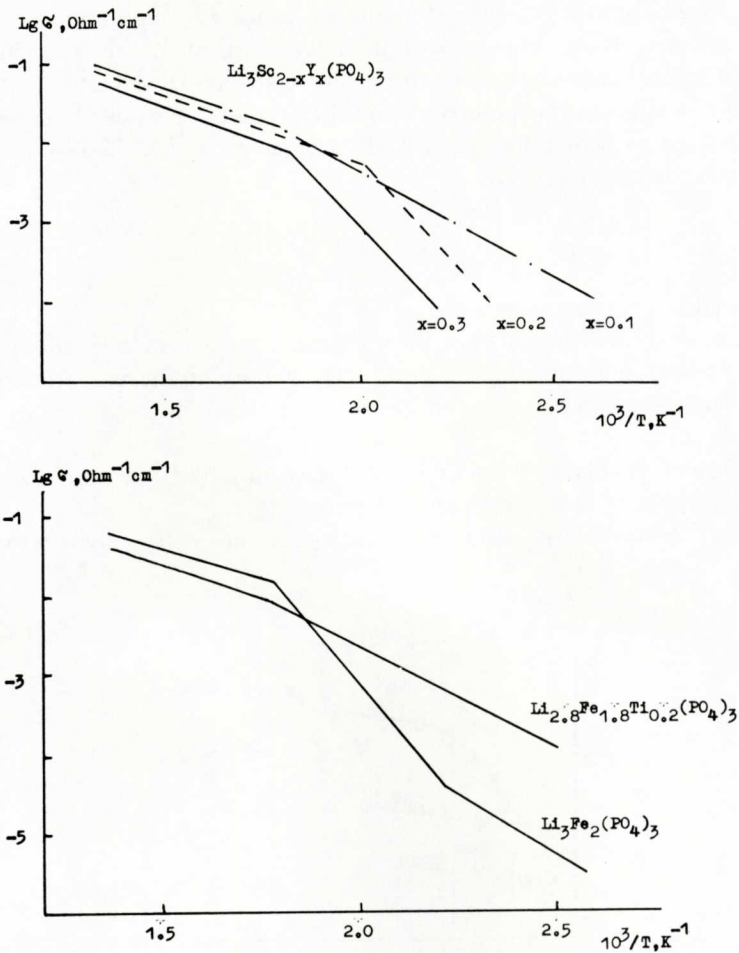
Fig. 9. Ionic conductivity of some solid solutions based on $Li_3M_2(PO_4)_3$.

It should be stressed that many of the above mentioned materials exhibit a phase transition to superionic state.

SUPERIONIC CONDUCTORS WITH IMPURITY-INDUCED STRUCTURE DISORDER

Non–stoichiometric phases belonging to the fluorite type structure are formed in all binary MF_2–RF_3 systems. The deviation from stoichiometry on the formation of heterovalent solid solutions attains record le-

vels– up to 50 mole % of the dopant. An unusually high concentration of structure defects in these phases attracts attention to the latter as model objects in physico– chemical and structure studies of defective solids.[16-18]

We studied the conductivity and dielectric properties of single crystal solid solutions. The conductivity of crystals at the 300-700K is described by the Arrhenius equation

$$\sigma T = \sigma_o \exp(-\Delta H/kT),$$

where ΔH is activation enthalpy.

These solid solutions are fluoride ion conductors and, therefore, we may expert a linear increase of conductivity with an increase in concentration of rare-earth elements and hence, an increase in the concentration of fluoride ions.

However, the experimental data for conductivity of non-stoichiometric phases show more complex behaviour.

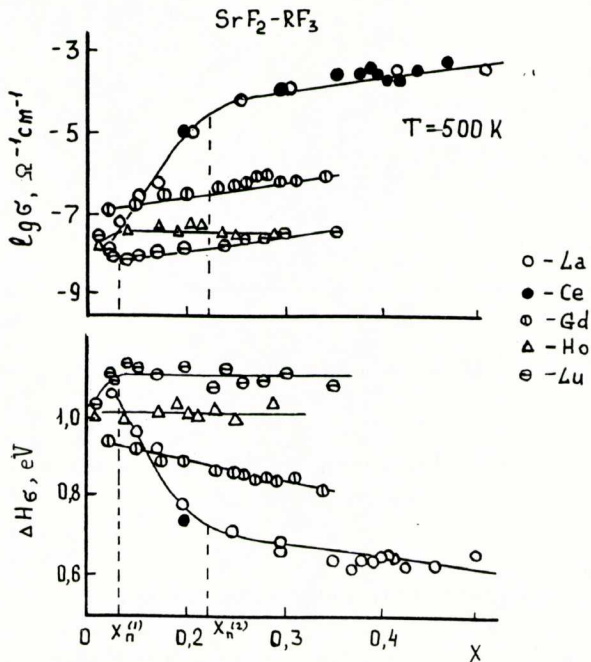Fig. 10 shows the concentration dependence of the conductivity and

Fig. 10. Concentration dependence of the conductivity and activation entaholpy of the $Sr_{1-x} R_x F_{2+x}$ solid solutions with fluorite structure.

enthalpy for solid solutions in the SrF_2 matrix. Systems with R = La, Ge, Pr manifest a pronounced σ change at x = 0.12 – 0.15.

These results can be explained by the "defect regions" model.[16] At large concentrations of the doped atoms the association of neutral dipoles and the formation of complex structure defects, so-called clusters, may take place. We suppose, that the defect region (Fig. 11) consists of a core (cluster) containing rare-earth ions and "frozen" fluoride ions. Also there is a periphery, which may have mobile anions weakly bound to the core. Thus, the composition and the local crystal structure of the defect region differ from those of the undistorted parent matrix.

With the rise of the concentration of dissolved rare-earth atoms in the solid solution the number of defect regions increases, and at concentration x_p spatial network of the domains is observed. The formation of three –dimensional defect phase network corresponds to the percolation threshold and is attended by a change of conductivity and other characteristics of the solid solutions.

Thus, the drastic conductivity change is related to the percolation threshold, x_p. At higher impurity level the observed $\sigma(x)$ and $\Delta H(x)$ plots should be explained taking into consideration interactons between defects. It should be noted that the concentration of charge carriers is independent of dopant concentration but is determined by the structure of defect region. The results of crystal structure studies suggest[19] that the so– called "small" cluster R_4F_{26} is built in the SrF_2 matrix instead of the M_2F_{23} group. In this case the following scheme for heterovalent substitution is possible
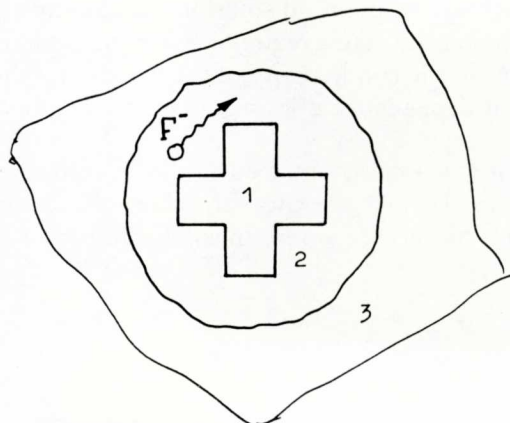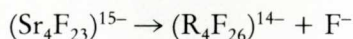
$$(Sr_4F_{23})^{15-} \rightarrow (R_4F_{26})^{14-} + F^-$$

Fig. 11. Defect region for $M_{1-x} R_x F_{2+x}$ solid solutions: 1– core; 2– periphery; 3– matrix.

Table 2. Parameters of anionic conductivity in solid solutions $M_{0.8} R_{0.2} F_{2.2}$

Composition	σ (500K), $Ohm^{-1} cm^{-1}$	$n_F \times 10^{21}$, cm^{-3}	μ (500K), cm^2/sV
M = Ba, R = (La, Ce, Pr)	$(4.4 \pm 1.6) \times 10^{-5}$	1	$(2.8 \pm 1.0) \times 10^{-7}$
M = Ba, R = (Gd – Tm)	$(1.3 \pm 0.3) \times 10^5$	0.5	$(1.6 \pm 0.4) \times 10^{-7}$
M = Sr, R = (La – Nd)	$(9.8 \pm 2.5) \times 10^{-5}$	2.2	$(2.8 \pm 0.7) \times 10^{-7}$
M = Sr, R = (Er, Lu, Y)	$(3.3 \pm 0.8) \times 10^{-8}$	0.66	$(3.1 \pm 0.48) \times 10^{-10}$
M = Ca, R = (La – Pr)	$(8.6 \pm 0.6) \times 10^{-7}$	3.3	$(1.6 \pm 0.1) \times 10^{-9}$
M = Ca, R = (Yb, Lu)	$(3.7 \pm 0.6) \times 10^{-8}$	0.74	$(3.1 \pm 0.5) \times 10^{-10}$

Thus, the electroneutrality condition implies the necessity of appearance of an additional mobile anion in the surroundings of the cluster.

Estimates give the following value of the concentration of mobile fluoride anions

$$n = 2.6 \times 10^{21} cm^{-3}.$$

Let us consider solid solutions of the second group with R = Er, Lu, Y. The conductivities of the solid solutions of the 1st and 2nd groups strongly differ in their behaviour: enthalpy in the 2nd group at x > 0.05 is independent of the concentration of the dopant and only a slight increase in conductivity is observed (Fig. 10). Crystal structure studies suggest[19] that the core is composed of cubooctahedral M_6F_{36-38} cluster. This cluster occupies the place of the Sr_6F_{32} group.

Low conductivity of the solid solutions can be explained on the basis of an assumption that the defect region is low conducting. In this case there is no difference in the conductivity of the matrix and the domain, hence the concentration dependence does not manifest any noticeable percolation threshold.

Similar results were also obtained for solid solutions based on BaF_2 and CaF_2 matrices. Table 2 presents the values of conductivity, mobility and concentration of fluoride anions in solid solutions with fluorite structure.

CONCLUSION

Studies of superionic conductors carried out in recent years have shown that fast ion transport in solids is a rather common occurrence. So

we can speak about a new direction that has been opened up in science, that is, solid state ionics, involving materials with anomalously high ionic conductivity. Search for superionic conductors can be made in various classes of inorganic compounds with structural disorder.

ABSTRACT

This article summarises, the results of the investigations conerning the solid-electrolyte properties of superionic conductors synthesized at the Institute of Crystallography, Moscow. New sodium–, lithium-conductors with intrinsic structure disorder have been found among phosphates, silicates and germanates. The solid solutions with fluorite structure in systems MF_2–RF_3 (M = Ca, Ba, Sr; R = rare earth element) are solid electrolytes with impurity-induced structure disorder.

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