High ionic conductivity in the compounds $Li_3Fe_2(PO_4)_3$ and $Li_3Sc_2(PO_4)_3$

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Orthorhombic modifications of the compounds $Li_3Fe_2(PO_4)_3$ and $Li_3Sc_2(PO_4)_3$
have been synthesized. The lithium-ion conductivity at 600 K reaches values
$(2 - 5) \times 10^{-2}$ mho/cm, which are comparable to those of the best reported
previously for solid electrolytes containing lithium. The atomic structure of the
compound $Li_3Fe_2(PO_4)_3$ has been determined.

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The $Li_3Fe_2(PO_4)_3$ and $Li_3Sc_2(PO_4)_3$ single crystals were synthesized by the hydrothermal method in the system $Li_2O - M_2^{3+}O_3 - P_2O_5 - H_2O$ (M = Fe, Sc) at a pressure of 1 kbar by the standard temperature-drop method, with a temperature of 520–720 K in the dissolution zone.

An unbounded isomorphism has been found by solid-phase synthesis in the $Li_3Fe_2(PO_4)_3$–$Li_3Sc_2(PO_4)_3$ system; significantly, the Fe atoms can be completely re-
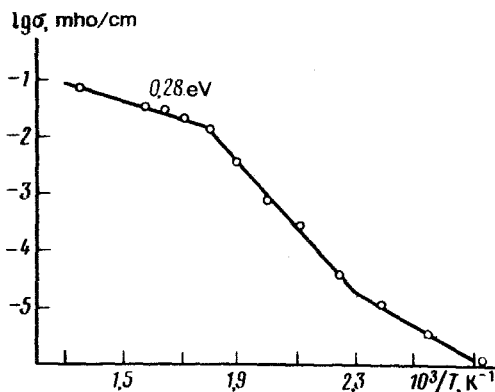
FIG. 1. Temperature dependence of the conductivity of $Li_3Fe_2(PO_4)_3$.

placed by Sc atoms without changing the structure of the compound. The introduction of other trivalent metals, in particular, rare earths, into this structure gives rise to the formation of a two-phase product with a narrow region of homogeneity: $Li_3(Fe^{3+}, TR^{3+})_2(PO_4)_3$. For the measurements of the thermal conductivity, tablets 5–7 mm in diameter were pressed from the synthesized powder and then annealed. The density of these tablets reached $\sim 90\%$ of the theoretical value.

The volume resistivity of $Li_3Fe_2(PO_4)_3$ was determined by analyzing the frequency dependence of the impedance. Figure 1 shows the temperature dependence of the conductivity. The curve of $\lg\sigma$ vs $1/T$ has two slope changes, at $T \sim 560$ and $T \sim 450$ K. The change in the activation energy E_σ corresponding to the lower temperature can be attributed to a region of a "nonintrinsic" conductivity.[1] The decrease in E_σ above 560 K can be linked in a natural way with a phase transition analogous to those in $Na_3Zr_2Si_2PO_{12}$ and $Na_3Sc_2(PO_4)_3$ (Ref. 2).

At 600 K the conductivity of these compounds reaches $(2-5) \times 10^{-2}$ mho/cm, which puts them in a class with the best lithium-conducting solid electrolytes, Li_3N and $Li_{14}Zn[GeO_4]_4$. Estimates of the electron component of the conductivity, σ_{el}, yield a figure of 10^{-5} mho/cm at 600 K. The conductivity in the compounds $Li_3Fe_2(PO_4)_3$ and $Li_3Sc_2(PO_4)_3$ is therefore ionic, and the results of the structural studies reported below show that this conductivity is due to the mobility of lithium ions.

For the x-ray structural studies we used an acicular $Li_3Fe_2(PO_4)_3$ single crystal with dimensions of $0.05 \times 0.06 \times 0.2$ mm. The x-ray diffraction pattern revealed the orthorhombic symmetry of the crystal: Laue class *mmm*, with unit-cell dimensions $a = 8.572(2)$, $b = 12,052(3)$, and $c = 8,599(3)$ Å. The integrated intensities of the features in the diffraction pattern were measured with a CAD-4F automatic x-ray diffractometer [Mo($K\alpha$) radiation, graphite monochromator, stepped scanning, ω method, $\sin\theta/\lambda \leqslant 0.8$ Å^{-1}, linear absorption coefficient $\mu = 34.4$ cm^{-1}]. Experiments were carried out at two temperatures: 295 K and in a high-conductivity state at 573 K. The low-temperature modification is characterized by the space group $P22_12_1$, while the high-temperature modification is characterized by the group *Pcan*. The structure is
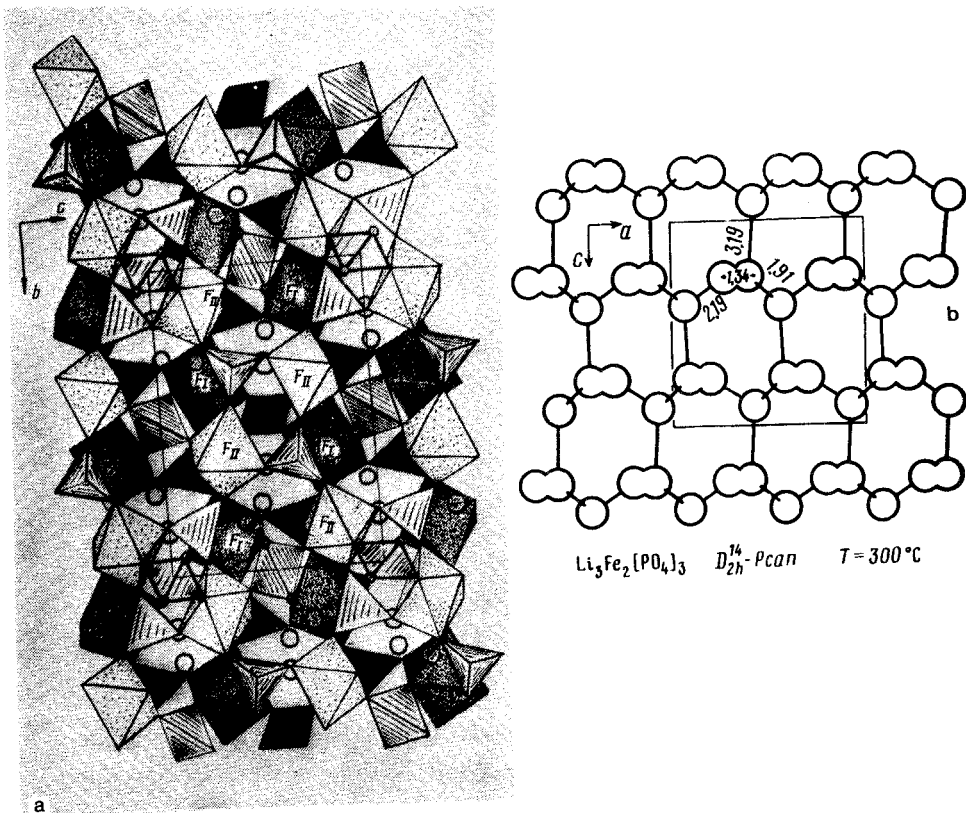
FIG. 2. Crystal structure of $Li_3Fe_2(PO_4)_3$. a—Fragment of the three-dimensional framework of PO_4 tetrahedra and FeO_6 octahedra; b—relative arrangement of the lithium ions in the structure at 573 K.

made up of $[PO]_4$ tetrahedra and $[FeO]_6$ octahedra, which join at vertices, forming a three-dimensional framework. Figure 2a shows one projection of this structure. The cavities of the framework hold singly charged lithium ions. At $T = 300\,°C$ only one of the three crystallographically independent positions of the Li atoms in the structure is 100% populated. The two other positions are filled with lithium at a probability of 1/4; this situation is characteristic of ionic conductors. Figure 2b shows the arrangement of Li atoms in the planes running parallel to the ac face of the unit cell of the crystal ($T = 300\,°C$). The relative arrangement of the Li atoms indicates an extremely probable and large anisotropy of the conductivity. The maximum conductivity should be expected along the direction of the a axis of the unit cell of the crystal.

A formula analog of the compound $Li_3Fe_2(PO_4)_3$ can be considered to be[3] $Na_3Fe_2(PO_4)_3$, whose structure differs from the model which we have found for the $Li_3Fe_2(PO_4)_3$ structure, even in terms of the architecture of the framework. In Ref. 3 there is also an indication of the syntheses of the compound $Li_3Fe_2(PO_4)_3$, which is characterized by an orthorhombic symmetry $R\bar{3}c$ or $R\,3c$. Comparing our results with

those of Ref. 3, we can assert that we have found a new orthorhombic modification of the compound $Li_3Fe_2(PO_4)_3$.

All the calculations which were carried out to determine and refine the structure were carried out on a computer with the help of the Rentgen programs.[4]

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