

# Influence of substitutions on the structure, ionic conductivity, and phase transitions in the system of $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$ ( $0 \leq x \leq 0.06$ ) solid solutions

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The article presents data on the study of the effect of substitutions of M-cations in the system of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions (in the concentration range  $0 \leq x \leq 0.06$ ) on the crystal structure, ionic conductivity, and also on the temperature of phase transitions  $T_{\alpha \rightarrow \beta}$ ,  $T_{\beta \rightarrow \gamma}$ . It is shown that samples of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) solid solutions are monoclinically distorted, and the structure parameters increase linearly with increasing dopant concentration. Moreover, in the studied samples of solid solutions, an increase in the conductivity of the  $\alpha$ -phase and a decrease in the  $\beta$ - and  $\gamma$ -phases are observed, as well as a decrease in the temperatures  $T_{\alpha \rightarrow \beta}$  and  $T_{\beta \rightarrow \gamma}$ . It is concluded that these changes are associated with both local deformations of the anionic part of the crystalline structure  $\left\{ [\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)]^{3-} \right\}_{3\infty}$ , and violation of the regularity of the crystal structure.

**Keywords:** polycrystal; structural parameters; ionic conductivity; phase transitions; solid solutions; dopant

## Introduction

Many crystals from the NASICON family have valuable properties and are structural materials for practical use. In particular, solid solutions based on  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  doped with erbium atoms can be used as phosphors [1].

Also, searches are underway for efficient ionic conductors from the NASICON family for practical application [2, 3]. The works [4–7] report on the possibility of using  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystals as an electrode material. In particular, it was found that  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystals can be promising cathode materials for creating sodium-ion batteries (SIBs), due to the uniqueness of the crystal structure and structural stability of this material [6, 7]. However, SIAs based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  cathode materials have low energy. Therefore, improving the conductive properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is important. One of the ways to increase the ion-conducting properties of orthophosphates is the creation of solid solutions on its basis [8, 9].

The most prominent representatives of the NASICON family are  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$ , where  $\text{M}=\text{Fe}, \text{Sc}$ , which are dielectrics in the low-temperature  $\alpha$ -phase, but after the  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$  phase transitions in the  $\gamma$ -phase, they have superionic ionic conductivity [10–14].

If the dipole ordering of  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is antiferroelectric (AFE), then  $\alpha$ - $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  is classified as ferroelectric (FE) [14, 15]. If the dipole ordering of  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is antiferroelectric (AFE), then  $\alpha$ - $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  is classified as FE [14, 15].

Despite the difference in the types of dipole ordering of these materials, the cause of the occurrence of polarization in them is the displacement of the cationic sublattice relative to the anionic one, due to the monoclinic distortion of their crystal structures [4]. These orthophosphates are similar in structure and properties [10, 12, 14–16], although the ionic radii of the considered M-cations differ (on  $\Delta r_{\text{M}}=0.18 \text{ \AA}$ ).

The structure of the  $\alpha$ - $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  crystal has a monoclinic distortion with sp. gr.  $C2/m$  and superstructure cell, the structure of the  $\alpha$ - $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  crystal is monoclinic distortion with sp. gr.  $Bb$ . To improve the conductive properties of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , it is advisable to conduct studies on the substitution of M-cations  $\text{Fe} \rightarrow \text{Sc}$  in this material [10]. Therefore, it was necessary to study the effect of the substitution of M-cations  $\text{Fe} \rightarrow \text{Sc}$  in the system of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) solid solutions on the structure, conductivity, and also on the transition temperatures  $T_{\alpha \rightarrow \beta}$  and  $T_{\beta \rightarrow \gamma}$  samples.

## Experimental part

Polycrystals of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  in the concentration range  $0 \leq x \leq 0.06$  were obtained using ceramic technology (from the charge:  $3\text{Na}_2\text{CO}_3 + 2(x-1)\text{Sc}_2\text{O}_3 + 2x\text{Fe}_2\text{O}_3 + 6\text{NH}_4\text{H}_2\text{PO}_4$ , taken in stoichiometric ratios) by two-stage firing.

The initial mixture was annealed at 970 K for 6 hours for phase formation. The resulting phases were ground, pressed into pellets, and then annealed to form polycrystals at 1070 K for 8 hours.

The study of the single-phase and crystal structures of the samples was performed by powder X-ray (using a DRON-3 diffractometer,  $\text{CuK}\alpha$ -radiation).

Determination of the parameters of ionic conductivity and dielectric permittivity of the samples was carried out according to the procedure given in [6]. To

create electrodes, silver was applied to the samples.

## Results and discussions

### Results of synthesis and X-ray study of $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$ ( $0 \leq x \leq 0.06$ ) polycrystals

The samples  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  were tablets 10 mm in diameter and 1 mm thick, dark brown in color, and polycrystals of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions, where  $x=0.02$ ;  $x=0.04$ ,  $x=0.06$  were light brown. X-ray measurements were obtained diffractograms of the studied polycrystals and single-phase samples of solid solutions  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  in the concentration range ( $0 \leq x \leq 0.06$ ) were established. Figure 1 shows the X-ray diffraction patterns of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) solid solution samples.

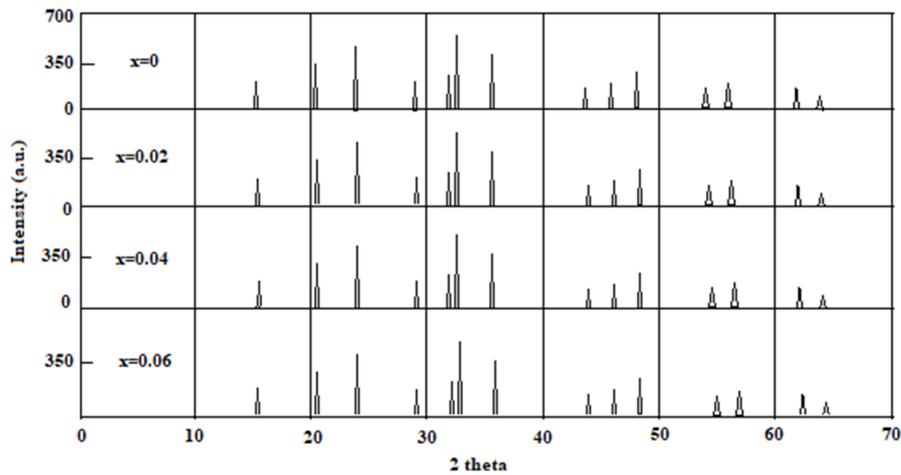


Figure 1. X-ray diffraction patterns of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solution samples, where  $x=0$ ;  $x=0.02$ ;  $x=0.04$ ;  $x=0.06$ .

The unit cell of the  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal at room temperature has a monoclinic-distorted structure (sp. gr.  $C2/m$ ) with the following parameters:  $a=8.7168 \text{ \AA}$ ,  $b=8.7168 \text{ \AA}$ ,  $c=21.5963 \text{ \AA}$ ,  $\gamma=90.37^\circ$ . Similar structural parameters possess solid solutions of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  compositions with  $x=0.02$ ;  $x=0.04$ ,  $x=0.06$ , because have the same peaks as those of  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , but slightly shifted to the right as the concentration increases (see Table 1), which indicates a linear increase in the structure parameters.

Table 1.

Structural parameters of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystals and  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions ( $0 \leq x \leq 0.06$ ).

Compounds	Temperature $T$ , K	Sp. group	Unit cell parameters					
			$a$ , $\text{\AA}$	$b$ , $\text{\AA}$	$c$ , $\text{\AA}$	$\alpha^0$	$\beta^0$	$\gamma^0$
$\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$								
$x=0$	295	$C2/m$	15.1230	8.7168	21.5963	90.0	90.37	90.0
$x=0.02$	295	$C2/m$	15.1234	8.7172	21.5965	90.0	90.38	90.00
$x=0.04$	295	$C2/m$	15.1238	8.7176	21.5967	90.0	90.39	90.00
$x=0.06$	295	$C2/m$	15.1242	8.7180	21.5969	90.0	90.40	90.0

The obtained structural parameters of solid solutions  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) show that the  $\left\{ [\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)]^{3-} \right\}_{3\infty}$  crystal frame allows replacement of M-cations of iron by much larger ionic radii of scandium atoms. These substitutions lead to a linear increase in the parameters of the structures of solid solutions as the concentration of dopants increases. It is possible that this is facilitated by the processes of local deformation of the "stretching" of the anionic framework during the substitution of M-cations  $\text{Fe} \rightarrow \text{Sc}$ .

## Ionic conductivity and phase transitions of polycrystals

### $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$ ( $0 \leq x \leq 0.06$ )

The conductivity of crystallites of polycrystals was determined by the impedance method [14], i.e. by analyzing the complex resistance  $Z^*(\omega)$  from the frequencies of harmonic electrical signals applied to the samples.

The conductivity of crystallites of the synthesized polycrystals was determined by the impedance method [14], i.e., by analyzing the complex resistance  $Z^*(\omega)$  obtained by the interaction of the sample with a harmonic electrical signal.

The impedance method makes it possible to separate the conductivities of crystallites and intercrystalline interlayers of polycrystalline samples of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions [14]. The impedance method makes it possible to separate the conductivities of crystallites and intercrystalline interlayers of polycrystalline samples of solid solutions [14].

The results of the study of the dependence of conductivity ( $\sigma(T)$ ) for crystallites of polycrystalline  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) samples are shown in Figure 2. Note that for these samples, the dependence  $\sigma(T)$  can be divided into three linear segments.

For  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  on the dependences  $\sigma(T)$ , separated by "oblique steps", corresponding to the phase transitions  $T_{\alpha \rightarrow \beta}$  and  $T_{\beta \rightarrow \gamma}$  (see Figure 1). For  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , the middle of the first "oblique step" (located between the  $\alpha$ - and  $\beta$ -phases) on the dependence  $\sigma(T)$  corresponds to the transition temperature  $T_{\alpha \rightarrow \beta} = 368$  K. In the case of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) solid solution samples, phase transitions were also determined from breaks. The dependences  $\sigma(T)$  established for these samples (see Figure 2) agree with the Arrhenius relation [14].

It should be noted that at the phase transition  $\alpha \rightarrow \beta$  for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  (curve 1 in Figure 2) is accompanied by a sharp change in the conductivity parameters, which can be associated with an increase in the crystal symmetry from monoclinic (sp. gr.  $C/2m$ ) to rhombohedral (sp. gr.  $3RC$ ) and the uniform distribution of disordered sodium cations over the A- and B-cavities [14]. The  $\beta \rightarrow \gamma$  phase transition is also accompanied by a change in the conductivity parameters, caused by the complete symmetrization of the rhombohedral crystal structure (sp. gr.  $3Rc$ )  $\gamma$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and the uniform distribution of disordered sodium cations over the A- and B-cavities.

In  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) solid solutions, an insignificant but consistent increase in conductivity in  $\alpha$ -phases is observed, and in  $\beta$ - and  $\gamma$ -

phases there is a gradual decrease in the conductivity of the samples. At the same time, the transition temperatures  $T_{\alpha \rightarrow \beta}$ ,  $T_{\beta \rightarrow \gamma}$  of the samples under study are gradually decreasing, which are represented by curves 2–4 in Figure 1 in the form of breaks in the  $\sigma(T)$  dependence.

It has been established that the conductivity of samples of  $\alpha$ - $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions in the polar phase increases as a result of a partial decrease in the degree of monoclinic distortion of the crystal structure caused by local deformations of the structure by dopants.

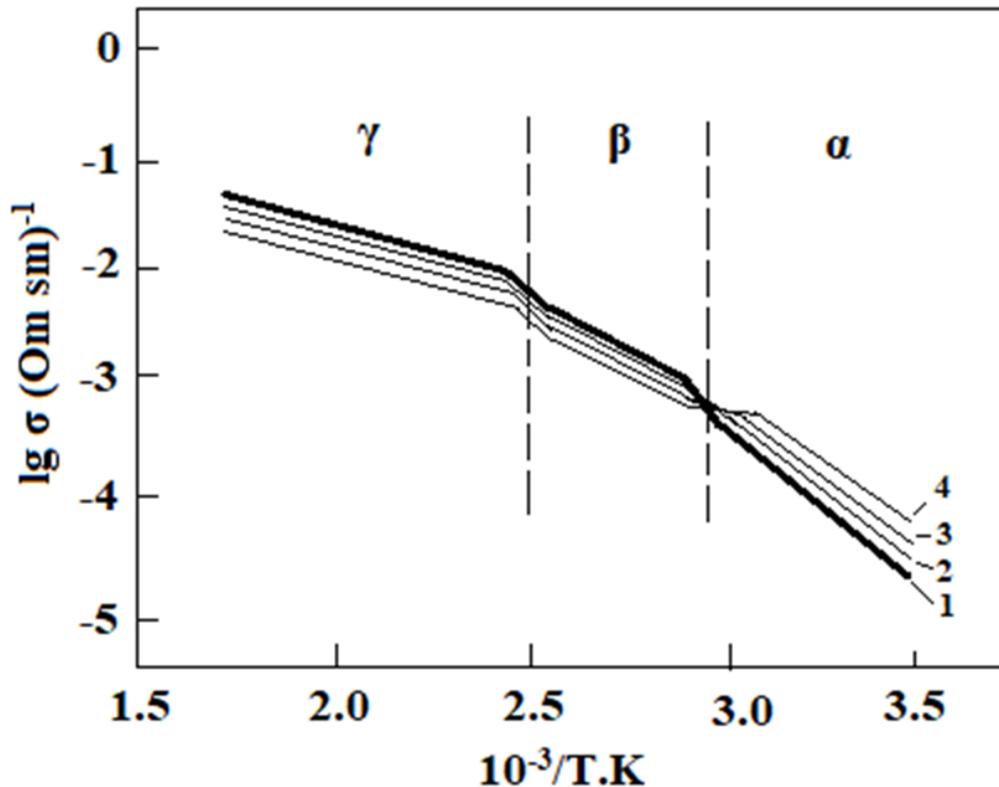


Figure 2. Temperature dependences of conductivity  $\sigma(T)$  for crystallites of polycrystalline samples of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$ , where:  $x=0$  (curve 1 is highlighted with a bold line);  $x=0.02$  (curve 2);  $x=0.04$  (curve 3);  $x=0.06$  (curve 4).  $T_{\alpha \rightarrow \beta}$  and  $T_{\beta \rightarrow \gamma}$  for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$ .

The decrease in the conductivity of solid solutions in superionic  $\beta$ - and  $\gamma$ -phases can be associated with a decrease in the statistical average "conduction channel" in the  $\left\{ [\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)]^{3-} \right\}_{3\infty}$  crystal frame due to local deformations stretching" of the structure and violation of the translational regularity of the crystal, when doped with scandium cations. More detailed data on the conductivity parameters and phase transition temperatures of the samples under study are given in Table 2.

Table 2.

Conductive parameters and phase transition temperatures for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions.

Sample/Options	$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$	$\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$		
The ionic radius of M-cation $r_i$ , Å	$R_{\text{Fe}}=0.64$	$R_{\text{Sc}}=0.83$		
Dopant concentrations $x$	0	0.02	0.04	0.06
Conductivity $\sigma_\alpha$ , $\Omega^{-1}\cdot\text{cm}^{-1}$ at $T=293$ K	$4.20\cdot 10^{-7}$	$4.35\cdot 10^{-7}$	$4.50\cdot 10^{-7}$	$5.65\cdot 10^{-7}$
Activation energy $\Delta E_\alpha$ , eV	0.63	0.61	0.59	0.56
Conductivity $\sigma_\beta$ , $\Omega^{-1}\cdot\text{cm}^{-1}$ at $T=345$ K	$5.9\cdot 10^{-5}$	$5.75\cdot 10^{-5}$	$5.60\cdot 10^{-5}$	$5.48\cdot 10^{-5}$
Activation energy $\Delta E_\beta$ , eV	0.46	0.45	0.44	0.43
Conductivity $\sigma_\gamma$ , $\Omega^{-1}\cdot\text{cm}^{-1}$ at $T=573$ K	$9.1\cdot 10^{-3}$	$8.8\cdot 10^{-3}$	$8.6\cdot 10^{-3}$	$8.3\cdot 10^{-3}$
Activation energy $\Delta E_\gamma$ , eV at $T=573$ K	0.39	0.37	0.35	0.33
Phase transition temperatures $T_{\alpha\rightarrow\beta}$ , K	368	367	366	365
Phase transition temperatures $T_{\beta\rightarrow\gamma}$ , K	418	417	416	415

The temperatures of phase transitions  $T_{\alpha\rightarrow\beta}$  of the studied polycrystals were also determined from the dependences  $\varepsilon(T)$  of solid solutions.

The permittivities  $\varepsilon$  were determined by analyzing the impedance  $Z^*(\omega)$  of the samples. On Figure 3 shows the temperature dependences of  $\varepsilon(T)$  at a frequency of  $5 \cdot 10^5$  Hz for  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  polycrystals ( $0 \leq x \leq 0.06$ ).

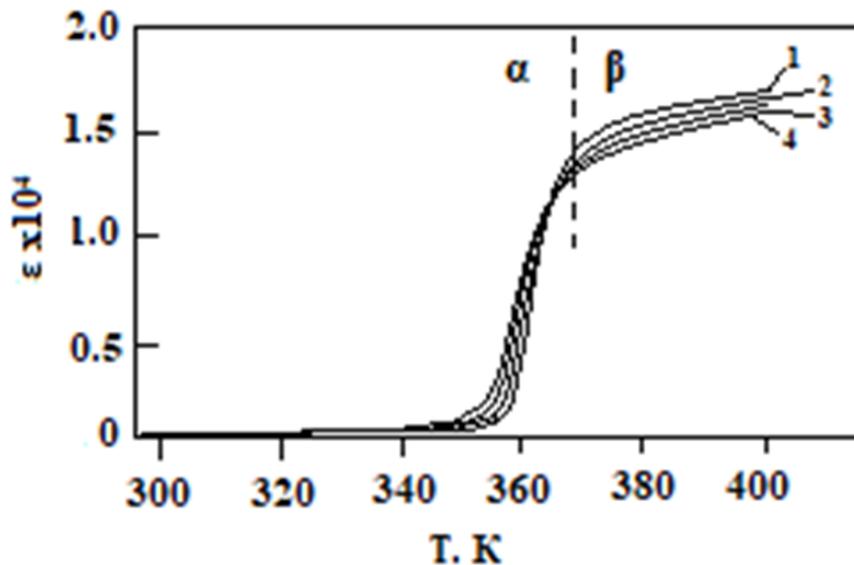


Figure 3.  $\varepsilon(T)$  at a frequency of  $3 \cdot 10^5$  Hz for polycrystalline samples of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$ , where  $x=0$  (curve 1);  $x=0.02$  (curve 2);  $x=0.04$  (curve 3)  $x=0.06$  (curve 4) for  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$ .

For the  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal in Figure 3, anomalies in the  $\varepsilon(T)$  dependence are clearly distinguished in the form of a dielectric permittivity jump at

a temperature of  $T=368$  K, which can be characterized as a phase transition from a dipole-ordered state to a paraelectric state  $T_{\alpha\rightarrow\beta}$ . Observed in Figure 3, a slight increase in the  $\varepsilon(T)$  up to  $T=368$  K characterizes the  $\alpha$ -phases of  $\alpha$ - $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions as dipole-ordered. All  $\alpha$ -phases of  $\alpha$ - $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions remain polar, despite the existing changes in the type of dipole ordering from AFE to FE upon substitution of M-cations.

According to Figure 3 it can be seen that the dependences  $\varepsilon(T)$  of samples of solid solutions  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) decrease, and the temperatures of phase transitions  $T_{\alpha\rightarrow\beta}$  ( $T_{\alpha\rightarrow\beta}$  are characterized by kinks) decrease monotonically with increasing dopant concentrations.

The observed decrease in the temperatures of phase transitions  $T_{\alpha\rightarrow\beta}$  of samples in this system of solid solutions can be explained by local deformations of the crystal structure as a result of the replacement of M-iron cations by scandium atoms with large ionic radius.

## Conclusion

1. It has been established that the crystal structure of orthophosphates  $\left\{ [\text{M}_2(\text{PO}_4)]^{3-} \right\}_{3\infty}$  (where  $\text{M} = \text{Fe}, \text{Sc}$ ) are very "elastic" since they allow deformations of monoclinic distortion of both AFE and FE types at low temperatures and creates conditions for superionic conductivity at high temperatures. In addition, the  $\left\{ [\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)]^{3-} \right\}_{3\infty}$  crystalline framework allows the replacement of M-iron cations by much larger ionic radii of scandium atoms.

2. It has been established that substitutions of M-cations  $\text{Fe} \rightarrow \text{Sc}$  in the system  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) do not change the symmetry of polycrystals, but the parameters of crystal structures increase linearly. Moreover, the ionic conductivities of samples of solid solutions increase in the  $\alpha$ -phases and decrease in the  $\beta$ - and  $\gamma$ -phases. These changes can be associated with local "stretching" deformations of the anionic framework, leading to a partial increase in the symmetry of the monoclinic  $\alpha$ -phases and a decrease in the conduction channel in the rhombohedral  $\beta$ - and  $\gamma$ -phases in the structure of  $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  solid solutions.

3. It has been established that the dipole ordering in samples of solid solutions  $\alpha$ - $\text{Na}_3\text{Fe}_{2(1-x)}\text{Sc}_{2x}(\text{PO}_4)_3$  ( $0 \leq x \leq 0.06$ ) is preserved despite the substitution of M-cations  $\text{Fe} \rightarrow \text{Sc}$ , but there is a gradual decrease temperature of phase transitions  $T_{\alpha\rightarrow\beta}$  and  $T_{\beta\rightarrow\gamma}$  with increasing concentration of dopants. Probably, these changes are caused by a violation of the order and regularity in the anionic and cationic parts of the crystal structure of the samples.

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