

# Phase Stability and Ionic Conductivity of NASICON-Like Phases in $\text{ScPO}_4$ - $\text{Na}_3\text{PO}_4$ - $\text{Li}_3\text{PO}_4$ Ternary System\*

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**Abstract** : Phase formation in ternary system of complex Sc , Na and Li phosphates was studied at 950 °C and synthesis of new phases of definite composition was carried out. Obtained specimens were investigated with X-ray powder diffraction , infrared and impedance spectroscopy. Compositions of fields of homogeneity with NASICON-like structure were discovered. Temperature dependency of ionic conductivity was measured.

**Key words** : phase diagrams ; solid solutions ; phosphates ; solid-state electrolytes

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There is a challenge of finding new solid-state electrolytes having high values of ionic conductivity at low working temperatures. Solid electrolytes are materials that have high ion mobility due to special crystal structure. Ions can move easily through their interstitials. High values of ionic conductivity are usually achieved by migration of alkaline cations. Such compounds as  $\beta$ -alumina ,  $\alpha$ -AgI and their derivatives with high values of ionic conductivity are well known. One of the promising materials for solid-state electrolytes , phosphosilicate of sodium and zirconium  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  , was discovered by Hong and Goode-nough<sup>[1,2]</sup>. The best electric properties are peculiar for  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  called NASICON ( Na Super Ionic Conductor ) , that exhibits a higher conductivity than  $\beta$ -alumina above 300 °C (  $\sigma = 0.25 \Omega^{-1} \cdot \text{cm}^{-1}$  ). These materials lend themselves to a wide range of applications , for example in solid-state batteries , fuel cells and gas sensors<sup>[3]</sup>. Big variety of NASICON-like compounds were intensively studied<sup>[4~7]</sup>. Later , it was found that binary system of  $\text{ScPO}_4$ - $\text{Na}_3\text{PO}_4$  also includes NASICON-like compounds :  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  and  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$ <sup>[8]</sup>. They possess relatively high values of ionic conductivity explained by their three-dimensional structure<sup>[9]</sup>. Its framework consists of  $(\text{PO}_4)$ -tetrahedra and  $(\text{ScO}_6)$ -octahedra shared on tops with interstitial space occupied by  $\text{Na}^+$ -cations. Significant

ionic conductivity of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$   $\sigma = 10^{-1} \Omega^{-1} \cdot \text{cm}^{-1}$  is achieved only at high temperature of 300 °C that limits its practical application. Properties of NASICON-like compounds are connected with statistic character of filling A- and B-type cavities by small  $\text{Na}^+$ -cations and their mobility in the system of channels<sup>[10,11]</sup>. These compounds have complex polymorphism.  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  has 3 polymorphous modifications ,  $\alpha \rightarrow \beta$  at  $\sim 50$  °C and  $\beta \rightarrow \gamma$  at  $\sim 168$  °C<sup>[12,13]</sup>.

It is known that high ionic conductivity can also be achieved by Li-cations.  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$  has 3-dimensional structure with Li-cation conductivity  $\sigma = 10^{-3} \sim 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$  at 300 °C<sup>[14~17]</sup>. Li-cations fill their crystallographic positions statistically. They have small size and can easily migrate through interstitials. Two phase transition were observed here :  $\alpha \rightarrow \beta$  at 177 ~ 222 °C and  $\beta \rightarrow \gamma$  at 222 ~ 257 °C. Polymorphous transitions and ionic properties of  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$  are similar to that of  $\text{A}_3\text{M}_2(\text{PO}_4)_3$  compounds : A = Li , Na , Ag , K ; M = Cr , Fe , In<sup>[18,19]</sup>.

The above-mentioned complex polymorphism makes it difficult to obtain NASICON-like compounds of high phase homogeneity and with good working characteristics at low temperature. It should also be noted here that high price of scandium does not serve well wide application of NASICON-like compounds.

The present work is addressed to a study on the

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subsolidal intersection of the quasiternary system of  $\text{ScPO}_4\text{-Na}_3\text{PO}_4\text{-Li}_3\text{PO}_4$  at 950 °C and aimed to understand how introduction of the third component could improve phase stability of NASICON-like compounds. Measurements of ionic conductivity would allow making a conclusion about practical application of obtained phases.

## 1 Experimental

Phase formation in ternary system of Sc, Na and Li phosphates was investigated by cross-sections:  $\text{ScPO}_4\text{-LiNa}_5(\text{PO}_4)_2$ ,  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3\text{-LiNa}_5(\text{PO}_4)_2$ ,  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3\text{-Na}_3\text{Sc}_2(\text{PO}_4)_3$ ,  $\text{Li}_2\text{Na}(\text{PO}_4)\text{-Na}_6\text{Sc}_3(\text{PO}_4)_5$ ,  $\text{Li}_3\text{PO}_4\text{-Na}_6\text{Sc}_3(\text{PO}_4)_5$ ,  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3\text{-Na}_6\text{Sc}_3(\text{PO}_4)_5$ . Samples were prepared through every 5% ~ 10% (mole fraction). As initial substances for complex phosphate synthesis, commercially available  $\text{Na}_3\text{PO}_4$  and  $\text{Li}_3\text{PO}_4$  (3N purity) were used.  $\text{ScPO}_4$  was synthesized using  $\text{Sc}_2\text{O}_3$  (3N purity). During this process  $\text{Sc}_2\text{O}_3$  was dissolved in concentrated HCl at heating, next sedimentation of scandium hydroxide by adding  $\text{NH}_4\text{OH}$  was conducted at pH = 9 and deposits were dissolved in 30%  $\text{H}_3\text{PO}_4$ . Obtained solution was left for 48 h at room temperature (RT) for ripening, condensation and evaporation. Finally, as-obtained deposits were washed out in hot water and dried at 200 °C followed by calcinations at 950 °C during 24 h.

Complex phosphates were obtained by ceramic method using stoichiometric amounts of simple phosphates. They were mixed and ground in a mortar with ethanol, then pressed in pellets ( $d = 10$  mm) and sintered in furnace at 950 °C during 100 ~ 200 h. After that samples were tempered in liquid nitrogen.

Identification of intermediate and final products of thermal processing was carried out by X-ray powder diffraction using a Shimadzu XRD-6000 diffractometer with Cu K $\alpha$ -radiation at RT. To determine unit cell parameters, the angle interval of  $10^\circ \leq 2\theta \leq 80^\circ$  with a scanning step of  $0.02^\circ$  and recording time 70 min, depending on the quality of reflections, was used. After indexing unit cell parameters were calculated and analyzed with Rietveld method.

Deformation of phosphate anion  $\text{PO}_4^{3-}$  caused by adding of 3d component ( $\text{Li}_3\text{PO}_4$ ) was estimated by infrared (IR)-spectroscopy. IR-spectra of single phase specimens were registered with spectrometer Bruker EQ-55 in the range of wavenumber 400 ~ 3600  $\text{cm}^{-1}$ . Samples were pressed in pellets with KBr.

Ionic conductivity was measured in temperature range 20 ~ 200 °C and frequency range 1 Hz ~ 1 MHz on impedance meter Agilent 4284A with thermal a-

nalysis system NETZSCH STA 449C Jupiter. Powder samples were pressed in pellets of 10 mm in diameter and thickness of 1 ~ 1.5 mm.

## 2 Results and Discussion

Ternary system  $\text{ScPO}_4\text{-Na}_3\text{PO}_4\text{-Li}_3\text{PO}_4$  was investigated by cross-sections. Six cuts were performed (Fig. 1):  $\text{ScPO}_4\text{-LiNa}_5(\text{PO}_4)_2$ ,  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3\text{-LiNa}_5(\text{PO}_4)_2$ ,  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3\text{-Na}_3\text{Sc}_2(\text{PO}_4)_3$ ,  $\text{Li}_2\text{Na}(\text{PO}_4)\text{-Na}_6\text{Sc}_3(\text{PO}_4)_5$ ,  $\text{Li}_3\text{PO}_4\text{-Na}_6\text{Sc}_3(\text{PO}_4)_5$ ,  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3\text{-Na}_6\text{Sc}_3(\text{PO}_4)_5$ .

It was found that the cross-section  $\text{ScPO}_4\text{-LiNa}_5(\text{PO}_4)_2$  cuts into 4 areas of homogeneity in the field of triangle. First small single-phase area with a structure of  $\text{LiNa}_5(\text{PO}_4)_2$  lies up to 8% of  $\text{ScPO}_4$  (structure of a mineral olympite). Extensive area of homogeneity on the basis of high-temperature cubic sodium phosphate stabilized by scandium cation  $\text{Na}_{3-x}\text{Sc}_{x/3}\text{PO}_4$  expands from 12% to 35% of  $\text{ScPO}_4$ . Third area of homogeneity with structure of complex phosphate  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$  exists from 60% to 72% of  $\text{ScPO}_4$ . Its structure is similar to that of NASICON-like  $\text{Na}_{4.5}\text{Yb}_{1.5}(\text{PO}_4)_3$ . The last small area of homogeneity (78% ~ 80% of  $\text{ScPO}_4$ ) has a structure of complex phosphate  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ , it is also of NASICON-like structure.

Other performed cross-sections confirm the existence of relatively large area of solid solutions on the basis of  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$  and allows to determine its borders. Cross-section  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3\text{-Na}_6\text{Sc}_3(\text{PO}_4)_5$  cuts into 2 areas: single-phase area with  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$  structure from 0% to 50% of  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$  followed by two-phase area up to 100% of  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$ . Diffraction patterns of two-phase area contain reflections of both initial compounds. Cross-section  $\text{Li}_2\text{Na}(\text{PO}_4)\text{-}$

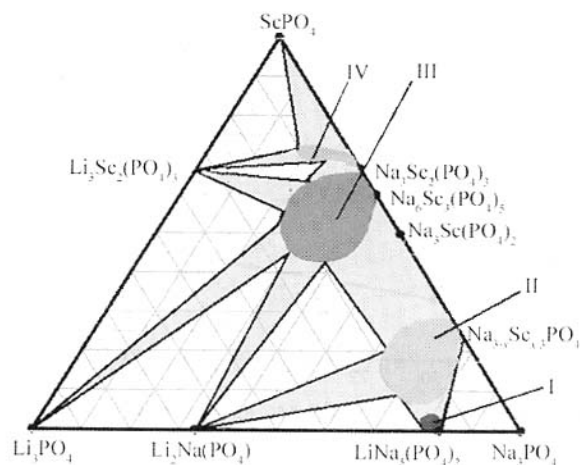


Fig. 1 Phase correlations in ternary system of  $\text{ScPO}_4\text{-Na}_3\text{PO}_4\text{-Li}_3\text{PO}_4$  at 950 °C

$\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$  also cuts into 2 areas. There are single-phase area with  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$  structure in the range of 0% ~ 70% of  $\text{Li}_2\text{Na}(\text{PO}_4)$  and two-phase area up to 70% ~ 100% of  $\text{Li}_2\text{Na}(\text{PO}_4)$ . Cross-section  $\text{Li}_3\text{PO}_4$ - $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$  cuts into single-phase area, which is from 0% to 60% of  $\text{Li}_3\text{PO}_4$ , and above mentioned area of homogeneity with a structure of  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$ . It lasts from 60% to 100% of  $\text{Li}_3\text{PO}_4$ . Cross-section  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$ - $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  cuts only into two-phase area. Finally, no homogeneity area was found for  $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$ - $\text{LiNa}_5(\text{PO}_4)_2$  cross-section. All samples obtained contain two phases, at least. Their diffraction patterns are rather complicated and a lot of unidentified reflections present. All obtained single-phase areas are not new compounds. They are analogs of compounds existing in forming system of double phosphates  $\text{ScPO}_4$ - $\text{Na}_3\text{PO}_4$ .

Lattice parameters of NASICON-like phase samples (Fig. 1, III) were calculated. On Fig. 2 lattice parameters dependences on  $\text{ScPO}_4$  content in cross-section  $\text{ScPO}_4$ - $\text{LiNa}_5(\text{PO}_4)_2$  can be seen. Linear character of dependences of  $a$  and  $c$  is observed in all range of solid solutions following to Vegard's law. Registered IR-spectra show strong distortion of phosphate anion  $\text{PO}_4^{3-}$  caused by introduction of Li-cations into crystal structure of complex Na-Sc phosphates. Distortion of a phosphate anion results in lowering of symmetry of  $\text{PO}_4$ -groups and change of selection rules. Such picture is observed on the spectra of NASICON-like phase with structure of  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$ .

As a result of experimental work performed quasi-ternary diagram was drawn in Fig. 1. It shows phase correlations in the system at 950 °C. We can see single-, two- and three-phase regions. Red-colored area (II) corresponds to cubic phase with structure of

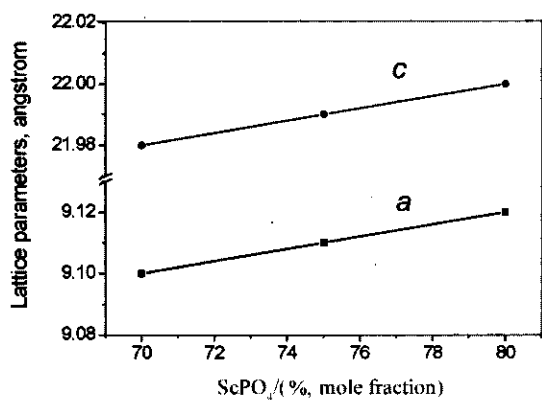


Fig. 2 Lattice parameters  $a$  and  $c$  of single-phase area with NASICON-like structure of  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$  in cross-section  $\text{ScPO}_4$ - $\text{LiNa}_5(\text{PO}_4)_2$

$\text{Na}_{3-x}\text{Sc}_{x/3}\text{PO}_4$  and single-phase area with NASICON-like structure of  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$  is marked by blue color (III). Small single-phase areas with NASICON-like structure of  $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$  (IV) and with mineral oympite structure (I) are marked by green and dark-blue colors, respectively.

Ionic conductivity measurements were carried out on samples of solid solutions area of NASICON-like structure  $\text{Na}_6\text{Sc}_3(\text{PO}_4)_5$ . For this purpose hodographs were plotted. Values of ionic conductivity were calculated with using formula:

$$\sigma = h / (R_v \cdot S)$$

where  $h$  denotes thickness of sample, cm;  $R_v$  denotes volumetric resistance,  $\Omega$ ;  $S$  denotes area of electrode contacts,  $\text{cm}^2$ .

According to calculated data temperature dependence of ionic conductivity was plotted (Fig. 3). Surprisingly, introduction of  $\text{Li}^+$ -cation has rather negative influence on ionic conductivity of obtained samples and will be the subject of a future investigation.

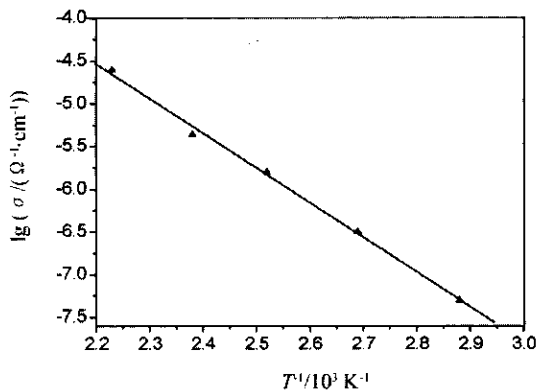


Fig. 3 Temperature dependences of ionic conductivity of NASICON-like single-phase

### 3 Conclusion

Phase formation in ternary system  $\text{ScPO}_4$ - $\text{Na}_3\text{PO}_4$ - $\text{Li}_3\text{PO}_4$  was investigated for the first time. Introduction of  $\text{Li}^+$ -cations in crystal structure of NASICON-like compounds does not result into forming new compounds, but significantly affects dimensions and phase stability of a solid solutions region. Four relatively large single-phase areas, analogs of compounds existing in forming binary systems, were found out. Compositions of high phase stability which allows obtaining ceramics with NASICON-like structure and desired electro-chemical properties were discovered. It would also enable to decrease expensive scandium content in NASICON-like compounds and makes them very interesting from economic point of view.

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