

CRYSTAL STRUCTURE OF THE SOLID ELECTROLYTE $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$
IN THE TEMPERATURE RANGE 27–350°C

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An x-ray structural study of $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ crystals has been carried out in the temperature range 27–350°C. It has been shown that the first phase transformation in the range 40–60°C is accompanied by an increase in the density and a change to the space group $R\bar{3}c$. The possible relationship between the observed temperature structural deformations and the change in the activation energy in the second phase transformation in the range 130–180°C has been discussed.

A study of the temperature dependence of the electrical conductivity of $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ crystals [1] revealed two temperature ranges in which there is a change in the activation energy: 50 and 60 and 130–180°C (Fig. 1). The first observed phase transformation leads to an abrupt change in the electrical conductivity, whereas the second is marked by an inflection on the curve giving the temperature dependence of the electrical conductivity and by a decrease in its activation energy. An analogous temperature dependence of the electrical conductivity was observed for $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$ [2, 3]. At room temperature, these crystals are stable as the monoclinic modification; above 95 and 140°C, their rhombohedral phases are stable. A second phase transformation is observed for these compounds at temperatures of 145 and 170°C. In accordance with the nature of the temperature dependence of the electrical conductivity, the structural study was carried out at 27, 65, 97, 147, 197, 247, 297, and 350°C using one single crystal; the study at room temperature was carried out to identify these and previously studied [4] crystals. Figure 1 also gives the temperature dependence of the unit cell parameters. The monoclinic structure is converted into a trigonal structure in the temperature range 40–60°, and the phase transformation is accompanied by a decrease in the volume. When the single crystal is heated further in the temperature range 150–200°C, there is a change in the slope of the lines characterizing the temperature dependence of the parameter c and the unit cell volume V with a parameter a which is constant over the first phase transformation. The numerical values of the parameters being discussed are given in Table 1. For convenience in comparison, the data for temperatures before the first phase transformation are given in the trigonal setting. A low-temperature phase transformation was also observed in [5, 6].

STRUCTURAL STUDIES AND DESCRIPTION OF THE STRUCTURES

The compound was synthesized in the form of poorly faceted single crystals of insufficient size for rolling. All the experimental material was obtained on a DAR-UM-BESM-6 automated system for x-ray structural studies. The monoclinic crystals in the temperature range before the first phase transformation in the space group Bb contain four molecules in the unit cell. The calculated density is 2.81 g/cm³; 998 reflections were recorded using $\text{CuK}\alpha$ radiation ($R = 7.2\%$), and subsequently the experiment and the calculations were repeated for $\text{MoK}\alpha$ radiation, where 2540 independent reflections were recorded ($R = 6\%$). Allowance was made for absorption [7] using the form of the specimen and transmission curves recorded using the 002, 004, and 006 reflections. The cell parameters were refined from the $\text{K}\alpha_1$ and $\text{K}\alpha_2$ wavelengths of the molybdenum radiation for the reflections 440, 660, $\bar{1}260$, $2\bar{0}.10.0$ in the monoclinic cell, which corresponds to the reflections 600, 900, 0.0.18, 0.0.30 in the hexagonal cell. For the recording at different temperatures we used the high-temperature assembly developed in the Section of the Institute of Chemical Physics of the Academy of Sciences of the USSR for a diffractometer of the sloping type, in which the temperature is established and kept constant to within $\pm 2^\circ$ [8]. The change from one temperature to another was carried

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TABLE 1. Cell Parameters, Number of Reflections, and Values of the R-Factor for the Temperatures Studied

T, °C	a, Å	c, Å	V, Å ³	Number of reflections for the structure studied	R, %
18	8,885	22,746	1555,2		
27	8,665	22,747	1555,2		
35	8,889	22,748	1556,6		
40	8,889	22,743	1556,3		
45	8,930(4)	22,308(7)	1540,5		
60 [4]	8,927(3)	22,34(4)			
65	8,931(4)	22,326(7)	1542,1	624	5,3
80	8,930(4)	22,351(7)	1543,7		
97	8,929(4)	22,383(7)	1545,5	652	4,3
147	8,926(4)	22,477(7)	1550,9	625	4,0
197	8,928(4)	22,575(7)	1558,4	605	4,8
247	8,928(4)	22,625(7)	1561,8	626	5,4
297	8,928(4)	22,674(7)	1565,2	581	4,3
350	8,929(4)	22,709(7)	1568,0	585	4,9

TABLE 2. Coordinates of the Atoms ($\times 10^4$) and Values of the Individual Thermal Vibrations ($\times 10^4$) for the Temperatures Studied

T°, C	65	97	147	197	247	297	350
Sc Z	3513(1)*	3512	3510	3508	3507	3506	3505
B ₁₁ =B ₂₂ =B ₁₂	24	24	29	30	33	34	37
B ₃₃	3	3	3	3	3	4	4
P Y	2948(1)	2944	2939	2935	2931	2929	2927
B ₁₁ =B ₁₂	30	28	32	32	33	35	39
B ₂₂	23	22	26	27	30	32	34
B ₃₃	7	6	6	6	6	6	6
B ₂₃	-7	-6	-6	-5	-5	-5	-5
B ₁₃	-14	-13	-12	-10	-10	-9	-10
O ₁ X	1729(2)	1729	1733	1736	1736	1741	1739
Y	1925(2)	1923	1935	1941	1943	1947	1951
Z	4113(1)	4110	4103	4094	4091	4089	4086
B ₁₁	52	50	53	54	62	63	67
B ₂₂	43	41	46	48	54	54	58
B ₃₃	10	10	11	11	12	12	13
B ₁₂	21	13	11	11	13	10	17
B ₁₃	-10	-14	-13	-13	-14	-11	-13
B ₂₃	-12	-16	-18	-16	-20	-20	-19
O ₂ X	243(3)	256	285	306	321	329	335
Y	2096(3)	2106	2116	2118	2123	2127	2129
Z	1944(1)	1943	1949	1953	1957	1956	1959
B ₁₁	119	114	131	135	138	154	161
B ₂₂	104	104	104	99	108	102	113
B ₃₃	20	19	17	16	16	15	16
B ₁₂	133	126	128	128	132	141	152
B ₁₃	-19	-14	-8	-2	-2	-3	-2
B ₂₃	-65	-61	-54	-49	-48	-46	-48
Na ₁ X	6372(2)	6368	6366	6358	5351	6358	6353
B ₁₁	48	54	41	72	74	96	106
B ₂₂ =B ₁₂	45	56	50	78	101	114	139
B ₃₃	32	38	45	63	66	75	85
B ₁₃	25	30	36	52	59	63	74
B ₂₃	50	59	73	103	119	125	148
Population	11,9	11,9	11,9	12,3	11,9	12,1	12,3
Na ₂ B ₁₁ =B ₂₂ = =B ₁₂	526	658	574	903	1035	1279	1289
B ₃₃	4	7	5	12	9	14	20
Population	5,3	5,6	5,5	5,5	5,2	5,5	5,2

*The error in the determination of the coordinates of the atoms is the same for all temperatures.

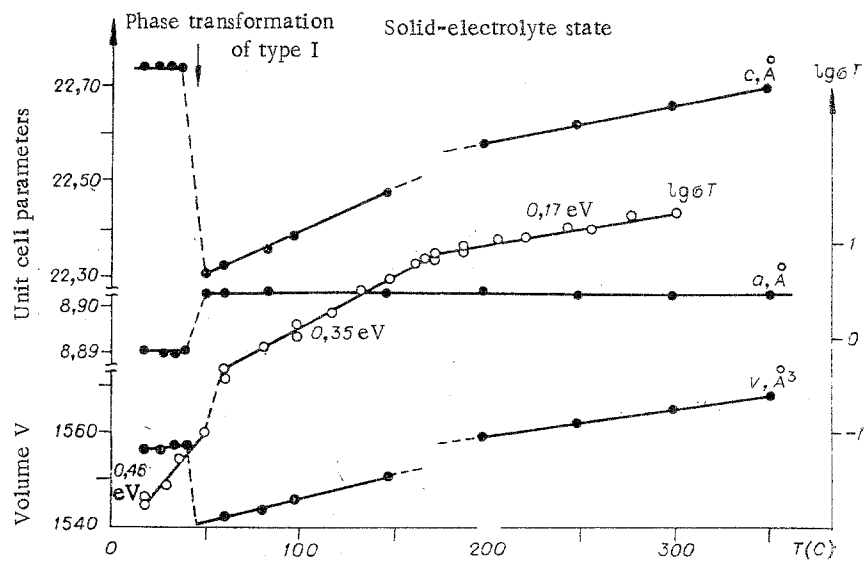
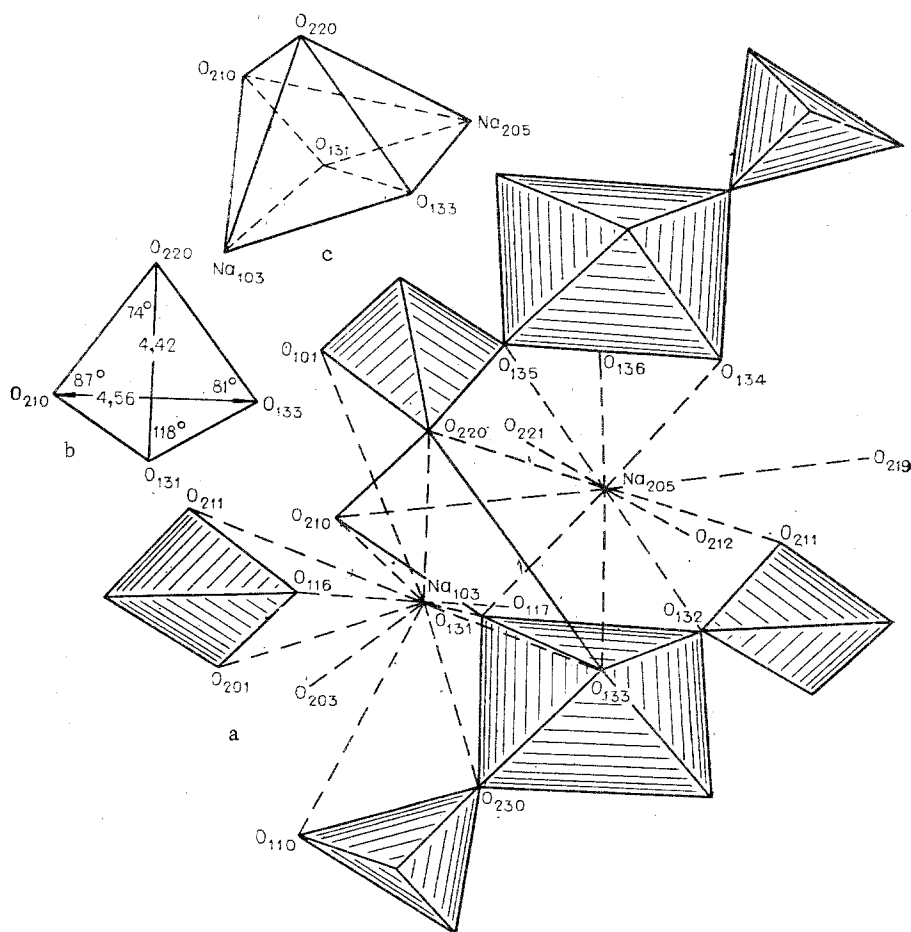


Fig. 1. Temperature dependence of the conductivity and lattice parameters of the solid electrolyte $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$.



with subsequent re-indexing and averaging of equivalent reflections for each temperature. The number of independent reflections and the final value of the R-factor for each of the temperatures studied are given in Table 1. The values of the independent coordinates and the anisotropic thermal parameters are given in Table 2. The changes taking place in the structure in the first phase transformation were discussed in [5] and agree with our data.

Figure 2a gives a fragment of the oxygen framework containing two sodium atoms of different kinds projected on the xOz plane. The broken lines indicate the distances from each sodium atom to the 12 nearest oxygen atoms. The two crystallographically independent oxygen atoms are numbered in such a way that the first figure of their number denotes the kind, and the last two figures of their number indicates the number of the symmetry matrix from [9]. A similar notation is used for the sodium atoms. Of all the oxygen atoms given in Fig. 2a, only four are common to two sodium atoms situated together: O_{220} , O_{210} , O_{131} , and O_{133} ; for clarity, they are joined by continuous lines. Figure 2b shows the details of the structure of this four-angle figure for a temperature of 197°C. The distances $r_{220}-r_{131}$ and $r_{210}-r_{133}$ for all temperatures are given in Table 3. Each sixfold position occupied by a sodium ion of the second kind is surrounded by six 18-fold positions occupied by sodium ions of the first kind; these positions are situated at the vertices of a trigonal antiprism, but the actual movement of the sodium ions takes place not along a straight line but as it were along the sand-glass shape formed. Since each 18-fold position adjoins two sixfold positions, the structural fragment of two sodium atoms and four oxygen atoms, multiplied by the symmetry elements, produces three-dimensional infinite channels in the crystal. The details of the structure of the fragment $Na_{205}O_{131}O_{133}O_{220}O_{210}Na_{103}$ (see Fig. 2c) are given in Table 3 for all temperatures. The errors in the determination of the distances do not exceed 0.007 Å. The last row gives the absolute magnitude of the change in the distance. The fragment being considered contains eight such distances for which Δr is greater than 3σ . Each distance changes regularly. The areas of the cross sections, the regular features of the displacement of the oxygen atoms from the common plane, and the values of the distances from the oxygen atoms to the center of the cross section for all temperatures were also analyzed. The absence of any other structural manifestations of the observed phase transformation lead to the conclusion that the change in the conductivity is due entirely to the change in the above distances. There is practically no change in the magnitude of the semi-axes nor in the orientation of the ellipsoids of the temperature vibrations of the oxygen atoms in the temperature range 65–350°C. For the sodium ions, while the orientation of the ellipsoids is preserved, their dimensions increase by a factor of two.

DISCUSSION OF RESULTS

The structural study established that in the range 50–60°C there is a phase transformation, as a result of which the monoclinic crystals (space group Bb) become rhombohedral (space group $R\bar{3}c$). The results of our studies at 65°C on the whole agree with the data in [6]. In the phase transformation, the $[Sc_2(PO_4)_3]^{3-}$ framework remains practically unchanged, since the maximum displacements of the atoms forming the framework do not exceed 0.2 Å, but an appreciable redistribution of the sodium ions is observed. In the monoclinic low-temperature modification, the sodium ions are distributed in five fourfold crystallographic positions. In the phase transformation, as a result of the displacement of the sodium ions, the symmetry

TABLE 3. Values of the Distances in the Fragment $Na_{103}O_{220}O_{210}O_{131}O_{133}Na_{205}$

T, °C	$O_{220}-O_{131}$	$O_{210}-O_{133}$	$O_{131}-O_{133}$	$O_{131}-O_{210}$	$O_{210}-O_{220}$	$O_{220}-O_{133}$	$Na_{103}-O_{131}$	$Na_{103}-O_{133}$	$Na_{103}-O_{210}$	$Na_{103}-O_{220}$	$Na_{205}-O_{131}$	$Na_{205}-O_{210}$	$Na_{103}-Na_{205}$
65	4.370	4.583	2.838	2.458	3.804	3.770	2.464	2.504	2.901	2.706	2.570	3.660	3.406
97	4.372	4.581	2.836	2.459	3.804	3.788	2.465	2.500	2.897	2.706	2.578	3.650	3.408
147	4.386	4.563	2.847	2.449	3.803	3.805	2.461	2.504	2.873	2.731	2.602	3.641	3.411
197	4.413	4.563	2.856	2.454	3.807	3.826	2.462	2.502	2.862	2.751	2.628	3.638	3.413
247	4.425	4.556	2.858	2.451	3.807	3.833	2.463	2.500	2.851	2.763	2.637	3.634	3.414
297	4.431	4.556	2.865	2.451	3.804	3.836	2.463	2.504	2.846	2.768	2.647	3.630	3.418
350	4.435	4.546	2.867	2.449	3.807	3.847	2.461	2.506	2.843	2.777	2.654	3.630	3.418
$ \Delta r $	0.065	0.037	0.031	0.010		0.059			0.058	0.071	0.084	0.020	

of the lattice increases to $R\bar{3}c$ with the formation of two crystallographically independent positions for the sodium ions: six- and 18-fold. According to our data, in contrast to [6], the sixfold position is completely populated. In the second position, 12 sodium ions are distributed randomly in the 18 equivalent positions. The redistribution of the sodium ions involves the ions denoted Na(B) and Na(C) in [2], whereas the ions Na(A) completely populate the fourfold position in the monoclinic modification together with the atoms of the $[\text{Sc}_2 \cdot \cdot (\text{PO}_4)_3]^{3-}$ framework, which undergo no significant change in position.

A recently published paper [10] described the synthesis and structure of the phase "NASICON" for $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ crystals. Analysis of the structure of this phase, studied by Hong at room temperature, confirmed completely that it is identical to the high-temperature phase which we studied. The x-ray diffraction patterns given in [10] for the phase "NASICON" agree with our $F(hk\bar{l})$ for the high-temperature modifications. Calculation shows that the monoclinic setting which we chose for the crystals studied at 97°C is converted by a simple transformation of the matrices (120, 001, 101) to the unit cell of [10] in the space group $c2/c$. The parameters of the transformed cell ($a = 15.487$, $b = 8.930$, $c = 9.040$ Å, $\beta = 124.8^\circ$) extrapolated to $t = 27^\circ\text{C}$, show satisfactory agreement with the parameters given in [10] ($a = 15.461$, $b = 8.913$, $c = 9.016$ Å, $\beta = 124.8^\circ$). We thus arrive at the conclusion that Hong was able to stabilize the high-temperature phase at room temperature. The possibility of this stabilization is indicated by our calorimetric measurements. On heating in an MKS-250 scanning isothermal calorimeter at a rate of scanning of 0.1 deg/min, beginning from room temperature, an endothermic peak of ~180-210 cal/mole is observed at 50°C; a second endothermic peak with a heat absorption of ~250 cal/mole appears at 169°C. On cooling, hysteresis of 35-40° is observed for both peaks, which is a characteristic of a phase transformation of type I [11].

The first phase transformation, associated with a redistribution of the sodium ions, for $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ crystals is characterized by a decrease in the unit cell volume, that is, by an increase in the density of the crystals from 2.81 g/cm³ (27°C) for the monoclinic modification to 2.88 g/cm³ (65°C) for the rhombohedral modification. It can be confidently stated that for $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$ crystals, the phase transformation is also accompanied by an increase in the density of the crystal. The volumes of the unit cells given for the monoclinic and rhombohedral modifications are 1395 and 1398 Å³, respectively. If, however, account is taken of the fact that the second value was obtained at a temperature of 205°C, whereas the transition takes place at 140°C [3], the increase in the density of the rhombohedral phase is obvious. It may be assumed that, for $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ crystals, an increase in the density also takes place in the phase transformation, since the slight increase in the unit cell volume from 1422 (25°C) to 1439 Å³ (200°C) is most probably the result of the volume thermal expansion (with the phase transformation at 95°C). In general, phase transformations of this kind, where the high-temperature phase is denser than the low-temperature phase, are very rare. Moreover, it is surprising that these transformations (in the compounds being considered) lead to a super-ion state, characterized by a channel structure. Analogous phase transformations are observed for AgI with an increase in density from 5.66 to 6.01 g/cm³ [12] and for RbAg_4I_5 with an increase in density from 5.36 to 5.43 g/cm³ (the calculation for the α -phase was carried out for -43°C) [13]. We assume that this phenomenon is characteristic of super-ion conductors with three-dimensional conductivity, in which the transformation to the super-ion state leads to a more uniform distribution of the conducting ion in the unit cell of the crystal, i.e., the conducting ion, as it were, "flows" through the cavities of the framework structure, leading to slight contraction of the crystal. In addition, the high density of the high-temperature phase indicates that it is a metastable state. This should apparently also be revealed in its physicochemical properties: high ionic conductivity, easy exchange of the conducting ions for other ions, etc. $\text{NaZr}_2(\text{PO}_4)_3$ crystals, which have the same structure as $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$, do not show the properties of the super-ion state, but the introduction of additional sodium ions in the 18-fold crystallographic position, including them in the overall system of sodium ions determining the ionic conductivity of the high-temperature phase, leads to the appearance of super-ion properties. According to the experimental data, in the temperature range 65-350°C there is no change in the populations of the positions of the ions Na_1 and Na_2 (within the limits of error of the measurement) (see Table 2). The analogous observation, that the population of the conducting ions is independent of temperature, was previously made for the solid electrolyte RbAg_4I_5 [14]. In the last case, however, no changes in the activation energy of the electrical conductivity were observed throughout the entire temperature range studied.

The concept of an order-disorder phase transformation, proposed to explain the inflection on the graph giving the temperature dependence of the electrical conductivity of PyAg_5I_6 crystals [15], cannot be used to explain the analogous phenomenon in $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ crystals, since in the last case the change in the populations of the crystallographic positions occupied by the conducting ions (Na_1 and Na_2) is independent of temperature.

To investigate the mechanism of the conductivity in crystals of the type being considered, a structural study of $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ crystals in which sodium ions have been replaced by silver ions by ion exchange is now being carried out.

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