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Zirconium Deficiency in Nasicon-Type Compounds: Crystal Structure of $Na_5Zr(PO_4)_3$

J. P. BOILOT,* G. COLLIN,† AND R. COMES†

**Groupe de Chimie du Solide, Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau, France and †Laboratoire de Physique des Solides, Université de Paris Sud, Bât 510, Orsay, France*

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Single crystals of $Na_5Zr(PO_4)_3$ have been prepared using a flux method. At high temperature (200°C), the crystal structure can be described as a 3D network of PO_4 tetrahedra corner shared with ZrO_6 and NaO_6 octahedra. In fact, this compound belongs to the Nasicon-type class which exhibits a large nonstoichiometry range by zirconium deficiency.

Introduction

Many compounds exhibit a Nasicon ($Na_3Zr_2Si_2PO_{12}$)-type structure (space group $R\bar{3}c$). The exceptional electrical properties of these materials are due to the high mobility of sodium ions through tunnels in a rigid structure made of SiO_4/PO_4 tetrahedra sharing corners with MO_6 octahedra (*1, 2*).

These compounds are either pure phosphates $Na_3M_2^{III}(PO_4)_3$ with M^{III}: Sc, Fe, Cr, Y . . . , or solid solutions in the system $NaZr_2(PO_4)_3$–$Na_4Zr(SiO_4)_3$. It has been shown that the existence range of Nasicon-type structures could be extended by partial substitution of Zr^{IV} ions by sodium ions. Moreover, other solid solutions can be obtained by mixing silicates and phosphates with a zirconium deficiency: $Na_{1+4y}Zr_{2-y}(PO_4)_3$, $0 < y < 1$ (*3*). Concerning compositions close to the pure phosphate $Na_5Zr(PO_4)_3$ ($y = 1$) and especially, $Na_{5.5}ZrP_{2.5}Si_{0.5}O_{12}$ we have, recently demonstrated the existence of two structural transitions at respectively, 86 and 129°C. These are usual characteristics for compounds with a Nasicon-type structure. The first transition corresponds to a change of correlations between off-centered zirconium atoms in octahedral sites, the second to a centering of these atoms and an occupation transfer between sodium sites. The order of these transitions and associated thermal effects is influenced by the nonstoichiometry and structural defects. The purpose of this paper is to report

(1) experimental conditions for the single crystal synthesis of $Na_5Zr(PO_4)_3$; and

(2) the conventional structure determination of the high temperature phase (200°C) from X-ray diffraction, i.e., above the two structural transitions.

Despite a different space group ($R32$ instead of $R\bar{3}c$) we demonstrate that the single crystal structure of $Na_5Zr(PO_4)_3$ still retains main features of the Nasicon-type structure.

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TABLE I

EXPERIMENTAL CONDITIONS FOR THE SYNTHESIS OF $Na_5Zr(PO_4)_3$ SINGLE CRYSTALS

	Experiment 1	Experiment 2	Experiment 3
		Experimental parameters	
T(°C)	1100	1150	1190
t(days)	1	3	9
x $Na_4P_2O_7/Na_5Zr(PO_4)_3$	10	4	3
τ(°C/hr)	3	3	3
		Crystal growth	
	No crystal	Crystallization in the bulk Small crystals grow in the shape of hexagonal platelets ($S \sim 1$ mm^2) with frequent twinning (Fig. 1a)	Surface nucleation Monocrystalline platelets with a great area (5 to 8 mm^2), in comparison with the thickness (0.1 to 0.5 mm). Crystals exhibit frequent twinning (Fig. 1b)
	Good dissolution in the flux	Good homogeneity of the dissolution	Partial dissolution in the flux

Experimental

1. Single Crystal Preparation

Single crystals have been obtained using the flux technique. The $Na_4P_2O_7$ compound was used as a solvent (melting point: 880°C) and the starting compound was composed of $Na_5Zr(PO_4)_3$ phase in a polycrystalline state, prepared from a solid state reaction between ZrO_2, Na_2CO_3, and $NH_4H_2PO_4$ at 900°C. Each mole of $Na_5Zr(PO_4)_3$ is mixed with x moles of $Na_4P_2O_7$ in a platinium crucible. This is placed in a furnace and held above T (°C) long enough (t days) to ensure complete reaction. Then the temperature is lowered at the rate of τ°C/hr to a temperature of 850°C. Next the crucible is removed from the furnace, allowed to cool, and the grown $Na_5Zr(PO_4)_3$ crystals are separated by leaching away the solidified flux with hot water and then with hot dilute HCl.

Three preparations, using different experimental parameters (T, t, x, τ), are summarized in Table I. Figures 1a and b, respectively, show monocrystalline platelets obtained from Experiments 2 and 3. It can be noted that experimental conditions which imply a high enough $Na_5Zr(PO_4)_3$ concentration in the flux and an important flux evaporation lead to best crystals (see Experiment 3 in Table I).

Single crystals were analyzed for their content of Na, Zr, P elements by atomic absorption spectrometry and only small variations (less than 0.1 wt%) have been observed in the element contents. The average composition deduced from the chemical analysis is of $Na_{4.94(4)}Zr_{.99(1)}P_{2.96(3)}O_{12}$.

2. X-Ray Data Collecting

Single crystals of the $Na_5Zr(PO_4)_3$ compound were studied at 200°C by taking precession photographs. A hexagonal (rhombohedral) symmetry was found and the reflections systematically absent are only $hkil$ with $-h + k + l = 3n$. The existence of $h\bar{h}0l$ reflections with $l = 2n$ clearly shows that these crystals do not have the same space group as the Nasicon-type structure ($R\bar{3}c$). The parameters of the hexagonal cell were refined at 200°C on a $P2_1$ syntex automatic four circle diffractometer: $a = 9.217$

Å, $c = 22.39$ Å. The crystal was heated using a hot air device (±2°C). Intensities of 1847 reflections were recorded on the same diffractometer between $2\theta = 0$ and $2\theta = 65°$, using Mo$K\alpha$ radiation with a graphite monochromator. Absorption corrections were performed with the ψ scan technique using 15 reflections. Equivalent reflections were averaged and refinement was carried out according to the ORJFLS routine with all the nonequivalent measured intensities (even zero values) (820 reflections) and using atomic scattering factors.

X-Ray Structure Determination

The Patterson function shows clearly that the positions of zirconium, phosphorus, and sodium atoms in the $Na_5Zr(PO_4)_3$ unit cell are similar to the ones observed for the Nasicon-type structure. Thus $3m$ and $\bar{3}m$ symmetries which would imply another distribution of phosphorus and sodium atoms are inconsistent with Patterson projections.

Initially the structure refinement was carried out in the $R3$ space group after transposition of positional coordinates previously reported for $R\bar{3}c$ Nasicon-type compounds (*1*, *4*). The filling of normal Nasicon sodium sites and the half substitution of zirconium by sodium atoms are imposed in order to respect the chemical composition. All this leads to a discrepancy index of 9.5%.

But after a shift of the cell origin ($\Delta z = \frac{1}{4}$) structural parameters exhibit a clear symmetry relation xyz, $yx\bar{z}$, corresponding to the $R32$ space group, in which structural refinements are then performed. In this way, a discrepancy index of 4.28% is obtained, after refinement of positions and anisotropic thermal parameters.

Successive refinements of the occupation factors for oxygen, sodium and zirconium atoms lead to $R = 4.06\%$. No significant change is found in oxygen site occupancies; the occupation of Na(1) site is only 0.96(1) whereas the Na(2) site seems fully occupied. An unexpected result is that the zirconium site is underoccupied (0.96(1)).

In fact, if we omit reflections close to the origin of the reciprocal space ($\sin \theta/\lambda < 0.30$), thus using only 740 independent refections, a similar refinement involves a full occupancy of the zirconium site (0.99(1)). Consequently, the previous zirconium deficiency seems to be an artifact, due to the use of the atomic scattering factors. Indeed, ionic scattering factors would be more accurate, but the P^{5+} table is still unknown.

A further investigation, by difference

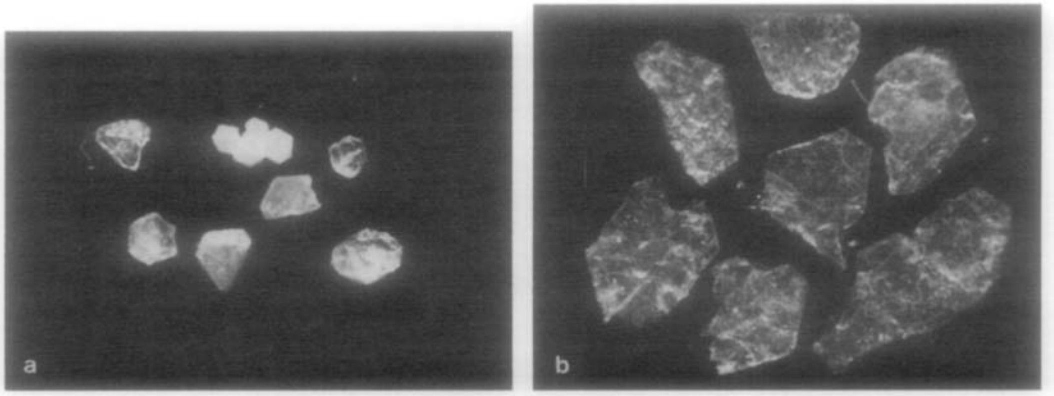

FIG. 1. Single crystals of $Na_5Zr(PO_4)_3$ (×1) (a) prepared from Experiment 2 in Table I, and (b) prepared from Experiment 3 in Table I.

TABLE II

$Na_5Zr(PO_4)_3$ (200°C): POSITION AND THERMAL PARAMETERS ($Z = 6$)

	Pos.	Occup.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	6*c*	0.858(3)	0.00000	0.00000	0.09736(2)	198(1)	198(1)	264(3)	99	0	0
Zrint1	6*c*	0.059(3)	0.00000	0.00000	0.7539(59)	609(46)					
Zrint2	6*c*	0.030(3)	0.00000	0.00000	0.12266(76)	565(60)					
P(1)	9*d*	1.500	0.29078(11)	0.00000	0.00000	151(4)	177(5)	408(15)	$U_{22}/2$	$U_{23}/2$	31(5)
P(2)	9*e*	1.50	0.67332(14)	0.00000	0.50000	215(7)	198(9)	447(8)	$U_{22}/2$	$U_{23}/2$	78(6)
O(1)	18F	3.00	0.20356(46)	0.02761(47)	−0.05375(19)	530(20)	775(23)	1081(23)	255(17)	−382(20)	285(19)
O(2)	18F	3.00	0.78307(42)	0.4196(51)	0.55339(18)	538(9)	794(24)	929(23)	59(18)	−346(20)	239(20)
O(3)	18F	3.00	0.16222(40)	0.18414(36)	−0.15608(14)	344(14)	392(17)	681(18)	−6(13)	−28(14)	222(15)
O(4)	18F	3.00	0.82163(30)	0.78917(32)	0.32441(13)	253(13)	245(12)	699(18)	52(11)	67(14)	53(13)
Na(3)	6*c*	1.00(1)	0.00000	0.00000	0.40424(10)	416(7)	416(7)	478(10)	$U_{22}/2$	0	0
Na(1)	6*c*	0.96(1)	0.00000	0.00000	0.25511(10)	621(12)	621(12)	395(13)	—	0	0
Na(21)	9*d*	1.50(1)	0.61713(23)	0.00000	0.00000	304(8)	351(12)	1037(18)	—	$U_{23}/2$	−38(13)
Na(22)	9*e*	1.49(1)	0.31473(41)	0.00000	0.50000	391(18)	342(22)	2597(35)	—	$U_{23}/2$	327(22)
Na(4)	9*d*	0.04(1)	0.1100(65)	0.00000	0.00000	90(200)	0	0	0	0	0

Note. U_{ij} (Å^2 × 10^4) is given by the formula exp $-2\pi^2 \Sigma_{i,j} h_i h_j a_i^* a_j^*$.

TABLE III

$Na_5Zr(PO_4)_3$: ANHARMONIC TERMS

Covariant Contracted Gamma and Delta Tensors for Oxygen Atom

	Gamma(1)	Gamma(2)	Gamma(3)	Delta(1.1)	Delta(2.2)	Delta(3.3)	Delta(1.2)	Delta(1.3)	Delta(2.3)
O(1)	0.17 − 001(10)	−0.21 − 001(7)	0.40 − 001(19)	0.70 − 001(18)	0.15 − 001(9)	0.21 + 000(7)	−0.32 − 001(11)	0.16 + 000(3)	−0.68 − 001(22)
O(2)	−0.28 − 001(6)	0.12 − 001(4)	−0.71 − 001(13)	0.37 − 001(9)	−0.37 − 002(34)	0.11 + 000(5)	0.77 − 003(500)	0.59 − 001(19)	0.12 − 002(112)
O(3)	0.73 − 002(50)	0.06 − 002(54)	0.48 − 001(9)	0.24 − 002(60)	0.29 − 002(67)	0.50 − 001(28)	0.12 − 002(48)	0.15 − 001(9)	−0.13 − 001(12)
O(4)	−0.32 − 002(47)	−0.16 − 001(5)	−0.96 − 002(56)	−0.10 − 002(74)	0.17 − 001(7)	0.14 − 001(12)	0.46 − 002(55)	−0.29 − 004(70)	0.26 − 002(78)

Covariant Contracted Gamma Tensor and Scalar Delta for Na + Ions

	Gamma(1)	Gamma(3)	Scal. delta
Na(1)	0.00	−0.20 − 001(9)	0.27 − 003(44)
Na(3)	0.00	0.12 − 001(7)	0.11 − 002(3)
Na(21)	−0.67 − 002(53)	0.00	0.41 − 003(38)
Na(22)	0.78 − 002(86)	0.00	0.16 − 003(72)

Full Tensors for Zr Atom

	Gamma 111	Gamma 333	Gamma 112	Gamma 113	Delta 1111	Delta 3333	Delta 1113	Delta 1133	Delta 1123
Zr	0.32 − 0.03(12)	0.15 − 004(17)	−0.88 − 003(24)	−0.02 − 004(42)	−0.36 − 003(17)	−0.34 − 005(47)	0.12 − 003(12)	−0.14 − 004(9)	−0.43 − 004(46)

Fourier analysis, shows a significant residual electron density about 0.6 Å from the Zr site in the ±*c* direction of the hexagonal cell. Using the orthogonalized Hermite polynomial expansion of the structure factor described by Johnson (*5*), anharmonic temperature factors up to the fourth order are applied to the Zr site. This leads to an improvement of the agreement index (4.06 → 3.55%). Nevertheless, the introduction of two interstitial zirconium sites, on both sides of the normal one in a refinement without anharmonic terms, gives a better description of the zirconium atom (3.20%) (Table IVa). This probably reveals a statical disorder which could be connected with the off-centering of these atoms at low temperature (*3*).

Another significant residual electron density, found between two ZrO_6 octahedra, has been interpreted as an interstitial sodium position (noted Na(4)), essentially because the occupation factor of this site is different in the low temperature phases (*3*). The introduction of this new sodium position in the refinement gives an agreement index of $R = 3.07\%$ (Table IVa) and a weighted value of $R_w = 2.66\%$. Finally a cycle with anharmonic terms leads to positions, anisotropic thermal parameters, and occupation factors which are summarized in Table II. Elements of full or contracted third and fourth rank tensor for atoms are given in Table III. Important anharmonic contributions were found, especially for O(1) and O(2) atoms. The Hamiltonian statistical test (Table IVb) shows that the improvement of the agreement index, arising from the introduction of anharmonic terms ($R_w = 2.30\%$), is significant.

Description of the Structure

The crystal structure of the Nasicon-type is usually described in terms of PO_4 tetrahedra and ZrO_6 octahedra which are linked by corners to give a three-dimensional network. Na atoms occupy the interstices. In $Na_5Zr(PO_4)_3$, half of the zirconium atoms are replaced by sodium atoms and four Na sites are occupied:

the regular Na_1 and Na_2 sites previously mentioned for Nasicon-type compounds, though the Na_2 is shifted into two independent sites (noted Na(21) and Na(22));

Na(3) sites taking the place of Zr sites in order to display the new atomic sequence along the threefold axis
Na(1)–Na(3)–Na(3)–Na(1)–Zr–Zr–Na(1)
to be compared with
Na(1)–Zr–Zr–Na(1)–Zr–Zr–Na(1)
for usual Nasicon compounds;

Na(4) interstitial site strongly off-centered in the six coordinated antiprism localized between two Zr sites and only slightly occupied at this temperature.

The values of thermal vibrations are rather high and anisotropic for all atoms of this material (Table II). This behavior can be compared with one of the other Nasicon-type compounds in which the same effect is generally observed (cf., for instance, $Na_3Sc_2(PO_4)_3$ (*6–7*)). However, the phenomenon is enhanced in this material, which is probably due to a highly disordered state following the two strong first-order phase transitions.

Interatomic distances are given in Table V. Normal *M*–O distances are found for ZrO_6 octahedra and PO_4 tetrahedra. However, the substitution of half the Zr atoms of the usual Nasicon by sodium on Na(3) sites, implies a formation of a dissymetric field around the Na(1) site. Consequently, sodium–oxygen distances are found to be long for Na(1)–O(3) (2.73 Å), O(3) belonging to the ZrO_6 octahedra, and short for Na(1)–O(4) (2.40 Å), O(4) belonging to the Na(3)–O_6 distorted octahedra. In the same way, sodium–oxygen distances are slightly

TABLE IV

HAMILTONIAN STATISTICAL TEST

(a) Level of significance for the introduction of a new interstitial atom compared to the minimum level $\alpha = 0.005$

Evolution of agreement index R		Number of additional parameters	$R1/R2$	Minimum level of significance $\alpha = 0.005$ Hamilton
4.06				
	Splitting of the Zr site introduction of Zr INT1 and Zr INT2	6	1.268	1.012
3.20				
	Introduction of the Na(4) atom	3	1.042	1.009
3.07				

(b) Level of significance for each introduction of a new set of anharmonic parameters compared to the minimum level $\alpha = 0.005$

Evolution of weighted R (R_w)			Number of additional parameters	$R1/R2$	Minimum level of significance $\alpha = 0.005$ Hamilton
2.66					
		Zr Full tensor	9	1.039	1.015
2.56					
	O(1)	Contracted tensor	18		1.023
	O(2)	3γ6δ		1.062	
2.41					
	O(3)	Contracted tensor	18		1.023
	O(4)	3γ6δ		1.039	
2.32					
	Na(1)				
	Na(21)	Contracted tensor	8	1.010	1.010
	Na(22)	1γ1δ			
	Na(3)				
2.30					

longer around Na(22) (⟨2.75⟩) close to Zr than around Na(21) (⟨2.69⟩) close to Na(3).

Sodium thermal parameters in different Nasicon-type structures are shown in Table VI. For all these compounds thermal vibrations are quite different: large in the trigonal phase, for Na(1), and, on the contrary, large in the c direction for Na(2). However, in the $Na_5Zr(PO_4)_3$-type structure, first the U_{11} thermal component of Na(1) is small, in comparison with the one in $Na_3Sc_2(PO_4)_3$ (9), and the U_{33} component of Na(22) (close to Zr) is higher than the one of Na(21) (close to Na(3)) showing that the substitution of zirconium atoms by sodium decreases the thermal anisotropy in Na(2) sites.

Conclusion

Single crystal synthesis of $Na_5Zr(PO_4)_3$ by the flux method has shown that Nasicon-

TABLE V

INTERATOMIC DISTANCES (Å)

			Average
Zr octahedron	O(1)	3 × 2.018	⟨2.046⟩
	O(3)	3 × 2.0743	
Na(1) antiprismatic	O(3)	3 × 2.732	⟨2.561⟩
	O(4)	3 × 2.390	
Na(3) octahedron	O(2)	3 × 2.419	⟨2.484⟩
	O(4)	3 × 2.548	
Na(21)	O(4)	2 × 2.511	⟨2.686⟩
	O(4)	2 × 2.535	
	O(2)	2 × 2.618	
	O(1)	2 × 3.080	
Na(22)	O(2)	2 × 2.594	⟨2.746⟩
	O(3)	2 × 2.651	
	O(3)	2 × 2.845	
	O(1)	2 × 2.895	
P(1) tetrahedra	O(4)	2 × 1.489	⟨1.512⟩
	O(1)	2 × 1.535	
P(2) tetrahedra	O(2)	2 × 1.481	⟨1.513⟩
	O(3)	2 × 1.545	

type compounds can be prepared with a large zirconium deficiency. This displays, in pure Nasicon phosphate $Na_5Zr_2(PO_4)_3$, a nonstoichiometry range by substitution in octahedral sites, with a formula $Na_{1+4y}Zr_{2-y}(PO_4)_3$, $0 < y < 1$.

This new nonstoichiometry mechanism associated with the traditional one (substitution of P^{5+} by Si^{4+} in tetrahedral sites) can probably lead to a large class of compounds with the Nasicon-type compound. Consequently other high conducting compounds may be found in the future. However, the easy replacement of Zr atoms by Na make the study of usual Nasicon-type compounds complicated and should imply a very accurate characterization of the ceramics used as solid electrolytes.

The crystal structure determination of $Na_5Zr(PO_4)_3$ at high temperature (200°C) reveals that this compound, in spite of a different space group, belongs to the Nasicon-type class. The dissymetric field around Na(1) and Na(2) sites introduces only some minor particularities.

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TABLE VI

Na–O DISTANCES (Å) AND THERMAL PARAMETERS (Å^2 × 10^4) OF CONDUCTING IONS IN DIFFERENT COMPOUNDS WITH A NASICON-TYPE STRUCTURE

	$Na_4Zr_2Si_3O_{12}$ (Ref. (*8*))		$Na_3Sc_2P_3O_{12}$ (Ref. (*7*))		$Na_5ZrP_3O_{12}$ (this study)	
	RT	300°C	RT	220°C		200°C
Na(1)–O	2.489	2.540	2.552	2.616		2.561
Na(2)–O	2.704	2.709	2.647	2.651	Na(21)	2.686
					Na(22)	2.746
Na(1)						
$U_{11} = U_{22}$	260	702	1514	1785		621
U_{33}	80	236	242	293		395
Na(2)						
U_{11}	162	368	231	380	Na(21)	304
					Na(22)	391
U_{22}	133	274	240	408	Na(21)	351
					Na(22)	342
U_{33}	590	1314	1029	1734	Na(21)	1037
					Na(22)	2537

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