A NIOBIUM PHOSPHATE WITH A NASICON STRUCTURE: $Na_{0.5}Nb_2(PO_4)_3$

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ABSTRACT
    A new niobium phosphate $Na_{0.5}Nb_2P_3O_{12}$, with the Nasicon structure has been isolated. The structure of this oxide has been determined from a X-ray diffraction study on single crystal and compared to that of the empty Nasicon, $Nb_2P_3O_{12}$ recently determined (14).
        MATERIALS INDEX : Sodium, Niobium, Phosphate, Nasicon.

INTRODUCTION

Oxides with the Nasicon structure have been extensivelystudied as solid electrolytes with high ionic conductivity. Numerous phosphats with this structure have indeed been synthesized, after the determination of the structure of $NaZr_2P_3O_{12}$ by Hagmanand Kierkegaard (1). Besides the nasicon type oxides $A_{1+x}(M,M')_2P_3O_{12}$ isolated for A = Li, Na ; M = Ti, Zr, Hf and M'= Mg, Cr, Ga, In, Yb (2-9), titanophosphates $Na_{1+x}Ti_2P_3O_{12}$ belonging to this structural type, and characterized by a mixed valence of titanium were recently synthesized by solid state reaction, by electrochemical reaction and reaction with organometallic compounds (10-11). Contrary to titanium quite a few number of nasicon type niobium phosphates have so far been isolated. Masse et al (12) succeeded to prepare an empty nasicon structure $NbTiP_3O_{12}$, involving Nb(V), whereas Subbarao et al (13) have shown the possibility to introduce cations in this latter opened framework. Recently an empty nasicon type phosphate $Nb_2P_3O_{12}$ was synthesized involving only niobium, with two oxidation states Nb(V) and Nb(IV) (14). We report here on the synthesis and crystal structure of a new niobium phosphate with the nasicon structure $Na_{0.5}Nb_2P_3O_{12}$.

RESULTS AND DISCUSSION

The synthesis of $Na_{0.5}Nb_2P_3O_{12}$ was performed in two steps. First, a stoechiometric mixture of Na_2CO_3, $H(NH_4)_2PO_4$ and Nb_2O_5 was heated to 673K in order to eliminate CO_2, NH_3 and H_2O. In the second step, the resulting finely ground product was mixed with an appropriate amount of niobium and sealed in an evacuated silica ampoule. This sample was then heated up to 1373K for 3 days and quenched at room temperature. The microcrystalline black powder obtained by this method corresponds to the pure nasicontype phase.

Single crystals were prepared from mixtures of composition $NaNb_2P_3O_{12}$. A black crystal of 0.075 x 0.072 x 0.036 mm was selected for the X-ray diffraction study. The crystal data and intensity measurements are given in table 1. It must be pointed out that the refinement of the atomic parameters and the anisotropic thermal factors was, in a first step, carried out for a fully occupation of the sodium site (x = 1), leading to R = 0.033, Rw = 0.0395 and Beq (Na) = 4.4. Subsequent refinements including the occupancy factor of sodium led to R = 0.0292, Rw = 0.0335 for the coordinates of table 2* and to the formula $Na_{0.5}Nb_2P_3O_{12}$ confirmed by microprobe analysis.

TABLE 1

Summary of crystal data, intensity measurements and structure refinement parameters for
$Na_{0.5}Nb_2(PO_4)_3$

1. Crystal data

Space group	R-3C
Cell dimensions	a = 8.7362(9) Å
	c = 22.093(2) Å
Volume	V = 1460.2(4) Å³
Z	6

2. Intensity measurement

(MoKα)	0.71073 Å
Scan mode	ω-2θ
Scan width (°)	1 + 0.35 tan θ
Slit aperture (mm)	1.06 + tan θ
Max θ (°)	45
Standard reflections	3 measured evey 2000 s (no decay)
Reflections with I > 3σ	1115

3. Structure solution and refinement

Parameters refined	32
Agreement factors	R = 0.0292, Rw = 0.0335

These results clearly show that $Na_{0.5}Nb_2P_3O_{12}$ has a nasicon frammework very similar to that obtained for the empty phosphate $Nb_2P_3O_{12}$ (14), with sodium located in the spacious cages formed by the 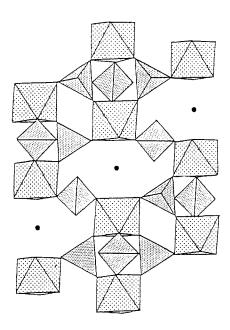PO_4 tetrahedra and the NbO_6 octahedra (Fig. 1). The Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as :
(4/3) * [a2*·(1.1) + b2*·(2.2) + c2*·(3.3) + ab(cos gamma)*·(1.2)+ ac(cos beta)*·(1.3) + bc(cos alpha)*·(2.3)]
PO_4 tetrahedra have the classical geometry observed in the monophosphate compounds i.e four equal P-O distances and O-P-O angles close to 109[(table 3). These distances and angles are equal in the limit of 3Å to those of $Nb_2P_3O_{12}$. The niobium atom is off-centered in its octahedron of about 0.07 Å along c, leading to tow sets of Nb-O distances significantly different at 3Å (Table 3). The Nb-O bonds (Table 4) are longer than in $Nb_2P_3O_{12}$ accordingly to the mean valence of the Nb atoms which is about 4.25 here instead of 4.5 in the empty compound. Since only one independant site is available for niobium a statistical distribution of Nb(V) and Nb(IV) on the octahedral sites can be proposed. The introduction of sodium in the cages induces only a small

TABLE 2

Parameters and their estimated standard deviations

Atom	x	y	z	B(A2)
Nb	0.0	0.0	0.14377(2)	0.455(4)
Na	0.0	0.0	0.0	2.1(1)
P	0.2882(1)	0.0	0.250	0.52(6)
O(1)	0.0202(3)	0.2006(3)	0.1932(1)	1.41(6)
O(2)	0.1949(3)	0.1696(3)	0.0881(1)	1.14(4)

FIG. 1

Projection of [210] layer showing the $Nb_2P_3O_{13}$ units.

TABLE 3

Distances (Å) et angles (°) in the PO_4 tetrahedron

P	O(1^i)	O(1^{ii})	O(2^{iii})	O(2^{iv})
O(1^i)	1.527(3)	2.532(4)	2.509(4)	2.463(2)
O(1^{ii})	112.1(2)	1.527(3)	2.463(2)	2.509(4)
O(2^{iii})	110.5(2)	107.5(1)	1.529(2)	2.487(3)
O(2i^v)	107.5(1)	110.4(2)	108.9(2)	1.529(2)

variation of the volume of the unit cell compared to that of the empty compound. This variation of about 11 $Å^3$ represents only 0.75 % of the all volume.

TABLE 4

Distances (Å) and angles (°) in the NbO_6 octahedron

Nb	O(1)	O(1^v)	O(1^i)	O(2)	O(2^v)	O(2^i)
O(1)	1.996(3)	2.897(4)	2.897(4)	2.897(4)	2.818(3)	4.014(4)
O(1^v)	93.0(1)	1.996(3)	2.895(4)	4.014(4)	2.863(4)	2.818(3)
O(1^i)	93.0(1)	93.0(1)	1.996(3)	2.818(3)	4.014(4)	2.863(4)
O(2)	90.9(1)	175.4(1)	89.1(1)	2.020(2)	2.777(3)	2.777(3)
O(2^v)	89.1(1)	90.9(1)	175.4(1)	86.8(1)	2.020(2)	2.777(3)
O(2^i)	175.4(1)	89.1(1)	90.9(1)	86.8(1)	86.8(1)	2.020(2)

Symmetry codes :	i	:	y-x	;	-x	;	z
	ii	:	y	;	x	;	1.-z
	iii	:	2/3-x	;	1/3-y	;	1/3-z
	iv	:	1/3-x+y	;	y-1/3	;	1/6+z
	v	:	-y	;	x-y	;	z

The Na-O distances of 2.522 Å are rather large in agreement with a possible mobility of Na+ through this framework.It is worth pointing out that the intercalation rate of sodium x, in $Na_xNb_2P_3O_{12}$ is rather low compared of other nasicon oxides, for which is generally equal or greater than one. This may be due to the greater difficulty to obtain Nb(IV). Electrochemical intercalation or reaction with organometallic should allow the sodium content to be increased. The investigation of the ionic conduction properties of this material will carried out.

CONCLUDING REMARKS

A new non stoichiometric nasicon $Na_{0.5}Nb_2 (PO_4)_3$, characterized by a mixed valence of niobium, Nb (V)-Nb (IV), has been isolated. It should be possible to extend the homogeneity range of this phase, and especially to increase the sodium content by electrichemical intercalation or by reaction with organometallic compounds. The investigation of the ionic conduction properties of this material will be carried out.

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