Na₂VP₂O₈: A Tetravalent Vanadium Diphosphate with a Layered Structure

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A new vanadium(IV) diphosphate, $Na_2VP_2O_8$, was isolated and its structure was determined from single-crystal X-ray diffraction data. This phase crystallizes in the monoclinic space group $P2_1/c$, with $a = 7.7178(6)$ Å, $b = 13.3233(8)$ Å, $c = 6.2871(3)$ Å, $\beta = 99.49(1)°$. This structure consists of $[VP_2O_8]_x$ layers parallel to (010), sandwiching sodium cations. The layers can be described either by $[VP_2O_{11}]$ units or by $[VPO_8]_x$ chains running along **c**. The $[VP_2O_{11}]$ units are built up from a P_2O_7 group sharing two of its apices with a VO_6 octahedron, whereas in the $[VPO_8]_x$ chains one VO_6 octahedron alternates with one PO_4 tetrahedron. An important feature of this structure deals with the existence of one free oxygen atom for each VO_6 octahedron and for each P_2O_7 group, pointing out the slabs. The VO_6 octahedron exhibits one abnormally short V–O bond characteristic of the vanadium(IV) ion. © 1992 Academic Press, Inc.

Introduction

Tetravalent vanadium, owing to its ability to form vanadyl groups, adopts various coordinations ranging from pure VO_5 pyramids to VO_6 distorted octahedra. This feature has allowed numerous vanadium(IV) phosphates with a three-dimensional framework to be synthesized (1–5). A number of layered V(IV) phosphates have also been obtained, but most of them are hydrates or hydrogenophosphates, in which the interlayer connection is made (in many cases) by hydrogen bonding. In this respect a very interesting chemistry has been developed for the two forms of hydrogenophosphate, α- and β-VO(HPO₄) · 2H₂O (6, 7), whereas phosphate hydrates with a new layered structure such as K₂ (VO)₂P₃O₉(OH)₃ · 1.125 H₂O (8) and Na₅V₂P₃O₁₄ · H₂O (9)

have been synthesized. On the other hand, very few anhydro vanadium(IV) phosphates with a layer structure have been isolated. The vanadyl diphosphates β-K₂V₃P₄O₁₇ (10) and A₂VP₂O₈ with A = K, Rb, Cs (11, 12) seem to be the only examples of layered materials. For this reason we have investigated the possibility of replacing potassium by a smaller cation, sodium. In the work presented herein, we report the synthesis and the crystal structure of a new vanadium(IV) diphosphate, Na₂VP₂O₈.

Synthesis

The vanadium(IV) diphosphate Na₂VP₂O₈ was synthesized as a pure phase in two steps. First, an adequate mixture of Na₂CO₃, V₂O₅, and H(NH₄)₂PO₄, corresponding to the composition "Na₂V$_{0.8}^V$P₂O₈"

TABLE I

Na$_2$VP$_2$O$_8$ POWDER PATTERN

hkl	d_{obs} (Å)	d_{calc} (Å)	I	hkl	d_{obs} (Å)	d_{calc} (Å)	I
020	6.671	6.662	100	−202	2.625	2.625	15
011	5.618	5.622	31	−212	2.577	2.576	20
120	5.018	5.013	20	122	2.517	2.517	26
−111	4.886	4.885	23	−132		2.516	
021	4.548	4.539	41	−222	2.444	2.442	19
−121	4.129	4.124	23	−241	2.417	2.417	13
130	3.837	3.836	66	−321	2.337	2.338	12
200	3.801	3.806		151	2.287	2.288	12
121	3.708	3.707	18	241	2.243	2.241	17
210	3.663	3.660	28	330	2.204	2.203	23
−211	3.396	3.396	29	212		2.200	
−131		3.391		−302	2.144	2.145	19
220	3.309	3.305	43	−312		2.117	
002	3.101	3.100	26	222	2.113	2.115	13
−102	3.054	3.053	61	061	2.091	2.091	15
140		3.051		−242		2.062	
012	3.023	3.020	25	−113	2.060	2.058	15
−112	2.976	2.976	32	251	2.001	2.001	15
211	2.959	2.953	26	−123		1.989	
230	2.893	2.890	24	331		1.988	
−141	2.813	2.813	33	161	1.988	1.988	17
022		2.811		023	1.974	1.974	15
221	2.756	2.757	66	260	1.918	1.918	23
−231		2.755		152	1.904	1.903	15
102	2.720	2.719	33	400		1.903	
112	2.666	2.664	15	−133	1.886	1.886	15
				033	1.874	1.874	17

to 1023 K for 24 hr; subsequent cooling at a rate of 1 K hr^{-1} down to 923 K was performed, followed by a quenching at room temperature.

Structure Determination

A blue crystal with dimensions 0.077 × 0.154 × 0.077 mm was selected for the structure determination. The cell parameters reported in Table II were determined and refined by diffractometric techniques at 21°C with a least-squares refinement based upon 25 reflections with $36° < \theta < 44°$. The systematic absences led to the $P2_1/c$ space group. The data were collected on a CAD-4 Enraf–Nonius diffractometer with the data collection parameters reported in Table II. The reflections were corrected for Lorentz and polarization effects; no correction was made for extinction and absorption.

Atomic coordinates of the vanadium atom were deduced by the heavy atom method, and the other atoms were located by subse-

was heated in air to 653 K in order to eliminate CO$_2$, H$_2$O, and NH$_3$. In the second step, the finely ground product was mixed with sufficient metallic vanadium to yield the appropriate metal stoichiometry (i.e., Na : V : P, 2 : 1 : 2), sealed in an evacuated silica ampoule, heated to 893 K for 1 day, and finally quenched to room temperature. The X-ray powder diffraction pattern of this phase was indexed in a monoclinic cell (Table I) deduced from the single crystal study.

The crystals of Na$_2$VPO$_8$ were isolated as a minor product from a mixture of nominal composition, "Na$_3$V$_2$P$_3$O$_{12}$," using a two-step thermal treatment. The first step, carried out for the composition "Na$_3$V$_{1.2}^V$P$_3$O$_{12}$," is identical to that described above. For the second step, the product added with 0.2 metallic vanadium was heated in an evacuated silica ampoule

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR Na$_2$VP$_2$O$_8$

1. Crystal data	
Space group	$P2_1/c$
Cell dimensions	$a = 7.7178(6)$ Å
	$b = 13.3233(8)$ Å
	$c = 6.2871(3)$ Å
	$\beta = 99.49(1)$ Å
Volume	637.6(6) Å
Z	4
2. Intensity measurements	
λ (MoKα)	0.71073 Å
Scan mode	$\omega - \frac{4}{3}\theta$
Scan width (°)	$1.05 + 0.35 \tan \theta$
Slit aperture (mm)	$1 + \tan \theta$
Max θ (°)	45°
Standard reflections	3 measured every 3000 sec
Reflections with $I > 3\sigma$	2927
μ (mm^{-1})	2.142 mm^{-1}
3. Structure solution and refinement	
Parameters refined	118
Agreement factors	$R = 0.025\ R_w = 0.028$
Weighting scheme	$w = f(\sin \theta/\lambda)$
Max Δ/σ	0.005

TABLE IIIA

POSITIONAL PARAMETERS AND THEIR ESTIMATED
STANDARD DEVIATIONS

Atom	x	y	z	B (Å^2)
V(1)	0.22827(3)	0.42441(2)	0.27003(4)	0.480(3)
P(1)	0.35999(5)	0.63441(3)	0.54265(6)	0.467(4)
P(2)	0.17255(5)	0.48123(3)	0.75090(6)	0.444(4)
Na(1)	0.0735(1)	0.70519(8)	0.1615(2)	1.57(1)
Na(2)	0.5190(1)	0.36430(8)	0.9288(2)	2.11(2)
O(1)	0.3635(2)	0.56316(9)	0.3562(2)	0.72(1)
O(2)	0.4659(2)	0.3591(1)	0.3033(2)	0.91(2)
O(3)	0.1118(2)	0.3265(1)	0.1913(2)	1.12(2)
O(4)	0.2299(2)	0.40891(9)	0.5899(2)	0.76(2)
O(5)	0.0227(2)	0.5227(1)	0.2451(2)	0.74(1)
O(6)	0.2803(2)	0.4643(1)	−0.0263(2)	0.96(2)
O(7)	0.2184(2)	0.59215(9)	0.6856(2)	0.89(2)
O(8)	0.2864(2)	0.73565(9)	0.4742(2)	0.89(2)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $B = \frac{4}{3}\Sigma_i\Sigma_j\mathbf{a}_i \cdot \mathbf{a}_j \cdot \beta_{ij}$.

quent Fourier synthesis. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.025$ and $R_w = 0.028$ and to the atomic parameters reported in Tables IIIA and IIIB.
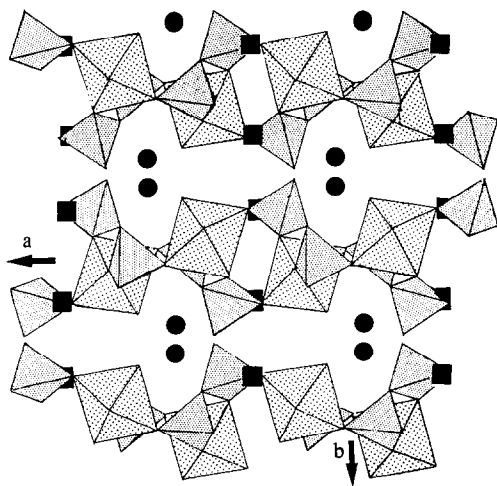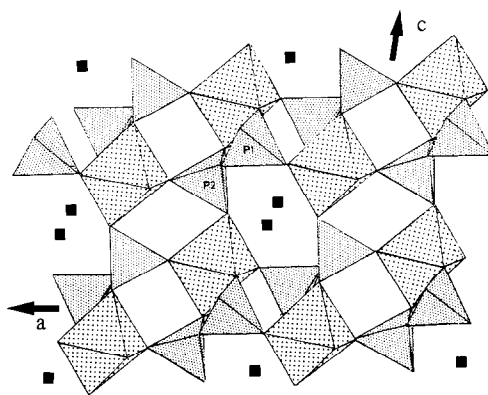

FIG. 2. Projection of the structure along *b*.

Description of the Structure and Discussion

As shown from the projection of the structure into the (001) plane (Fig. 1), $Na_2VP_2O_8$ is, like the other phosphates with a similar formula, $A_2VP_2O_8$, a layered material. Its $[VP_2O_8]_\infty$ layers are built up from diphosphate groups; however, unlike these oxides they do not exhibit VO_5 pyramids but VO_6 octahedra.

The $[VP_2O_8]_\infty$ slabs parallel to (010) (Fig. 2) can be described in terms of $[VP_2O_{11}]$ units similar to the $[MP_2O_{11}]$ units observed, for example, in $NaTiP_2O_7$ (*13*), $NaMoP_2O_7$ (*14*), and $Ba_{0.5}MoP_2O_8$ (*15*), i.e., built up from one P_2O_7 group sharing two of its apices with the same VO_6 octahedron (Fig. 3). The entire $[VP_2O_8]_\infty$ layer consists of
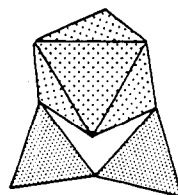

FIG. 1. Projection of the structure along *c*: (●) Na(1); (■) Na(2).

FIG. 3. MP_2O_{11} unit.

TABLE IIIB

REFINED DISPLACEMENT PARAMETER EXPRESSIONS—β's

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
V(1)	0.00170(2)	0.00092(1)	0.00253(3)	0.00006(3)	0.00065(4)	−0.00043(3)
P(1)	0.00178(4)	0.00075(1)	0.00289(5)	0.00002(4)	0.00039(8)	0.00023(5)
P(2)	0.00161(4)	0.00091(1)	0.00209(5)	0.00005(4)	0.00082(7)	0.00014(5)
Na(1)	0.0057(1)	0.00306(5)	0.0077(2)	−0.0023(1)	0.0010(2)	0.0003(2)
Na(2)	0.0098(1)	0.00373(5)	0.0112(2)	0.0077(1)	0.0131(2)	0.0065(2)
O(1)	0.0032(1)	0.00129(5)	0.0035(2)	−0.0011(1)	0.0021(2)	−0.0013(2)
O(2)	0.0023(1)	0.00192(5)	0.0050(2)	0.0010(2)	−0.0007(3)	−0.0021(2)
O(3)	0.0040(1)	0.00144(5)	0.0091(2)	−0.0014(2)	0.0010(3)	−0.0023(2)
O(4)	0.0045(1)	0.00101(4)	0.0037(2)	0.0008(1)	0.0030(3)	−0.0002(1)
O(5)	0.0016(1)	0.00134(4)	0.0060(2)	0.0002(1)	0.0015(2)	0.0006(2)
O(6)	0.0025(1)	0.00274(6)	0.0021(2)	0.0010(2)	0.0000(2)	0.0008(2)
O(7)	0.0048(1)	0.00101(4)	0.0067(2)	−0.0012(1)	0.0073(3)	−0.0008(2)
O(8)	0.0043(2)	0.00098(4)	0.0061(2)	0.0008(2)	0.0007(3)	0.0016(2)

Note. The form of the anisotropic displacement parameter is $\exp[-(B(1,1) * h^2 + B(2,2) * k^2 + B(3,3) * l^2 + B(1,2) * + hk\ B(1,3) * hl + B(2,3) * kl)]$.

[VP$_2$O$_{11}$] units only, sharing their corners in such a way that each P$_2$O$_7$ group of one unit shares three of its apices with the octahedra of three other units. As a result, each VO$_6$ octahedron shares five of its apices with four P$_2$O$_7$ groups and has one free apex pointing out of the layer. In the same way, each P$_2$O$_7$ has one free apex pointing out of the [VP$_2$O$_8$]$_\infty$ layer, as shown from the view of this layer along **b** (Fig. 2). The latter view shows also that this assemblage of polyhedra forms six-sided windows built up from two octahedra and two P$_2$O$_7$ groups.

Another description of the [VP$_2$O$_8$]$_\infty$ layers deal with the [VPO$_8$]$_\infty$ chains running along **c** (Fig. 2). Such chains (Fig. 4a), in which one MO$_6$ octahedron alternates with one PO$_4$ tetrahedron, have been found in many phosphates of transition elements (5, 16–33). In the [VP$_2$O$_8$]$_\infty$ slabs, two successive [VPO$_8$]$_\infty$ chains share the corners of their polyhedra in such a way that a PO$_4$ tetrahedron of one chain is linked to a VO$_6$ octahedron of the other chain, forming double chains [V$_2$P$_2$O$_{14}$]$_\infty$ (Fig. 4b) similar to those already observed in sev-

eral vanadium(IV) phosphates such as VO(HPO$_4$) · 4H$_2$O (*16*). These double chains are linked by PO$_4$ tetrahedra P(1), which share two of their corners with the VO$_6$ octahedra of two different double chains, the third one being linked to the P(2) tetrahedron of the chain to form the P$_2$O$_7$ group.

Succeeding [VP$_2$O$_8$]$_\infty$ layers along **b** are related by a *c* glide plane parallel to (010).
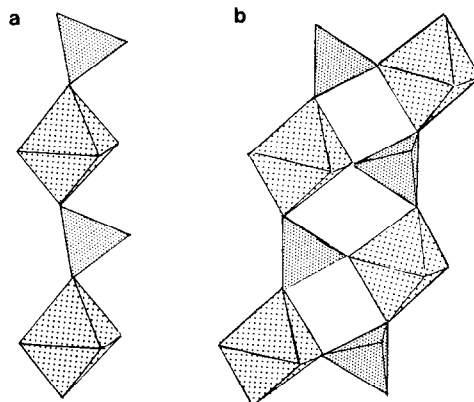
FIG. 4. (a) [VPO$_8$]$_\infty$ chain; (b) [V$_2$P$_2$O$_{14}$]$_\infty$ chain.

TABLE IV

DISTANCES (Å) AND ANGLES IN THE PO_4 TETRAHEDRA AND IN THE VO_6 OCTAHEDRON

P(1)	O(1)	O(2^i)	O(7)	O(8)
O(1)	1.512(1)	2.542(2)	2.541(2)	2.516(2)
O(2^i)	113.68(8)	1.524(1)	2.512(2)	2.515(2)
O(7)	108.11(7)	105.71(8)	1.626(1)	2.435(2)
O(8)	113.38(8)	112.59(8)	102.30(8)	1.499(1)

P(2)	O(4)	O(5^ii)	O(6^iii)	O(7)
O(4)	1.515(1)	2.525(2)	2.491(2)	2.520(2)
O(5^ii)	113.01(8)	1.512(1)	2.516(2)	2.502(2)
O(6^iii)	110.17(8)	111.96(8)	1.523(1)	2.475(2)
O(7)	108.47(7)	107.52(8)	105.32(9)	1.589(1)

V(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	2.148(1)	2.866(2)	3.758(7)	2.819(2)	2.663(2)	2.725(2)
O(2)	87.09(6)	2.009(1)	2.742(2)	2.844(2)	4.021(7)	2.708(2)
O(3)	174.42(7)	97.72(7)	1.614(1)	2.750(2)	2.737(2)	2.742(2)
O(4)	85.05(5)	89.80(6)	97.72(7)	2.020(1)	2.900(2)	4.025(7)
O(5)	78.86(5)	165.79(6)	96.21(7)	91.09(5)	2.043(1)	2.931
O(6)	81.12(6)	83.93(6)	96.54(7)	165.07(6)	91.74(6)	2.040(1)

Note. P(1)–O(7)–P(2) = 131.55°. The V–O or P–O distances are on the diagonal. Above it are O(i) . . . O(j) distances and below it are the O(i)–V–O(j) or O(i)–P–O(j) angles.

Each P tetrahedron is characterized by one long P–O bond (1.589 and 1.626 Å) between P and the bridging oxygen (Table IV). The other three P(2)–O distances are almost equal (1.512, 1.515, 1.523 Å). The other three P(1)–O distances show more variety, being 1.524, 1.512, and 1.499 Å; the shortest distance represents the "free" P–O bond pointing into the interlayer.

The vanadium atom is located inside an almost regular "O_6" octahedron. However, this atom is displaced from the center of its polyhedron, along **b** toward the free oxygen atom, forming a short V–O bond of 1.61 Å, characteristic of the vanadyl ion observed in all vanadium(IV) phosphates, regardless of V coordination. The four other equatorial V–O distances are almost equal (Table IV), ranging from 2 to 2.04 Å, whereas the sixth V–O bond, opposite the vanadyl bond, is much longer (2.148 Å), as previously observed for other V(IV) phosphates.

The Na^+ cations, located between the layers, exhibit two kinds of coordination. The Na(1) cations, which sit about half-distance between two successive layers (Fig. 1) exhibit a sevenfold coordination, with Na–O distances ranging from 2.312 to 3.031 Å (Table V). Note that four of the

TABLE V

OXYGEN ATOMS SURROUNDING Na^+ WITH Na–O < 3.2 Å

Na(1)–O(1)	= 3.031(2) Å	Na(2)–O(1^i)	= 2.346(2) Å
Na(1)–O(3^iv)	= 2.469(2) Å	Na(2)–O(2^iii)	= 2.456(2) Å
Na(1)–O(3^v)	= 2.440(2) Å	Na(2)–O(2^vii)	= 3.089(2) Å
Na(1)–O(5)	= 2.532(2) Å	Na(2)–O(4)	= 2.881(2) Å
Na(1)–O(7^vi)	= 2.917(2) Å	Na(2)–O(6^iii)	= 2.328(2) Å
Na(1)–O(8)	= 2.380(2) Å	Na(2)–O(6^i)	= 2.771(2) Å
Na(1)–O(8^vi)	= 2.312(2) Å	Na(2)–O(7^viii)	= 2.950(2) Å
		Na(2)–O(8^ix)	= 2.294(3) Å

Note. Symmetry code: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $x, y, 1 + z$; (iv) $-x, 1 - y, -z$; (v) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $+x, \frac{3}{2} - y, -\frac{1}{2} + z$; (vii) $+x, \frac{1}{2} - y, +\frac{1}{2} + z$; (viii) $1 - x, 1 - y, 2 - z$; (ix) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$.

oxygen atoms surrounding Na(1) belong to the same layer, whereas the three others belong to the next one.

The Na(2) cations sit much closer to the [VP$_2$O$_8$]$_\infty$ layers, i.e., on both sides of the six-sided windows (Fig. 1). These cations exhibit an eightfold coordination in which are involved six oxygens of one layer and two oxygens of the next layer, the Na–O distances ranging from 2.294 to 3.089 Å (Fig. 1). It is worth pointing out that the shortest Na–O bonds (2.29–2.31 Å) correspond to the free oxygen atom O(8) of the P(1) tetrahedron, whereas the free oxygen atom O(3) of the VO$_6$ octahedron is linked only to Na(1), with longer distances ranging from 2.44 to 2.469 Å (Table V).

Concluding Remarks

The synthesis of this new sodium vanadium phosphate, together with the previous results obtained for other alkaline vanadium phosphates with a similar formula, shows the great ability of the vanadium(IV) phosphates A_2VP$_2$O$_8$ to form a layer structure. One must also emphasize the variety of the structures since only two of them, rubidium and cesium phosphates, are isostructural. Moreover, the sodium compound differs from the other phases by the existence of VO$_6$ octahedra instead of VO$_5$ pyramids. The ion-exchange properties and ionic conductivity of this original structure will be investigated.

References

1. A. LECLAIRE, H. CHAHBOUN, D. GROULT, AND B. RAVEAU, J. Solid State Chem. 77, 170 (1988).
2. L. BENHAMADA, A. GRANDIN, M. M. BOREL, A. LECLAIRE, AND B. RAVEAU, Acta Crystallogr. C 47, 1138 (1991).
3. L. BENHAMADA, A. GRANDIN, M. M. BOREL, A. LECLAIRE, AND B. RAVEAU, C. R. Acad. Sci. Paris 314, 585 (1992).
4. A. GRANDIN, J. CHARDON, M. M. BOREL, A. LECLAIRE, AND B. RAVEAU, J. Solid State Chem., 99, 297 (1992).
5. A. GRANDIN, J. CHARDON, M. M. BOREL, A. LECLAIRE, AND B. RAVEAU, Acta Crystallogr., C48 (1992).
6. A. LE BAIL, G. FEREY, P. AMOROS, AND D. BELTRAN-PORTER, Eur. J. Solid State Chem. 26, 419 (1989).
7. A. LE BAIL, G. FEREY, P. AMOROS, D. BELTRAN-PORTER, AND G. VILLENEUVE, J. Solid State Chem.79, 176 (1989).
8. K.-H. LII AND H.-J. TSAI, Inorg. Chem. 30, 446 (1991).
9. L. BENAMADA, A. GRANDIN, M. M. BOREL, A. LECLAIRE, AND B. RAVEAU, J. Solid State Chem. 96, 390 (1992).
10. K. H. LII, H. J. TSAI, AND S. L. WANG, J. Solid State Chem. 87, 396 (1990).
11. YU. E. GORBUNOVA, S. A. LINDE, A. V. LAVROV, AND I. V. TANANAEV, Dokl. Akad. Nauk SSSR 250(2), 350 (1980).
12. K. H. LII AND S. L. WANG, J. Solid State Chem. 82, 239 (1989).
13. A. LECLAIRE, A. BENMOUSSA, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, J. Solid State Chem. 77, 299 (1988).
14. A. LECLAIRE, M.M. BOREL, A. GRANDIN, AND B. RAVEAU, Z. Kristallogr. 184, 247 (1988).
15. G. COSTENTIN, M. M. BOREL, A. LECLAIRE, AND B. RAVEAU, J. Solid State Chem. 89, 83 (1990).
16. M. E. LEONOWICZ, J. W. JOHNSON, J. F. BRODY, H. F. SHANNON, JR., AND J. M. NEWSAM, J. Solid State Chem. 56, 370 (1985).
17. A. V. LAVROV, V. P. NIKOLAEV, G. G. SADIKOV, AND M. A. PORAI-KOSHITS, Dokl. Akad. Nauk SSSR 266, 343 (1982).
18. I. TORDJMAN, R. MASSE, AND J. C. GUITEL, Z. Kristallogr. 139, 103 (1974).
19. A. LECLAIRE, A. BENABBAS, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, J. Solid State Chem. 83, 245 (1989).
20. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, Eur. J. Solid State Chem. 26, 45 (1989).
21. A. BENMOUSSA, M. M. BOREL, A. GRANDIN, A. LECLAIRE, AND B. RAVEAU, Ann. Chim. Fr. 14, 181 (1989).
22. C. DELMAS, R. OLAZGUAGA, F. CHERKAOUI, R. BROCHU, F. LE FLEM, AND P. HAGENMULLER, Mater. Res. Bull. 16, 285 (1981).
23. C. DELMAS, J. C. VIALA, R. OLAZCUAGA, G. LE FLEM, F. CHERKAOUI, R. BROCHU, AND P. HAGENMULLER, Mater. Res. Bull. 16, 83 (1981).
24. C. DELMAS, J. C. VIALA, R. OLAZGUAGE, G. LE FLEM, F. CHERKAOUI, R. BROCHU, AND P. HAGENMULLER, Solid State Ionics 3/4, 209 (1981).

25. L. S. CHEN AND L. Z. XIANG, *Solid State Ionics* **9/10,** 835 (1983).

26. L. Z. XIANG, Y. H. JUN, L. S. CHUN, AND T. S. BAO, *Solid State Ionics* **18/19,** 549 (1986).

27. S. HAMDOUNE, D. TRANQUI, AND E. J. SCHOULER, *Solid State Ionics* **18/19,** 587 (1986).

28. S. HAMDOUNE, M. GONDRAND, AND D. TRANQUI, *Mater. Res. Bull.* **21,** 237 (1986).

29. M. A. SUBRAMANIAN, R. SUBRAMANIAN, AND A. CLEARFIELD, *Solid State Ionics* **18/19,** 562 (1986).

30. C. DELMAS, R. OLAZGUAGA, F. CHERKAOUI, R. BROCHU, AND G. LE FLEM, *C.R. Acad. Sci.* **287,** 169 (1978).

31. A. NADIRI, Doctoral thesis, University of Bordeaux (1986).

32. R. MASSE, A. DURIF, J. G. GUITEL, AND J. TORDJMAN, *Bull. Soc. Fr. Miner. Crystallogr.* **95,** 47 (1972).

33. G. V. SUBBARAO, U. V. VARADARJU, K. A. THOMAS, AND B. SIVASANKAR, *J. Solid State Chem.* **70,** 101 (1987).