JOURNAL OF SOLID STATE CHEMISTRY **31**, 321–328 (1980)

Nonstoichiometric Oxides with a Layer Structure: The Compounds $A_{1-x}(Ti_{1-x}M_{1+x})O_5$

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Received November 30, 1978; in revised form April 5, 1979

New nonstoichiometric oxides $A_{1-x}(Ti_{1-x}Nb_{1+x})O_5$ and tantalates ATiTaO$_5$ with a layer structure of the KTiNbO$_5$ type have been isolated, with A = K, Rb, Tl, Cs. These oxides, which are orthorhombic, space group *Pnma*, are characterized by a preferential occupation of one type of site 4*c* by the titanium atoms. The structural evolution as a function of composition and the stability of these compounds are discussed.

Introduction

Among the oxides characterized by a host lattice, and showing a nonstoichiometry on the guest cations, the layer structures are, to our knowledge, the least numerous. From this point of view, the alkali titanoniobate KTiNbO$_5$ described by Wadsley (*1*) has attracted our attention. For the layer structure of this oxide, where each sheet $(TiNbO_5)_n^{n+}$ consists of double zigzag strings of octahedra-sharing corners, suggests the possibility of nonstoichiometry on the potassium ion sites. The present study is thus concerned with new titanoniobates $A_{1-x}(Ti_{1-x}Nb_{1+x})O_5$, with A = K, Rb, Tl, Cs. For comparison, the titanotantalates have also been studied.

Experimental

The starting materials used for the synthesis of the oxides $A_{1-x}(Ti_{1-x}M_{1+x})O_5$ were the carbonates A_2CO_3 (A = K, Rb, Tl, Cs) and the oxides TiO$_2$ and M_2O_5 (M = Ta, Nb). The dry mixed reactants were fired in air in a platinum crucible. After total decomposition of the carbonates, the mixtures were heated at temperatures ranging from 750 to 1250°C.

The samples were then examined by X-ray diffraction, using a Philips diffractometer employing nickel-filtered copper radiation.

Results

In the case of niobium, four nonstoichiometric oxides $A_{1-x}(Ti_{1-x}Nb_{1+x})O_5$ were isolated. The potassium and rubidium compounds have a wider homogeneity range ($0 \leq x \leq 0.15$) than those of thallium and cesium ($0 \leq x \leq 0.10$).

In the case of tantalum, only the oxides KTiTaO$_5$ and RbTiTaO$_5$ could be prepared. The X-ray powder spectra of these compounds were indexed on an orthorhombic cell (Table I), in agreement with the results previously obtained by Wadsley (*1*) for KTiNbO$_5$. All efforts to isolate single crystals of good quality were unsuccessful; the structural evolution of these compounds was thus studied from the X-ray powder

0022-4596/80/030321-08$02.00/0

TABLE I

PARAMETERS, DENSITIES, AND SYNTHESIS TEMPERATURES OF THE ORTHORHOMBIC OXIDES: $A_{1-x}Ti_{1-x}M_{1+x}O_5$

Compounds	a (Å)	b(Å)	c(Å)	d_{exp}	d_{cal} ($Z=4$)	Temperature of synthesis (°C)
$KTiNbO_5$	6.447	3.797	18.431	3.83	3.826	1100
$K_{0.90}Ti_{0.90}Nb_{1.10}O_5$	6.471	3.800	18.667	3.76	3.769	1100
$K_{0.85}Ti_{0.85}Nb_{1.15}O_5$	6.474	3.800	18.765	3.76	3.752	1100
$RbTiNbO_5$	6.472	3.814	18.943	4.32	4.350	1100
$Rb_{0.90}Ti_{0.90}Nb_{1.10}O_5$	6.482	3.803	19.212	4.26	4.247	1100
$Rb_{0.85}Ti_{0.85}Nb_{1.15}O_5$	6.499	3.812	19.360	4.24	4.231	1100
$TlTiNbO_5$	6.456	3.806	18.844	6.11	6.098	800
$Tl_{0.90}Ti_{0.90}Nb_{1.10}O_5$	6.457	3.799	18.919	5.88	5.856	800
$CsTiNbO_5$	6.498	3.826	19.908	4.74	4.742	750
$Cs_{0.90}Ti_{0.90}Nb_{1.10}O_5$	6.507	3.815	20.119	4.61	4.586	750
$KTiTaO_5$	6.437	3.797	18.474	5.10	5.118	1250
$RbTiTaO_5$	6.451	3.812	19.000	5.63	5.605	1200

diffraction data except for the cesium niobates for which preferential orientation was observed. For each compound, the intensities of the first 45 visible reflections, i.e., about 136 *hkl*, were used for the structure determination. The scattering factors of the ions used in the calculation of intensities were those given by Cromer and Waber (*2*), corrected for anomalous dispersion. The refinement of the atomic positions was made using a program perfected in this laboratory (*3*). On account of the systematically absent reflections, the intensities were computed in the first step using the data given by Wadsley (*1*) for $KTiNbO_5$; all the atoms were located in $4c$ positions of the space group *Pnma*, titanium and niobium or tantalum being statistically distributed over two sites $4c$ in this case, B_1 and B_2. In this first hypothesis, the values of the discrepancy factors calculated on the intensities ($R_I = \sum |I_o - I_c| / \sum I_o$) remained high after refinement. The best value was obtained for $Rb_{0.85}(Ti_{0.85}Nb_{1.15})O_5$ ($R_I = 0.08$), and the worst one for $KTiTaO_5$ ($R_I = 0.306$). As a result of the difference observed between niobium and tantalum compounds, the distribution of the titanium and niobium or tantalum atoms was then examined. Unlike the results obtained by Wadsley, we observed a preferential distribution of the titanium atoms on the B_1 sites, while the niobium (or tantalum) atoms were mainly located on the B_2 sites. After several cycles of refinement, of the atomic coordinates and of the occupancy factors of the B_1 and B_2 sites, the temperature factors first fixed at 1 Å^2 were then refined; they were stabilized to values ranging from 0.5 to 2.12 for the metallic atoms and from 0.80 to 2.0 for the oxygen atoms.

The final atomic parameters for all these compounds are given in Table II. The values of R ranging from 0.062 to 0.073 are quite acceptable. The atomic positions are not very different from one compound to another, and are relatively close to those obtained by Wadsley for $KTiNbO_5$. It is worth noting that for every composition except for $Rb_{0.85}(Ti_{0.85}Nb_{1.15})O_5$, the occupancy factors of the B_1 and B_2 sites by the metallic atoms are approximately the same: About three-quarters of the B_1 site is occupied by the titanium atoms. Figure 1, which represents the evolution of R_I as a function of the occupancy factor of the B_1 site by the titanium atoms for some examples, shows

TABLE II

FINAL ATOMIC PARAMETERS[a] FOR $A_{1-x}(Ti_{1-x}Nb_{1+x})O_5$ AND $ATiTaO_5$

Compounds		$KTiNbO_5$[b]	$K_{0.85}Ti_{0.85}Nb_{1.15}O_5$	$RbTiNbO_5$	$Rb_{0.85}Ti_{0.85}Nb_{1.15}O_5$	$TlTiNbO_5$	$Tl_{0.90}Ti_{0.90}Nb_{1.10}O_5$	$KTiTaO_5$	$RbTiTaO_5$
A	x	0.791(1)	0.794(2)	0.799(1)	0.778(2)	0.773(1)	0.783(2)	0.794(2)	0.798(1)
	z	0.8040(3)	0.8042(4)	0.8032(3)	0.8015(5)	0.8024(2)	0.8017(4)	0.8112(8)	0.8033(3)
	$B(Å)^2$	0.80	1.69	0.88	1.52	1.35	2.12	0.75	0.96
B_1	x	0.323(1)	0.317(1)	0.312(2)	0.307(2)	0.313(2)	0.325(5)	0.329(2)	0.317(1)
Ti+Nb	z	0.0314(3)	0.0351(3)	0.0354(5)	0.0292(7)	0.0339(6)	0.0333(7)	0.0308(6)	0.0338(4)
or (Ta)	τ_1	0.75	0.72	0.80	0.51	0.80	0.68	0.75	0.75
B_2	x	0.764(1)	0.769(1)	0.765(1)	0.766(2)	0.766(3)	0.751(2)	0.763(2)	0.765(1)
Ti+Nb	z	0.1112(2)	0.1105(2)	0.1063(3)	0.1063(3)	0.1082(3)	0.1081(3)	0.1097(2)	0.1071(2)
or (Ta)	τ_2	0.25	0.13	0.20	0.34	0.20	0.22	0.25	0.25
O_1	x	0.088(4)	0.069(3)	0.045(6)	0.064(5)	0.059(7)	0.075(6)	0.069(6)	0.057(6)
	z	0.078(1)	0.081(1)	0.060(2)	0.073(1)	0.069(3)	0.069(3)	0.059(3)	0.067(2)
O_2	x	0.668(3)	0.644(3)	0.623(4)	0.650(5)	0.645(5)	0.662(5)	0.669(5)	0.619(4)
	z	0.002(1)	−0.002(1)	0.004(1)	−0.002(1)	0.001(2)	0.005(3)	−0.008(3)	−0.002(1)
O_3	x	0.464(3)	0.460(2)	0.458(6)	0.472(5)	0.469(6)	0.461(6)	0.466(6)	0.470(5)
	z	0.119(1)	0.125(1)	0.116(1)	0.116(1)	0.119(2)	0.119(3)	0.110(2)	0.118(2)
O_4	x	0.828(3)	0.837(4)	0.808(6)	0.795(1)	0.823(3)	0.821(5)	0.903(5)	0.799(5)
	z	0.207(1)	0.210(1)	0.203(1)	0.201(1)	0.204(1)	0.202(3)	0.189(3)	0.203(1)
O_5	x	0.234(5)	0.221(5)	0.198(7)	0.223(6)	0.230(5)	0.245(6)	0.279(7)	0.197(7)
	z	0.923(1)	0.924(1)	0.928(1)	0.922(1)	0.920(1)	0.922(3)	0.923(2)	0.928(1)
$R_I = \frac{\sum \lvert I_o - I_c \rvert}{\sum I_o}$		0.064	0.064	0.073	0.066	0.063	0.065	0.068	0.071

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[a] From the space group $y = 0.25$. τ_1 and τ_2 represent the fraction of occupancy of the B_1 and B_2 sites by the titanium atoms.

[b] For homogeneity our results are given here: They are close to those of Wadsley (*1*), except for the distribution of titanium and niobium.

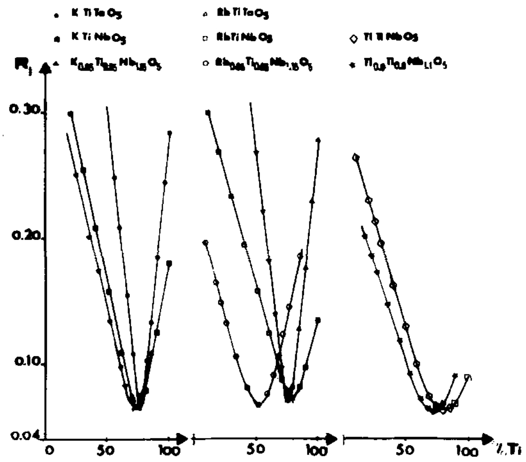

FIG. 1. Evolution of the discrepancy factor R_I as a function of the occupancy factor of the B_1 sites by the titanium atoms.

that these results are very significant; the tantalum oxides are the most convincing due to the higher scattering factor of this element compared to that of niobium. In a similar way the R value is more affected by the distribution of the metallic ions on the B_1 and B_2 sites for potassium than for rubidium or for thallium, in agreement with the atomic numbers of these elements.

Discussion

The analysis of the structure of these oxides (Fig. 2a) shows that the octahedral sheets $(B_2O_5)_n^{n-}$ are built up from structural units of two octahedra-sharing edges. These distorted octahedra (Fig. 2b) differ from one another mainly in the position of the metallic atom B with regard to the surrounding oxygen atoms. The B_1 atom is indeed much more strongly thrown off center in its octahedron (I) than the B_2 atom in the octahedron (II). The interatomic distances B–O (Table III) clearly show these differences. These results can easily be explained by the geometry of the framework: The octahedron (I) shares its

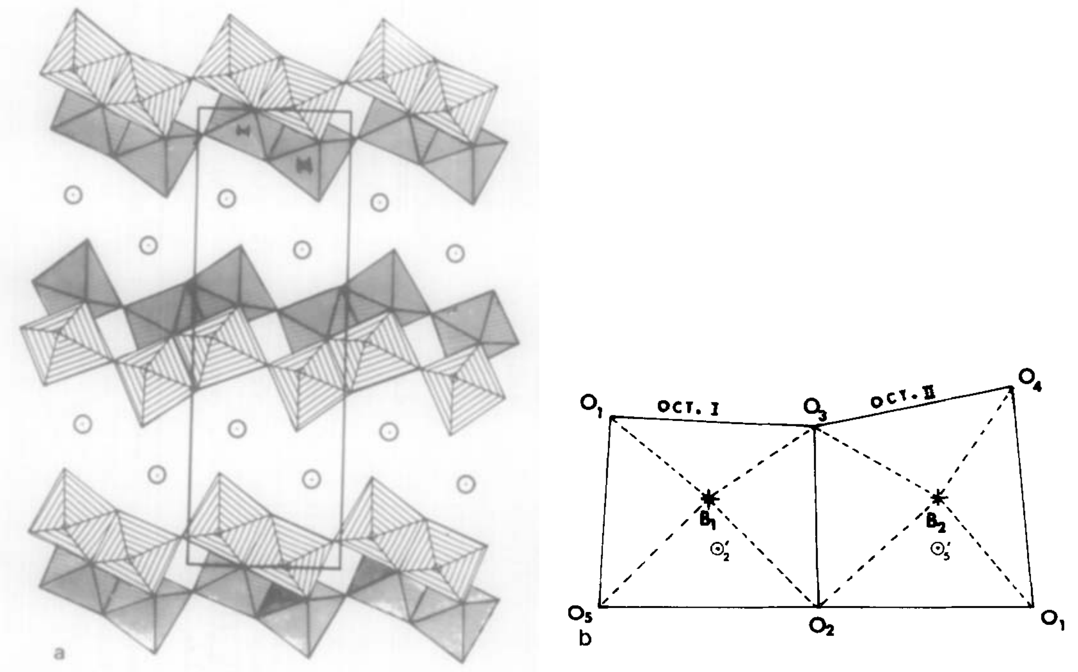

FIG. 2. Structure of $RbTiNbO_5$ drawn as octahedra: (a) projection onto the (010) plane; (b) the distorted I and II octahedra projected onto the (010) plane.

edges with five octahedra, while the octahedron (II) shares its edges with three octahedra (Fig. 3a). As a result of this stacking, the B_1 atom is much more repulsed by its five neighbors than B_2 is by its three neighbors, giving B–B distances rather close to one another and ranging from 3.19 to 3.38 Å (Table III). Moreover, the direction of the displacement of B toward the outside of the sheet is in agreement with the arrangement of the surrounding B atoms (Fig. 3b). This results in minimum B_1–O distances shorter than the B_2–O distances (Table III). It is thus comprehensible that the titanium atoms preferentially occupy the B_1 sites due to their size, which is smaller than that of niobium and tantalum. The statistical distribution of niobium and titanium found by Wadsley for $KTiNbO_5$ is not inconsistent with our results; it is possible that the transition temperature which leads to the disordered state is not much higher than 1100°C. The crystals studied by Wadsley were prepared at slightly higher temperatures (1150°C), and the author noted their poor quality and the existence of numerous diffuse streaks which he assumed to be caused by "disorder of some kind." The factors governing the stability of this structure are not yet well established. Nevertheless, the more limited number of tantalates and especially the absence of a homogeneity range for these compounds indicate that the tantalum, more ionic than the niobium, plays a greater part in the repulsion between neighboring atoms and thus decreases the stability of the structure. These observations are in agreement with our previous results on niobates and tantalates with formula $A_3M_8O_{21}$ (*4, 5*), which are equally characterized by edge-sharing octahedra. In a similar way, it seems that, due to the presence of edge-sharing octahedra, the stability of this structure should be favored by B elements with electronic configuration d^0. The very short B_1–O distances observed for all these oxides

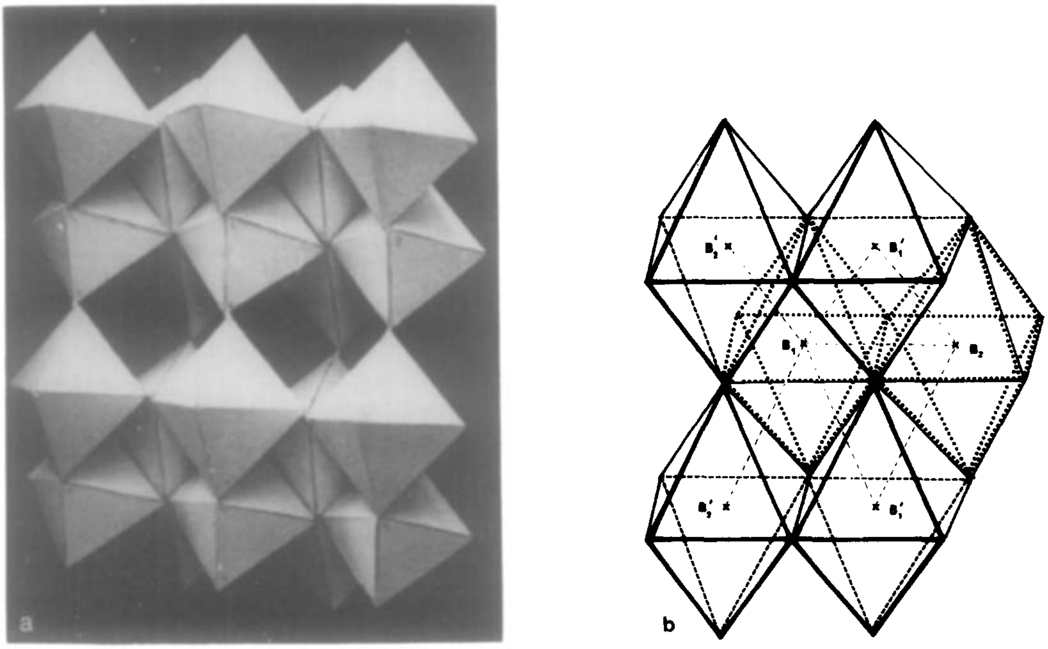

FIG. 3. Stacking of the octahedra along the **b** axis: (a) a sheet $(B_2O_5)_n$; (b) arrangement of the B atoms in the structure.

TABLE III

INTERATOMIC DISTANCES (Å) FOR $A_{1-x}(Ti_{1-x}Nb_{1+x})O_5$ AND ATiTaO

Distances	$KTiNbO_5$	$K_{0.85}Ti_{0.85}Nb_{1.15}O_5$	$KTiTaO_5$	$RbTiNbO_5$	$Rb_{0.85}Ti_{0.85}Nb_{1.15}O_5$	$RbTiTaO_5$	$TlTiNbO_5$	$Tl_{0.9}Ti_{0.9}Nb_{1.1}O_5$
Tunnel								
O_3–O_4	3.31(3)	3.20(3)	3.73(7)	3.57(3)	3.73(3)	3.58(4)	3.46(4)	3.51(7)
O_4–O_4	3.59(3)	3.57(3)	3.93(6)	3.70(5)	3.77(2)	3.69(4)	3.66(3)	3.71(6)
K–O_1	2.99(2)	3.00(2)	3.17(4)	3.37(3)	3.24(2)	3.25(3)	3.26(4)	3.23(4)
K–O_3	2.88(1)	2.84(2)	2.92(3)	2.96(2)	2.97(2)	2.98(3)	2.87(3)	2.89(4)
K–O_4	2.72(1)	2.74(2)	2.72(2)	2.78(2)	2.77(2)	2.77(2)	2.73(1)	2.76(4)
K–O_4	3.11(1)	3.06(2)	3.21(4)	3.18(3)	3.36(1)	3.22(3)	3.22(1)	3.18(3)
Octahedron I								
B_1–O_1	1.74(2)	1.82(2)	1.76(4)	1.78(4)	1.79(3)	1.79(4)	1.76(5)	1.75(5)
B_1–O_3	1.86(2)	1.92(2)	1.71(4)	1.79(3)	1.99(3)	1.88(4)	1.90(4)	1.84(5)
B_1–O_2	2.29(2)	2.20(2)	2.30(4)	2.14(3)	2.31(3)	2.06(3)	2.23(3)	2.24(4)
B_1–O_5	2.07(2)	2.18(2)	2.01(6)	2.16(3)	2.14(3)	2.16(3)	2.21(2)	2.17(6)
B_1–O_2'	1.99(1)	2.04(1)	1.94(1)	2.04(1)	2.00(1)	2.04(1)	2.03(1)	2.03(2)
O_1–O_3	2.54(3)	2.66(2)	2.72(5)	2.87(5)	2.77(4)	2.83(5)	2.81(6)	2.67(6)
O_3–O_2	2.53(3)	2.59(4)	2.55(6)	2.50(3)	2.56(3)	2.48(4)	2.50(5)	2.51(7)
O_2–O_5	3.15(3)	3.10(4)	2.81(6)	3.04(5)	3.13(4)	3.02(5)	3.09(4)	3.11(6)
O_5–O_1	2.99(3)	3.10(3)	2.86(7)	2.68(4)	3.10(3)	2.80(4)	3.02(6)	2.99(7)
O_1–O_2'	2.87(2)	3.08(3)	2.71(4)	3.06(4)	3.03(3)	3.08(3)	3.00(4)	2.90(5)
O_3–O_2'	3.06(2)	3.12(3)	2.81(5)	2.90(2)	3.03(3)	2.96(3)	3.06(4)	3.12(6)
O_2–O_2'	2.88(2)	2.66(2)	2.90(3)	2.49(2)	2.73(3)	2.45(2)	2.67(3)	2.83(3)
O_5–O_2'	2.43(2)	2.51(3)	2.49(5)	2.64(3)	2.58(3)	2.65(3)	2.54(3)	2.43(5)

Octahedron II								
B_2–O_3	1.94(2)	2.02(2)	1.91(4)	1.99(4)	1.91(3)	1.91(3)	1.93(4)	1.88(4)
B_2–O_4	1.82(2)	1.91(2)	1.72(5)	1.84(2)	1.84(3)	1.83(2)	1.84(2)	1.83(5)
B_2–O_1	2.17(2)	2.02(2)	2.18(4)	2.01(4)	2.04(3)	2.02(4)	2.03(5)	2.21(4)
B_2–O_2	2.11(2)	2.19(4)	2.26(5)	2.27(2)	2.22(3)	2.28(2)	2.16(4)	2.03(5)
B_2–O_5'	2.00(1)	2.00(1)	2.01(2)	2.03(1)	1.99(1)	2.03(1)	1.97(1)	1.98(2)
O_2–O_3	2.53(3)	2.59(4)	2.55(6)	2.50(3)	2.56(3)	2.48(4)	2.50(5)	2.51(7)
O_3–O_4	2.85(3)	2.91(3)	3.16(5)	2.80(4)	2.66(3)	2.66(4)	2.78(4)	2.80(6)
O_4–O_1	2.92(3)	2.84(3)	2.62(7)	3.11(4)	3.02(3)	3.07(4)	2.96(6)	3.00(7)
O_1–O_2	3.04(3)	3.12(3)	2.87(5)	2.98(4)	3.06(4)	3.12(4)	2.96(6)	2.92(5)
O_2–O_5'	2.43(2)	2.51(3)	2.49(5)	2.64(3)	2.58(3)	2.65(3)	2.54(3)	2.43(5)
O_3–O_5'	2.83(3)	2.95(3)	2.58(4)	3.04(4)	2.84(3)	2.99(4)	2.81(3)	2.79(4)
O_4–O_5'	3.10(2)	3.16(2)	3.04(6)	3.12(2)	3.06(3)	3.13(2)	3.03(2)	3.04(6)
O_1–O_5'	2.81(3)	2.67(3)	2.96(4)	2.49(4)	2.67(3)	2.52(4)	2.68(4)	2.81(4)
B_1–B_2	3.21(1)	3.25(1)	3.15(2)	3.23(4)	3.33(2)	3.21(1)	3.25(2)	3.10(3)
B_1–B_1'	3.19(1)	3.30(1)	3.12(1)	3.37(1)	3.35(2)	3.29(1)	3.33(1)	3.21(3)
B_1–B_2'	3.29(1)	3.38(1)	3.27(1)	3.33(1)	3.28(2)	3.33(1)	3.33(1)	3.32(1)

indicates, on the other hand, that the size of the *B* atoms should play a part in the existence of the structure. The substitution of the *B* elements has not yet been systematically studied. The first results are, however, in favor of these hypotheses: Several attempts to substitute antimony V which has a d^{10} configuration, for niobium and zirconium which is larger, for titanium were indeed unsuccessful.

Although the cohesion of the structure is assured by the *A* ions, it is worth noting that an appreciable defect of *A* ions has been observed. The behavior of these compounds is quite different from that of other layer structures characterized by edge-sharing octahedra like titanates $Na_2Ti_3O_7$ (*6*), $A_2Ti_6O_{13}$ (*7*), and $A_2Ti_4O_9$ (*1, 8, 9*) for which a nonstoichiometry on the *A* ions has not, to our knowledge, been pointed out.

The evolution of the cell parameters as a function of x (Table I) shows clearly the influence of the *A* ions on the stability of the structure. The **a** and **b** parameters are not appreciably influenced by the variation of x, contrary to **c**, which increases drastically with x. This anisotropy is explained well by the decrease in the cohesion between the B_2O_5 sheets which extend normally to **c**, due to the defect of *A* ions.

The existence of nonstoichiometry in these oxides indicates the possibility of ion-exchange properties. From this point of view, the ionic conductivity of these compounds will be investigated.

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