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# Synthesis, structural, magnetic and transport properties of layered perovskite-related titanates, niobates and tantalates of the type $A_nB_nO_{3n+2}$, $A'A_{k-1}B_kO_{3k+1}$ and $A_mB_{m-1}O_{3m}$

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**Abstract**

This article represents a continuation of a paper on $A_nB_nO_{3n+2} = ABO_x$ compounds which was published in 2001 in this journal. This work reports also on oxides of the type $A'A_{k-1}B_kO_{3k+1}$ (Dion–Jacobson type phases) and hexagonal $A_mB_{m-1}O_{3m}$. The title materials have in common a layered perovskite-related structure whose layers are formed by corner-shared $BO_6$ octahedra. The three homologous series differ structurally in their orientation of the $BO_6$ octahedra with respect to the $c$-axis. This can be considered as a result from cutting the cubic perovskite $ABO_3$ structure along different directions followed by an insertion of additional oxygen, namely along the [100], [110] and [111] direction for $A'A_{k-1}B_kO_{3k+1}$, $A_nB_nO_{3n+2}$ and $A_mB_{m-1}O_{3m}$, respectively. The materials, with emphasis on electrical conductors, were prepared by floating zone melting and characterized by thermogravimetric analysis, X-ray powder diffraction and magnetic measurements. On crystals of five different compounds the resistivity was measured along the distinct crystallographic directions. Concerning $A_nB_nO_{3n+2}$ this work is focussed on two topics. The first are materials with paramagnetic rare earth ions at the $A$ site or transition metal ions such as $Fe^{3+}$ at the $B$ site. The second are non-stoichiometric compounds. Furthermore, we discuss issues like occupational order at the $B$ site, the proximity of some materials to the pyrochlore structure, potential magnetic ordering, and a possible coupling between magnetic and dielectric properties. The oxides $A'A_{k-1}B_kO_{3k+1}$ gained attention during a study of the reduced Ba–(Ca,La)–Nb–O system which lead to conducting Dion–Jacobson type phases without alkali metals. Concerning hexagonal $A_mB_{m-1}O_{3m}$ the emphasis of this work are conducting niobates in the system Sr–Nb–O. The title materials have in common a quasi-2D (layered) structure and they are mainly known as insulators. In the case of electrical

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conductors, however, their transport properties cover a quasi-1D, quasi-2D and anisotropic 3D metallic behavior. Also temperature-driven metal-to-semiconductor transitions occur. A special feature of the quasi-1D metals of the type $A_nB_nO_{3n+2}$ is their compositional, structural and electronic proximity to non-conducting (anti)ferroelectrics. We speculate that these quasi-1D metals may have the potential to create new (high-$T_c$) superconductors, especially when they are viewed from the perspective of the excitonic type of superconductivity. Referring to literature and results from this work, a comprehensive overview on the title oxides and their properties is presented.


*Keywords:* Titanates; Niobates; Tantalates; Perovskite-related crystal structures; Layered materials; Crystal growth; Floating zone melting; Low-dimensional conductors; Resistivity; Magnetic susceptibility; Magnetic ordering; Ferroelectrics; Antiferroelectrics; Superconductivity; Excitonic superconductivity

## 1. Introduction and overview

### *1.1. Preliminaries and general survey*

This article represents a continuation of a paper on $A_nB_nO_{3n+2} = ABO_x$ compounds which was published in 2001 in this journal [127]. This special group of oxides comprises the highest-$T_c$ ferroelectrics such as $n = 4$ $SrNbO_{3.50}$ [151] and quasi-1D metals such as $n = 5$ $SrNbO_{3.40}$ [110–113,127,136,244] which are in compositional, structural and electronic proximity to non-conducting (anti)ferroelectrics. This suggests the possibility to realize materials with an intrinsic coexistence of metallic conductivity and high dielectric polarizability. Therefore this group of oxides represents an important field of research.

In addition to the $A_nB_nO_{3n+2} = ABO_x$ materials this work reports also on Dion–Jacobson type phases $A'A_{k-1}B_kO_{3k+1}$ and hexagonal $A_mB_{m-1}O_{3m}$. There were several reasons for this extension. First, during a study exploring the substitution of Ca by Ba in $n = 4$ niobates $(Ca,La)NbO_{3.50}$, an additional phase appeared whose type was assigned as $A'A_{k-1}B_kO_{3k+1}$. This lead to the synthesis of $A'A_{k-1}B_kO_{3k+1}$ compounds in the reduced Ba–(Ca,La)–Nb–O system. They represent Dion–Jacobson type phases without any alkali metal. Secondly, associated with structural discussions the hexagonal $A_mB_{m1}O_{3m}$ oxides are sometimes cited in papers about $A_nB_nO_{3n+2}$ materials, e.g. in the publication by Levin et al. [122]. In addition to that, sometimes an $A_mB_{m-1}O_{3m}$ compound occurred as impurity phase in $A_nB_nO_{3n+2}$ compositions. That way the $A_mB_{m-1}O_{3m}$ phases gained attention and the question for the preparation of electrical conductors of this type did raise. Thirdly, the $A'A_{k-1}B_kO_{3k+1}$, $A_nB_nO_{3n+2}$ and $A_mB_{m-1}O_{3m}$ compounds represent three related structural modifications of the cubic perovskite $ABO_3$. They emerge from the latter by cutting it along its [100], [110] and [111] direction, respectively, followed by an insertion of additional oxygen. The resulting structures constitute layered, perovskite-related, homologous series whereby the layers along the $c$-axis are $k = n = m - 1$ $BO_6$ octahedra thick. The layers are formed by corner-shared $BO_6$ octahedra along the $ab$-plane. Their structural difference is mainly given by the kind of orientation of the $BO_6$ octahedra with respect to the $c$-axis. This suggests to study and compare the physical properties of related materials of these three series.

Before considering the three title series in detail, we cite two further structure types which are worth mentioning in their context. The first is given by the Ruddlesden–Popper phases $A_{j+1}B_jO_{3j+1}$ which represents a perovskite-related, layered, homologous series. Like the