Strontium Tantalates with a Perovskite Structure: Their Conductivity and High-Temperature Interaction with Water

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Abstract—The interaction of perovskite-like solid solutions \( \text{Sr}_6\text{–}x\text{Ta}_{2+x}\text{O}_{11+x} \) \( (x = 0–0.28) \) with water is studied, along with dependences of the solutions’ conductivity on their composition and the atmosphere’s temperature and humidity. The \( \text{Sr}_6\text{–}x\text{Ta}_{2+x}\text{O}_{11+x} \) phases with high concentrations of structural oxygen vacancies are high-temperature mixed oxygen–hydrogen ionic conductors whose conduction is sensitive to the presence of water vapor up to 900°C. According to a thermogravimetric study, the amount of water incorporated into the complex-oxide matrix is proportional to the concentration of structural oxygen vacancies. The process of water incorporation is considered in terms of crystalline and chemical properties of the structure. The oxygen-deficient perovskites containing coordination-unsaturated metal atoms can reconstruct their coordination polyhedron by adding water molecules, with subsequent partial dissociation of water to hydroxyl groups. The proposed mechanism explains different states of water in the oxide and a two-stage nature of its removal: water molecules coordinating the metal atom and those surrounding OH⁻ leave the core in the first and second stages, respectively.

INTRODUCTION

A large number of oxide phases with a perovskite structure or its derivative, which exhibit high-temperature proton conduction, have been synthesized and investigated within the last twenty years [1].

To date, the most promising proton conductor is the complex nonstoichiometric perovskite \( \text{Ba}_3(\text{Ca}_{1.18}\text{Nb}_{1.82})\text{O}_{6.5} \) (BCN18), where \( \delta = 0.27 \). Its proton conductivity exceeds the electroconductivity of typical high-temperature conductors and reaches 0.013 S cm⁻¹ at 600°C [2]. The share of electron conduction of this phase is vanishingly small in a wide range of partial oxygen pressures. The phase and its structural analogues are derivatives of complex perovskites \( A'B'B''O_9 \) or \( A'B'B'O_6 \), where \( B' \) is an alkaline-earth element and \( B'' \) is either niobium or tantalum. The latter group of compounds is extremely numerous, because the sum of charges \( A + B \) may be obtained not only as the sums \( 1 + 5, 2 + 4, \) or \( 3 + 3 \) in \( \text{ABO}_3 \), but also as more complex combinations, such as \( 2 + (3 + 5) \) or \( 3 + (2 + 4) \) for \( A'B'B'O_6 \). These compounds have been sufficiently well described in the literature, as they have a number of various application important properties. For example, a wide class of piezo- and ferroceramic materials was obtained on the basis of these compositions [3]. On the other hand, the high tolerance of the perovskite structure and the possibility of varying the composition by filling positions \( A \) (cubical octahedron) and also positions \( B \) (octahedron) with atoms of different types stimulate a search for new structural analogues with better properties.

With increasing the ratio \( B/B'' \), the stoichiometric perovskites become oxygen-deficient, because the excess low-charge cation \( B' \) is counterbalanced by the emergence of oxygen vacancies. In turn, this makes it possible to incorporate water and leads to the emergence of hydrogen defects. This means that the formation of oxygen vacancies occurs at the expense of an acceptor doping by the intrinsic dopant, as opposed to classical high-temperature proton conductors, such as \( \text{BaCe}_{1–x}\text{M}_x\text{O}_3–\alpha \), where \( M \) is a rare-earth metal.

Perovskite phases include compounds of the composition \( \text{Me}_x\text{M}_2\text{O}_{11} \) \( (V)O \) \( (\text{Me} = \text{Sr, Ba}; M = \text{Nb, Ta}) \), in which \( 1/12 \) of positions in the oxygen sublattice are vacant. As shown for the first time in [4, 5], the electroconductivity of the \( \text{Sr}_6\text{Nb}_2\text{O}_{11} \) phase is sensitive to the presence of water vapor at temperatures reaching 1000°C. Systematic research into the hydrogen transfer in such phases was commenced later [6–8]. It was found that solid solutions \( \text{Sr}_6\text{–}x\text{Nb}_{2+x}\text{O}_{11+x} \) \( (x = 0–0.28) \) with a high content of strontium and, consequently, structural oxygen vacancies are capable of dissolving water in their matrices; such solutions are predominantly proton conductors up to 600°C [6–8].

This work is devoted to studying the interaction between water and perovskite-like phases of the \( \text{SrO–Ta}_2\text{O}_5 \) system and their conductivity as a function of the composition and the atmosphere’s temperature and humidity.
THE STRUCTURE AND THE PHASE EQUILIBRIUMS

In the domestic scientific literature, perovskites ABO$_3$ are usually classified by the type of the B cations. The classification includes perovskite derivatives structured as cryolite (mineral Na$_3$AlF$_6$) or elpasolite (mineral K$_2$[NaAlF$_6$]). The general formula for elpasolite-structured oxides is A$_2$B’B’’O$_6$; they are also known as ordered 1 : 1 perovskites. An elementary cell contains four formula units. The larger the differences in the charges and radii of cations in the B sublattice, the more probable the cation ordering by octahedrons [9, 10].

Cryolites include compounds described by the general formula Me$_6$(Me$_2$M$_2$)$_2$O$_{11}$, where Me is Sr or Ba and M is Nb or Ta. Such compounds may be viewed as derivatives of a perovskite structure. If this is true, then their composition may be written in the following form:

$$\text{Me}_d(\text{Me}_2\text{M}_2)\text{O}_{11} = \text{Me}(\text{Me}_{0.5}\text{M}_{0.5})\text{O}_{2.75}(V_O)^{0.25}.$$

Here, $(V_O)\text{^d}$ denotes a structural oxygen vacancy. Thus, 8.33% of positions in the oxygen sublattice are vacant. It is exactly these specific features of the structure of such phases that create conditions for facilitated oxygen-ionic transport. Electric properties of Sr$_6$Nb$_2$O$_{11}$ and Sr$_6$Ca$_4$Nb$_2$O$_{11}$ were studied for the first time in [11]. Even that long ago, the authors of [11] attributed the high conductivity to the migration of oxygen ions. However, due to lack of comprehensive crystallographic investigations, these researchers failed to describe the conduction mechanism in more detail. Phase equilibriums and crystallographic features of phases that form in systems based on alkaline-earth-metal oxides and pentaoxides of niobium or tantalum were studied later. According to [12, 13], atoms of an alkaline-earth metal are crystallographically nonequivalent and occupy two types of positions with cubical-octahedral and octahedral coordination Me$_{\text{cub}}$(Me$_2$M$_2$)$^{0.5}$$\text{O}_{11}$. Atoms of an alkaline-earth metal in octahedral positions may partially be replaced by niobium or tantalum. This ensures the existence of homogeneity regions in phases Me$_6$M$_2$O$_{11}$, which is expressed by the Me$_{6–2}$M$_2$O$_{11}+3h(V_O)^{2–3}$. As seen, with increasing content of M$_2$O$_5$, the structural oxygen vacancies become occupied. This model of disordering was confirmed by measuring pycnometric densities and studying electric properties [14]. The Me$_6$M$_2$O$_5$ phases, the neighbors in the phase equilibrium diagram, have a perovskite-derivative structure with the oxygen sublattice completely occupied [13].

The homogeneity-region width of cryolite Sr$_6$Nb$_2$O$_{11}$ is heavily dependent on the temperature and does not include the 6 : 1 stoichiometric composition below 800°C. The widest homogeneity region is intrinsic to the phase based on Sr$_6$Ta$_2$O$_{11}$ (81–85.7 mol % SrO at 1200°C) [13], which corresponds to the interval from Sr$_6$Ta$_3$O$_{11}$ to Sr$_6$Ta$_{5.4}$Ta$_{0.6}$O$_{11.84}$. Phases Me$_6–2$M$_2$O$_{11}+3h$ and Me$_6$M$_2$O$_{11}$ are separated by a narrow two-phase region that does not exceed 1 mol % in the case of SrO–Ta$_2$O$_3$ [13].

The authors of [15–17] have an opposite viewpoint on the mechanism of formation of solid solutions in such systems. They view the region of compositions Sr$_6$Nb$_2$O$_{11}$ to Sr$_4$Nb$_2$O$_9$ as a continuous series of solid solution Sr(Sr$_{1/3}$+$_x$Nb$_{2/3}$–$_x$)$_6$O$_{11}$–(3/2)x on the basis of the Sr$_6$Nb$_2$O$_9$ structure, which is a perovskite with a completely occupied oxygen sublattice. The authors of [15–17] believe that oxygen vacancies V$_O$ emerge when the SrO content increases at the expense of the formation of substitutional defects of the type Sr$_{\text{Nb}}^+(3c_{\text{Sr}^{\text{Na}}}=2c_{\text{V}_O})$. In other words, such phases are viewed in [15–17] by analogy with classical doped solid electrolytes on the basis of ZrO$_2$ and CeO$_2$. To our minds, describing properties of phases with structural vacancies in terms of traditional point-defect models is counterproductive. In the electrolytes with a dopant type of disordering, oxygen vacancies are created by an acceptor dopant. As opposed to such electrolytes, phases of the type Me$_6$M$_2$O$_{11}$ with narrow homogeneity regions contain structural oxygen vacancies that are intrinsic to their structures; these require no charge compensation and are not point defects in a traditional sense. Following an insignificant deviation from the composition, such phases dramatically change their properties. For example, in the region of homogeneity of Sr$_6–2$Nb$_2$O$_{11}+3h$, below 1100°C, the electroconductivity drops by 2.5 orders of magnitude, and the activation energy increases from 1.0 to 1.4 eV, due to a decreased concentration of oxygen vacancies [14]. In other words, such solid solutions may formally be classified with doped solid electrolytes (with intrinsic dopants). However, by their nature and properties, these are closer to solid electrolytes with structural disordering. Such phases have a large amount of an alkaline-earth metal oxide in their composition, and the authors of [14–17] who experimented with them reported a poor quality of the ceramics, its cracking, short storage times, and property degradation. All this probably suggests a high affinity of these phases to water.

Thus, phases with the largest content of MeO and a maximum content of structural oxygen vacancies are most interesting, due to the possibility of realizing a hydrogen conduction. In this work, we present data for the solid solution Sr$_6–2$Ta$_2$O$_{11}+3h$, obtained in thermogravimetric studies and when measuring its conductivity in atmospheres with different water vapor activities. The data indicate the existence of a link between the water content and the concentration of structural oxygen vacancies.