Phase Transitions in Nonstoichiometric Strontium Tantalates with the Cryolite Structure


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Abstract—The structural transformations of SrTa₂O₁₁ and Sr₅.₉₂Ta₃.ₐ₆O₁₁.₁₂ oxygen-deficient cryolites with variations in the partial pressures of oxygen \( p(O_2) \) and water vapor \( p(H_2O) \) are investigated using X-ray diffraction, thermogravimetry, and electrical conductivity measurements. It is found that a change in the oxygen partial pressure leads to a phase transition accompanied by the transformation of the cubic cell into the tetragonal cell, most probably, due to ordering of oxygen vacancies. The intercalation of water into the matrix of the complex oxides under investigation results in a structural–chemical transformation during which the solid solution undergoes a transition to an oxyhydrate phase of variable composition and the cubic cell transforms into the orthorhombic cell. © 2002 MAIK “Nauka/Interperiodica”.

INTRODUCTION

In recent years, oxygen-deficient complex oxides of the general formula \( ABO_{3-\delta} \) with a perovskite-like structure have been investigated extensively, because these materials can possess a considerable oxygen ion conductivity at high temperatures and a protonic conductivity at low temperatures [1, 2]. The nature of the predominant charge carriers depends on the ambient conditions \([T, p(O_2), p(H_2O)]\). Within the quasi-chemical formalism, the formation of these carriers can be described by the following reactions of dissolution of oxygen or water vapors in the oxide, provided the matrix structure is retained:

\[
\begin{align*}
1/2O_2(g) + V_0^\circ &\leftrightarrow O_0^\circ + 2h^+, \quad (1) \\
H_2O(g) + V_0^\circ + O_0^\circ &\leftrightarrow 2OH_0^-, \quad (2)
\end{align*}
\]

where \( V_0^\circ \) is the oxygen vacancy, \( O_0^\circ \) is the oxygen atom at a regular lattice site, \( OH_0^- \) is the hydroxy group with an effective positive charge in the oxygen sublattice, and \( h^+ \) is the hole. Consequently, the oxides can either absorb or release \( O_2 \) (or \( H_2O \)), depending on the partial pressure of oxygen (or water vapors) in the atmosphere.

In the general case, apart from the ambient conditions responsible for the charge carrier concentration, the degree of disordering \( \delta \) of the oxide (concentration of oxygen vacancies) also directly correlates with the particular (oxygen ion or protonic) type of conduction. From this viewpoint, it is of interest to consider oxides with a large oxygen deficit for the purpose of attaining an appreciable degree of unipolar ionic conduction.

However, since the structure is capable of accumulating high concentrations of defects, the interaction of the oxide with components of the gaseous medium \( (O_2 \) and \( H_2O) \) can be accompanied by different phase transformations. In turn, these transformations can manifest themselves in an anomalous (i.e., nonlinear) behavior of the phase-sensitive properties.

Among the materials with a perovskite-like structure, there are oxygen-deficient cryolites (double perovskites) of the general formula \( Me_9M_5O_{11} \), where \( Me \) is an alkaline-earth metal and \( M \) is Nb or Ta. The unit cell of these compounds contains four formula units \( ABO_3 \); hence, one in every twelve sites in the oxygen sublattice is unoccupied [3, 4]. It is these specific structural features that provide unipolar oxygen ion transfer at high temperatures in dry atmospheres and proton transfer at temperatures below 600°C in moist atmospheres [5, 6]. Therefore, by varying the thermodynamic parameters over a wide range, it is possible to determine the stability range of a particular structure, on the one hand, and to reveal the factors responsible for the formation of new structures, on the other.

In the present work, we elucidated how the changes in the temperature \( T \) and the partial pressures of oxygen \( p(O_2) \) and water vapor \( p(H_2O) \) affect the electrical and...
The electrical measurements were carried out by the two-point probe method with the use of samples prepared in the form of pellets with fired Pt electrodes under variations in the temperature and the partial pressures of oxygen and water vapors. The resistance of the studied samples was measured using impedance spectroscopy on a Zahner Electric IM6 impedance spectrometer in the frequency range from 0.5 Hz to 1 MHz with ac voltage amplitudes ranging from 10 to 50 mV. The bulk resistance was calculated according to the Bouckamp program.

The thermogravimetric measurements were performed by continuous weighing in an atmosphere with a specified moisture content on a setup consisting of an ADV-200 analytical balance, a furnace, and a temperature controller.

In order to produce the dry atmosphere, atmospheric air was passed sequentially through a concentrated sulfuric acid and a P$_2$O$_5$ powder [$p$(H$_2$O) $= 10^{-5}$ atm]. The moist atmosphere was obtained by bubbling atmospheric air through a saturated KBr solution [$p$(H$_2$O) $= 0.023$ atm]. Atmospheres with intermediate moisture contents were prepared by bubbling atmospheric air through a temperature-controlled vessel with water at a specified temperature.

The partial pressure of oxygen was varied and controlled with the use of a pump and a detector prepared from stabilized ZrO$_2$.

RESULTS AND DISCUSSION

The electrical conductivity of Sr$_6$Ta$_2$O$_{11}$ and Sr$_{5.92}$Ta$_{2.08}$O$_{11.12}$ samples was investigated in a dry air atmosphere [$p$(H$_2$O) $= 10^{-5}$ atm] at temperatures of 500–1300°C over a wide range of oxygen partial pressures. It was found that the electrical conductivity does not depend on the oxygen partial pressure $p$(O$_2$). This confirms the assumption that the electrical conduction predominantly occurs through the oxygen ion mechanism without a noticeable contribution of electron transfer (Fig. 1a). However, in the limited temperature range 700–1100°C at low pressures $p$(O$_2$) $< 10^{-12}$ atm, the conductivity undergoes a reversible jumpwise decrease to a constant value and then remains unchanged; i.e., no noticeable increase in the electronic component of the conductivity occurs in the low-conduction state. This allows us to assume that the observed effect is unrelated to changes in the oxidation states of elements that are in the highest stable oxidation states in the compounds. The temperature of the transition under investigation regularly increases with an increase in the oxygen partial pressure $p$(O$_2$). X-ray diffraction analysis of the Sr$_{5.92}$Ta$_{2.08}$O$_{11.12}$ sample quenched at a temperature of 800°C and an oxygen partial pressure $p$(O$_2$) $< 10^{-12}$ atm revealed insignificant tetragonal distortions ($a = b = 8.2602 \pm 0.0003$ Å and $c = 8.3017 \pm 0.0003$ Å) as compared to the initial cubic

![Dependences of the conductivity isotherm of Sr$_6$Ta$_2$O$_{11}$ on the partial pressures (a) $p$(O$_2$) and (b) $p$(H$_2$O). Temperature, °C: (a) (1) 500, (2) 600, (3) 700, (4) 800, (5) 885, and (6) 1200 and (b) (1) 475, (2) 500, and (3) 600.](image)

![Experimental setup for the electrical measurements.](image)