Composition and structure of tungsten antimony acid

P. V. Timushkov1*, V. A. Burmistrov1, M. N. Ulyanov1, V. N. Semenov2

1Chelyabinsk State University, 70b ul. Molodogvardyetsev, Chelyabinsk 45402, Russian Federation
2Voronezh State University, 1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

Tungsten antimony acids (TAA) with the composition $H_{2(2-x)}Sb_{2}W_{x}O_{6+n}H_{2}O$ ($0 < x \leq 1.45; 0 < n \leq 2.0$) have been synthesized by hydrolysis of antimony trichloride pre-oxidized with nitric acid in the presence of varying amounts of Na$_{2}$WO$_{4}$. To obtain TAA protonated forms, the samples were kept in a 96% solution of sulphuric acid, the precipitate was washed until reaction became neutral and dried in air. The amount of tungsten, antimony, and silver ions in TAA was determined using energy dispersive analysis. Changes in structural parameters upon doping of AA with tungsten ions were studied using a Bruker D8 ADVANCE X-ray diffractometer (Cu$K_{α}$-radiation). The number of oxonium ions in TAA was determined by the substitution of these ions by silver ions in equivalent amounts (Ag$^{+}$-TAA forms).

All obtained TAA samples and Ag$^{+}$-TAA forms had a pyrochlore-type structure, space group symmetry $Fd3m$. Refinement of the arrangement of atoms in the structure using the Rietveld method showed that tungsten ions replace antimony ions and are statistically located in 16c, oxygen anions in 48f, and oxonium ions and water molecules in 16d and 8b positions, respectively.

When tungsten ions were introduced into samples, the structural parameters of the resulting phases changed. There was a decrease in the unit cell parameter and the distance between antimony ions and oxygen anions, while an increase in the distance between oxonium ions and oxygen anions located in 48f positions was observed. This allowed the removal of a proton from oxonium molecules and its transport via a system of hydrogen bonds formed by water molecules.

Keywords: Solid electrolytes of antimony oxide, Tungsten oxides, Antimony acid, Pyrochlore type structure

1. Introduction

Materials with high proton conductivity can be used for the production of electrochemical current sources [1–2]. One of these compounds is antimony acid (AA), which has a pyrochlore-type structure (space group symmetry $Fd\bar{3}m$) [3]. The peculiarity of AA is the structure formed from jointed antimony-oxygen octahedra with a negative charge. The compensation of negative charge requires the presence of positively charged particles, such as oxonium, silver, potassium, sodium ions, etc. [4]. In this case, water molecules are located in some positions located in hexagonal cavities and can form oxonium ions or diaquahydrogen ions with protons [4]. The amount of proton conductivity of AA depends on the number of water and oxonium molecules [5]. Studies [6–9] demonstrated that the substitution of antimony ions Sb(V) with W(VI) in complex antimony oxides creates defects in the oxygen sublattice and promotes an increase in ionic conductivity. Probably, the creation of additional vacancies, which can be filled with water molecules, should lead to a restructuring of the proton hydrate sublattice of AA, as a consequence, to an increase in proton conductivity. The formation of vacant positions is possible by introducing W(VI) ions with a similar ionic radius [5] but having a different valence from Sb(V) ions into the structure of AA. However, data on the synthesis and study of the structure of complex antimony oxides doped with tungsten, sodium, and potassium ions are limited and refer to samples synthesized by the solid-phase method [5–10]. Protonated forms obtained by substitution of monovalent ions in these compounds with oxonium ions [11] are not fully hydrated compounds.

Therefore, the goal of the study was to develop a method for the synthesis of tungsten antimony acid (TAA) with different contents of W(VI) ions, determination of the concentration range of stability of the resulting phases and their structural parameters.

2. Experimental

The synthesis of TAA samples was carried out by hydrolysis of pre-oxidized SbCl$_5$ with nitric acid in the presence of Na$_2$WO$_4$. The resulting precipitate was boiled for 6 hours, kept in the mother solution for seven days, washed with distilled water and dried. The W/Sb ratio in the resulting phases was varied by changing the amount of Na$_2$WO$_4$ in the original solutions.

To obtain the protonated form, the samples were kept in a 96% solution of sulphuric acid at room temperature for a long time, the precipitate was washed until neutral and dried in air.

The resulting TAA samples were a white powder and had a composition that can be described by the chemical formula:

$$H_{(2)}\text{Sb}_{(2)}\text{W}_{X\cdot6}\cdot n\text{H}_2\text{O} (0 < x \leq 1.45; 0 < n \leq 2.0).$$

The number of protons (oxonium) in the structure of the obtained TAA phases was determined using an ion exchange. For this, the sample was placed in a concentrated AgNO$_3$ solution and kept for 24 hours, after which it was washed from excess of silver and nitric acid until there was no reaction to Ag$^+$ ions. The amount of silver, antimony and tungsten ions in the structure was determined by energy-dispersive X-ray fluorescence spectroscopy using an EDXRF spectrometer (AR QUANT’X from Thermo Fisher Scientific) according to standard methods.

The phase composition was monitored using Bruker D8 ADVANCE diffractometer (CuK$_{α1}$-radiation) in the range of diffraction angles 2$θ$ from 10 to 70° with a step of 0.01°. The structure of the resulting compounds was refined by the Rietveld approach using the PowderCell software package. For generation of the linear shape of the diffraction maxima, pseudo-Voigt function was used. For calculation of the distance between the 16d, 16c, and 48f positions, the formulas provided in [12] was used.

3. Results and discussion

The X-ray diffraction patterns of the AA and TAA samples have the same set of diffraction maxima, the totality of which is satisfactorily described by the extinction laws for crystals with cubic structure of the pyrochlore type of space group symmetry $Fd\bar{3}m$ [13]. As the amount of tungsten ions in the TAA increases, no significant redistribution of the relative intensities of reflections with even and odd indices was observed. In this case, the reflections shift toward larger angles (Fig. 1). This may indicate the
substitution of some antimony ions with tungsten ions and a change in structural parameters.

Elemental analysis of TAA showed that with an increase in the concentration of tungsten ions in the initial solutions, they increase with a simultaneous decrease in the number of antimony ions in the solid phase. In this case, the dependence of the change in W/Sb ratios according to X-ray spectral analysis data coincides with those calculated using formula (1) (Fig. 2). Taking into account X-ray analysis, this allows us to confirm the substitution of Sb(V) ions with W(VI) in the same crystallographic positions and consider the resulting TAA samples.
as substitutional solid solutions. Under the assumption that the number of oxygen anions in the octahedra does not change, and the number of protons should correspond to the electrical neutrality of the compounds, chemical formulas have been proposed that describe the compositions of the resulting TAA phases (Table 1).

For experimental clarification of the number of protons in TAA, additional studies on samples in which hydrogen ions in solutions of silver nitrate were substituted by silver ions (Ag forms of TAA) were carried out.

As follows from the X-ray analysis data, during ion exchange the set of diffraction maxima does not change, but a decrease in the relative intensities of reflections with even and odd indices was observed (Fig. 3). This indicates the substitution of protons (oxonium) with silver ions in TAA [11] without changing the symmetry of the crystal lattice. The number of silver ions in TAA samples decreases with an increase in the number of substituted antimony ions for tungsten ions (Fig. 2), which indicates a decrease in the number of protons in TAA samples with the introduction of tungsten ions.

The data obtained on the composition of the samples allow to propose a model for the arrangement of ions along a regular system of points in a pyrochlore-type structure. The main framework of the structure is formed by antimony-oxygen and tungsten-oxygen octahedra, connected by vertices. In this case, antimony and tungsten ions are located in the centre of the octahedra (16c positions), and oxygen anions are located at their vertices (48f positions). Oxonium ions and water molecules are statistically located in the 16d and 8b positions.

A full-profile analysis of the TAA showed good agreement between the proposed model of ion distribution over positions of a pyrochlore-type structure and experimental data (Table 2). At the same time, with an increase in the number of tungsten ions in the TAA samples, the unit cell parameter decreased from 10.337 Å to 10.254 Å for TAA with composition $H_{0.55}Sb_{0.55}W_{1.45}O_6\cdot nH_2O$ (Table 2). At the same time, a decrease in the distance between 16c(Sb,W) – 48f(O) positions was observed, as well as an increase in the distance between 16d(H_3O^+) – 48f(O) positions.

![Figure 2](image.png)

**Figure 2.** Change in the ratio of Ag/ (Sb + W) (a) and W/Sb (b) ions when doping AA with tungsten ions according to data of X-ray fluorescent spectroscopy and calculated (solid lines) according to formula (1) for TAA and Ag-forms of TAA with an average degree of proton substitution by silver ions equal to 0.93

<table>
<thead>
<tr>
<th>No</th>
<th>H-form of TAA</th>
<th>Ag-form of TAA</th>
<th>Gross formula of TAA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sb, at.%</td>
<td>W, at.%</td>
<td>W/Sb</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>87.5</td>
<td>12.5</td>
<td>0.142</td>
</tr>
<tr>
<td>3</td>
<td>85.0</td>
<td>15.0</td>
<td>0.176</td>
</tr>
<tr>
<td>4</td>
<td>75.0</td>
<td>25.0</td>
<td>0.333</td>
</tr>
<tr>
<td>5</td>
<td>61.5</td>
<td>38.5</td>
<td>0.626</td>
</tr>
<tr>
<td>6</td>
<td>46.0</td>
<td>54.0</td>
<td>1.173</td>
</tr>
<tr>
<td>7</td>
<td>41.5</td>
<td>58.5</td>
<td>1.409</td>
</tr>
<tr>
<td>8</td>
<td>27.5</td>
<td>72.5</td>
<td>2.636</td>
</tr>
</tbody>
</table>

Table 1. The number of Sb(V) and W(VI) ions in TAA samples and silver ions in Ag-forms of TAA obtained by X-ray fluorescence spectroscopy

149
An increase in the parameter x of oxygen atoms was recorded (Table. 2). This may be due to the fact that tungsten ions have a higher electronegativity than antimony ions and change the electron density near oxygen anions, which led to distortion of antimony-oxygen octahedra, a decrease in interionic distances and the unit cell parameter. An increase in the distances between oxonium and oxygen anions makes the removal of proton from oxonium molecules and its transport via the system of hydrogen bonds formed by water molecules more probable.

4. Conclusions

The conditions for the synthesis of TAA samples with the composition $H_{x+y}Sb_{1-x}W_xO_{y+1-n}nH_2O$ $(0 < x \leq 1.45; 0 < n \leq 2.0)$ were established for a wide range of concentrations and it was shown that the TAA phases have a pyrochlore-type structure, with antimony and tungsten ions statistically located in 16c, oxygen anions located in 48f, and oxonium ions and water molecules located in 16d and 8b positions, respectively. The substitution of some antimony ions with tungsten ions in AA led to a decrease in the unit cell parameter and a change in interionic...
distances, which was caused by a change in the interaction energy in tungsten-oxygen octahedra and a decrease in the number of protons in the structure.

Contribution of the authors
The authors contributed equally to this article.

Conflict of interests
The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

Fig. 4. The distance between the 16d, 16c, and 48f positions from the ratio of substitution with tungsten calculated using formula 2. $R(H_3O^-O)$ – distance between the 16d and 48f positions, $R(Sb(W)-O)$ – distance between the 16c and 48f positions
Information about authors

Pyotr V. Timushkov, Assistant at the Department of Solid State Chemistry and Nanoprocesses, Chelyabinsk State University (Chelyabinsk, Russian Federation).
https://orcid.org/0009-0005-2226-3076
p.timushkov@mail.ru

Vladimir A. Burmistrov, Dr. Sci. (Phys.-Math.), Full Professor, Department of Solid State Chemistry and Nanoprocesses, Chelyabinsk State University (Chelyabinsk, Russian Federation).
https://orcid.org/0000-0002-7862-6017
burmistrov@csu.ru

Maxim N. Ulyanov, Cand. Sci. (Phys.-Math.), Assistant Professor at the Department of General and Theoretical Physics Chelyabinsk State University (Chelyabinsk, Russian Federation).
https://orcid.org/0000-0003-0066-9559
max-39@yandex.ru

Victor N. Semenov, Dr. Sci. (Chem.), Full Professor, Head of the Department of General and Inorganic Chemistry, Voronezh State University (Voronezh, Russian Federation).
https://orcid.org/0000-0002-4247-5667
office@chem.vsu.ru

Received 28.04.2023; approved after reviewing 19.05.2023; accepted for publication 15.06.2023; published online 25.03.2024.

Translated by Valentina Mittova