Thermionic Electron Emission of Tungsten Bronzes. K\(_{0.30}\)WO\(_3\) and Rb\(_{0.30}\)WO\(_3\)

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The work functions and thermionic constants of the hexagonal tungsten bronzes K\(_{0.30}\)WO\(_3\) (\(\phi = 1.76\) eV, \(A = 3\) A/\(\text{cm}^2\) K\(^2\)) and Rb\(_{0.30}\)WO\(_3\) (\(\phi = 1.88\) eV, \(A = 10\) A/\(\text{cm}^2\) K\(^2\)) are determined and compared with those of the corresponding alkaline metals and hexagonal Cs\(_{0.30}\)WO\(_3\).

Key words: Work function – Tungsten bronzes.

Tungsten bronzes, \(M_x\)WO\(_3\), where \(M\) is a metal and \(x < 1\), are non-stoichiometric compounds [1] which have a remarkable importance in several fields such as electrochemistry, catalysis, crystallography, etc. In a previous paper [2] the thermionic electron emission of the hexagonal bronze Cs\(_{0.30}\)WO\(_3\) was studied. Also bronzes K\(_x\)WO\(_3\) and Rb\(_x\)WO\(_3\) can crystallize in the hexagonal system [3]. Hexagonal alkaline tungsten bronzes have similar structures based on a framework of corner sharing WO\(_3\) octahedra forming hexagonal tunnels where alkaline atoms are located. Hussain [4] has shown that hexagonal \(M_x\)WO\(_3\), where \(M\) is K, Rb or Cs, has the same composition range (0.19 \(\leq x \leq 0.33\)) in the phase diagram. Therefore it seemed interesting to measure the thermionic electron emission of K\(_{0.30}\)WO\(_3\) and Rb\(_{0.30}\)WO\(_3\) and to compare the data with those [2] of the hexagonal cesium bronze.

K\(_{0.30}\)WO\(_3\) and Rb\(_{0.30}\)WO\(_3\) were prepared according to the method of Conroy and Podolsky [5] by heating a mixture of alkaline halide (in excess), WO\(_2\) and WO\(_3\) in a sealed quartz tube under a vacuum at 900 °C for 3 h. 99.998% KCl (Koch and Light), 99.99% RbCl (Aldrich), 99.9% WO\(_2\) (Noah), and 99.99% WO\(_3\) (Atomergic Chemetals) were used as reactants. The methods of purification and analysis of the products and also the experimental apparatus and procedure have already been described [2].

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The thermionic electron emission of K\(_{0.30}\)WO\(_3\) was studied in the temperature range 459–625 °C. The study of the electron emission of Rb\(_{0.30}\)WO\(_3\) was carried out in the 440–603 °C range.

Figure 1 shows the experimental data. \(J_{0_{\text{sat}}}\) is the zero field saturation current density and \(T\) the absolute temperature. From the slopes of the straight lines of Fig. 1 we obtain the values of the work function of K\(_{0.30}\)WO\(_3\) and Rb\(_{0.30}\)WO\(_3\). Extrapolation of the straight lines for \(1/T\) approaching zero gives the values of the thermionic constant for these bronzes.

Table 1 shows the work function and thermionic constant of K\(_{0.30}\)WO\(_3\) and Rb\(_{0.30}\)WO\(_3\) and also the corresponding data for Cs\(_{0.30}\)WO\(_3\) and alkaline metals. Surprisingly, while the work functions of the alkaline metals are in the order \(\phi_{\text{Cs}} < \phi_{\text{Rb}} < \phi_{\text{K}}\), the work functions of the hexagonal alkaline tungsten bronzes follow the reverse order. We can advance the hypothesis that, under the operating conditions, the surface of a hexagonal alkaline bronze is covered with...
Table 1. Work function and thermionic constant of hexagonal alkaline tungsten bronzes and corresponding alkaline metals.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Work function (eV)</th>
<th>Thermionic constant (A/cm² K²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₀.₃₀WO₃</td>
<td>1.76</td>
<td>3</td>
<td>this work</td>
</tr>
<tr>
<td>Rb₀.₃₀WO₃</td>
<td>1.88</td>
<td>10</td>
<td>this work</td>
</tr>
<tr>
<td>Cs₀.₃₀₅WO₃</td>
<td>2.12</td>
<td>115</td>
<td>[2]</td>
</tr>
<tr>
<td>K</td>
<td>2.39</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>Rb</td>
<td>2.21</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>Cs</td>
<td>2.14</td>
<td></td>
<td>[6]</td>
</tr>
</tbody>
</table>

a film of alkaline metal [7]. Moreover, even if the interpretation is not simple, we should admit that the interaction of the alkaline metal film with the WO₃ octahedra of the substrate is the greater, the smaller the alkaline metal. Actually, the interaction of the cesium film with the substrate should be small; in fact, as it can be seen in Table 1, the work function of Cs₀.₃₀₅WO₃ is practically equal to that of metallic cesium. The thermionic constant of Cs₀.₃₀₅WO₃ is close to the universal constant 120 A/cm² K², therefore indicating that the whole surface participates to the electron emission. K₀.₃₀WO₃ and Rb₀.₃₀WO₃, instead, show rather low values of the thermionic constant, so indicating a patch emission. With the aim of explaining these anomalies, a theoretical work will be undertaken. It will take into account both the energy of the dipole alkaline metal-oxygen in WO₃ (that could explain the observed reverse order of the work function) and the aggregation energy of an alkaline metal film onto WO₃, which could explain the patch emission of potassium and rubidium hexagonal bronzes.