

## A new class of thermionic electron emitters: Cesium tungsten bronzes, Cs x WO<sub>3</sub>

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Citation: [Journal of Applied Physics](#) **56**, 2972 (1984); doi: 10.1063/1.333765

View online: <http://dx.doi.org/10.1063/1.333765>

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# A new class of thermionic electron emitters: Cesium tungsten bronzes, $\text{Cs}_x\text{WO}_3$

F. Zocchi

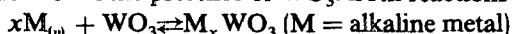
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(Received 14 March 1984; accepted for publication 11 June 1984)

A polycrystalline sample of  $\text{Cs}_{0.305}\text{WO}_3$  was heated in the temperature range 390–630 °C in a UHV chamber. The values for the work function and thermionic constant are, respectively,  $2.12 \pm 0.01$  eV and  $115 \text{ A/cm}^2 \text{ K}^2$ . The use of cesium tungsten bronzes as thermionic cathodes is limited to temperatures up to 630 °C, since at higher temperatures these materials deteriorate because of considerable loss of cesium. Tungsten bronzes, however, are suitable materials for systematic studies of the dependence of the work function on composition and structure.

Tungsten bronzes,  $\text{M}_x\text{WO}_3$ , are nonstoichiometric compounds whose structural, electrochemical, and catalytic properties have been extensively studied.<sup>1,2</sup> Their opto-electronic properties have also been investigated, but relatively few papers have been published on the UV photoemission<sup>3–5</sup> and no work at all has been done on the thermionic emission of these materials.

It is known<sup>1,2,6</sup> that tungsten bronzes can be prepared by reacting  $\text{WO}_3$  with alkali metal vapors and that the reverse reaction can be obtained by reducing the content in alkaline metal of a bronze, such as  $\text{Na}_x\text{WO}_3$ , by heating it in vacuum or in the presence of  $\text{WO}_3$ . Both reactions



can occur under operating conditions of some cathodes like cesium on oxygen or tungsten, Cs-O-W, and play a role in their electron-emitting behavior. During the operation of these cathodes, the appearance of a blue phase has been attributed<sup>7–8</sup> to the formation of a cesium bronze of the type studied by Magneli.<sup>9</sup>

The above results and considerations prompted the present study of the thermionic emission of cesium tungsten bronzes,  $\text{Cs}_x\text{WO}_3$ , with the aim of both clarifying their role in the functioning of the mentioned cathodes and investigating their possible applications.

The thermionic emission experiments were carried out in a UHV chamber at a pressure of  $2 \times 10^{-10}$  mbar obtained by means of an Edwards 700  $\ell/\text{s}$  diffusion pump of the Diff-stack type. A cylindrical molybdenum crucible (12 mm diameter) holding a bronze sample in the form of a pellet was used as cathode. The crucible temperature was measured with a quartz-insulated, chromel-alumel thermocouple. The cathode was faced by a cylindrical molybdenum anode at a distance of 1 mm. The cathode was mounted on a vertical 1-mm-diam tungsten rod. The anode was held by a 3-mm-diam tantalum rod. Both cathode and anode were heated by a tantalum ribbon. The whole system was surrounded by several tantalum thermal shields. The various parts of the vacuum chamber were washed with acetone in an ultrasonic bath and were treated, where necessary, with pickling solutions and then thoroughly washed with distilled water and acetone.

A cesium tungsten bronze was prepared according to the method of Conroy and Podolsky<sup>10</sup> by heating a mixture

of CsCl,  $\text{WO}_3$ , and  $\text{WO}_2$ , using excess CsCl and  $\text{WO}_2$  as the reactant limiting the  $x$  cesium coefficient in the bronze. 99.9999% "Ventron" CsCl, 99.99% "Atomergic Chemicals"  $\text{WO}_3$ , and 99% "Ventron Alfa Products"  $\text{WO}_2$  were used as reactants. In the latter, the main impurities were tungsten (0.5%) and tungsten oxides. Tungsten does not negatively interfere in the preparation of bronzes since at high temperature it reacts with  $\text{WO}_3$  to form  $\text{WO}_2$ . The mixture of CsCl,  $\text{WO}_3$ , and  $\text{WO}_2$  was heated in vacuum ( $10^{-5}$  mbar) in a quartz tube at 900 °C for 3 h. The blue product was ground and washed four times with hot distilled water in order to remove the excess CsCl. The x-ray powder diffraction analysis of the product indicated that it was identical with the hexagonal phase of  $\text{Cs}_x\text{WO}_3$  investigated by Magneli. No Bragg reflection in the diffraction pattern could be attributed to another phase. The cesium content in the bronze was determined by dissolving an accurately weighed sample of ca. 0.13 g by alkaline oxidizing melting with a mixture of 0.5 g  $\text{K}_2\text{CO}_3$  and 0.5 g  $\text{KNO}_3$  and using flame spectroscopy. This analysis indicated the composition  $\text{Cs}_{0.305}\text{WO}_3$ . A purified sample was pressed at 11 ton/cm<sup>2</sup> with the resulting pellet (10 mm diameter and 1.2 mm thick) showing a density of about 95% of the value previously reported.<sup>9</sup> The crucible with the bronze pellet was heated until it reached a constant temperature ( $\pm 0.5$  °C). The emitted thermionic current was measured by a Keithley 610 C electrometer which was connected with the cathode, while the anode was grounded.

In preliminary tests, full activation of the cathode was obtained by keeping its temperature at 500 °C for a period of about 10 min with an electric field of 500 V/mm between the two electrodes. It is worth noting that while for conventional barium oxide cathodes an activation period at 1000 °C is necessary in order to obtain maximum electron emission, in the case of  $\text{Cs}_{0.305}\text{WO}_3$  at 500 °C one obtains emission immediately and the activation process increases the electron current by only 50%.

A typical Schottky plot, obtained after full activation of the cathode, is shown in Fig. 1. Linear extrapolation for the electric field  $E$  going to zero gives the zero field saturation current density,  $J_{\text{sat}}$ . By plotting  $J_{\text{sat}}/T^2$  as a function of the reciprocal of the absolute temperature one obtains the diagram shown in Fig. 2. Extrapolation of the straight line

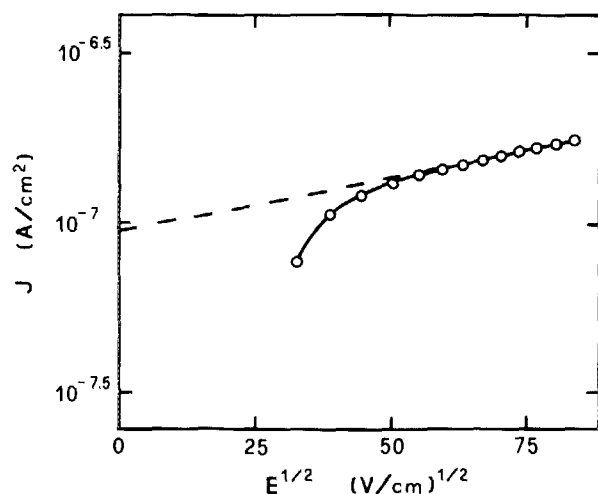


FIG. 1. Schottky plot of the current density  $J$  as a function of the square root of the electric field  $E$  in the space between cathode and anode.  $T = 721$  K.

for  $1/T$  approaching zero gives  $J_{\text{osat}}/T^2 = 115 \text{ A/cm}^2 \text{ K}^2$ , a value almost equal to the one ( $120.4 \text{ A/cm}^2 \text{ K}^2$ ) of the Sommerfeld universal constant.<sup>11</sup> From the slope of this straight line a value of  $2.12 \pm 0.01 \text{ eV}$  is obtained for the work function. The electron emission of  $\text{Cs}_{0.305}\text{WO}_3$ , in the considered temperature range (390–630 °C), was comparable with that of the barium oxide cathodes. However, the use of  $\text{Cs}_{0.305}\text{WO}_3$  for practical cathodes is unsuitable since, at temperatures higher than 630 °C, the electron emission was found to decrease swiftly due to a loss of cesium. Indeed the color of the surface of the pellet changed to brown and its structure was shown by x-ray diffraction to be that of  $\text{WO}_2$ . This result is in agreement with the assignment by Desplat and Papageorgopoulos<sup>7,8</sup> of an observed second cesium desorption peak, beginning at about 630 °C and with maximum at ca. 780 °C, to the decomposition of a cesium tungsten bronze.

The fact that the extrapolated value of  $J_{\text{osat}}/T^2$  in Fig. 2 is practically coincident with the Sommerfeld universal constant indicates that patch emission is rather limited in these polycrystalline materials. Moreover, the possibility of varying the cesium content in a wide range ( $0 < x < 0.33$ ) and the existence of various crystalline phases for  $\text{Cs}_x\text{WO}_3$  make these substances (and, possibly, tungsten bronzes in general) particularly suitable for studying the dependence of the work function on composition and structure. Indeed, as was

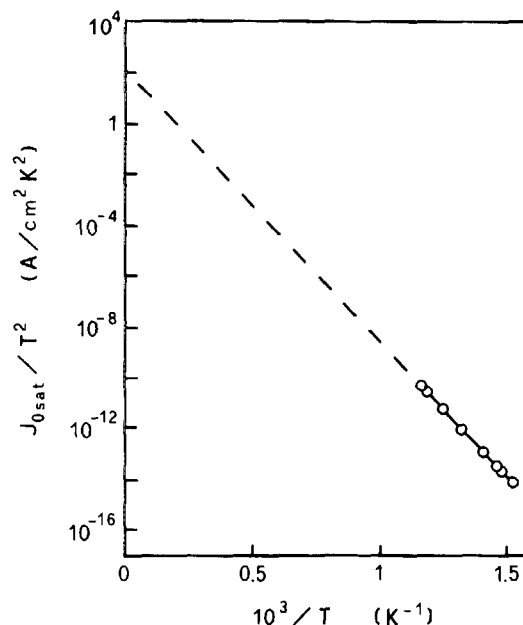


FIG. 2.  $J_{\text{osat}}/T^2$  as a function of the reciprocal of the absolute temperature.

pointed out recently,<sup>12</sup> this kind of investigation is of the utmost importance both from a theoretical point of view and for improving the performance of the cathodes.

Systematic work is in progress on the thermionic emission of various tungsten bronzes.

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