

Experimental Investigation of Bulk and Thin Film Perovskite SrVO₃ as a Thermionic Cathode Material

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Abstract: First-principles calculations based on Density Functional Theory (DFT) previously revealed that perovskite SrVO₃ is a promising candidate for thermionic emission applications. In this work, polycrystalline bulk and epitaxial thin film SrVO₃ samples have been experimentally examined. Both bulk and epitaxial SrVO₃ can exhibit low work function, consistent with DFT calculations and corresponding promising thermionic emission behavior. SrVO₃ is a potentially good thermionic emitter material and points more broadly to perovskite materials as a family of compounds which may further the development of next-generation thermionic electron emitters.

Keywords: thermionic emission; work function; perovskite; SrVO₃; X-ray photoelectron spectroscopy; thin film.

Introduction

The last few decades have witnessed the significant development of thermionic electron emission cathodes, which are widely used in vacuum electronic devices (VEDs) including traveling wave tubes, magnetrons, klystrons, and gyrotrons. Despite the success of various types of cathodes achieving practical low work function cathode surfaces, such as oxide cathodes, B-type and M-type impregnated cathodes and scandate cathodes, there is still an increasing need to search for new classes of materials for thermionic emitters due to the shortcomings of existing cathodes, including volatile barium oxide contamination, non-uniform emission current, and device performance drift.

To find new materials that can overcome such shortcomings, we have chosen to focus on perovskite materials (chemical formula ABO₃) because of their high compositional tunability, intrinsically polar surfaces with no added volatile dipole layer, and experimentally verified high stability under cathode operating conditions (T = 1000 °C, P(O₂) = 10⁻⁹ Torr) by many experiments on different perovskite systems. By varying the A- and B-site elements of a perovskite, its bulk electronic structure, surface dipole and stability can be tuned, making a stable perovskite with low work function likely obtainable. Our previous computational work examined a representative set of ~20 perovskite compounds with density functional theory (DFT), and SrVO₃ stood out from our screening because of its low predicted work function (1.9 eV on (001) AO-terminated surface, which also is expected to be a stable surface), high electrical conductivity (~10⁵ S/cm, comparable to graphite), and high predicted stability under cathode operating conditions.

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In this work, we experimentally evaluate aspects of multiple types of SrVO₃. In particular, we synthesized both polycrystalline bulk and highly oriented single crystal thin film samples, and characterized the structure using X-ray diffraction (XRD) and the surface chemistry and work function using X-ray photoelectron spectroscopy (XPS) with and without surface treatment. The consistent experimental results from bulk and thin film samples and corresponding consistency with DFT-calculated work function strongly suggests that SrVO₃ is a promising candidate for thermionic emission applications.

Polycrystalline Sample: Surface Oxidation and Recognition of Low Work Function

Polycrystalline SrVO₃ sample has been prepared via a sol-gel synthesis continued with a high temperature annealing under 5% H₂/95% Ar atmosphere. The powdered sample has then been pressed into pellets and sintered in the same reducing atmosphere for further characterization.

Powder XRD was used to assess the structure of SrVO₃, and a high purity (~99%) bulk perovskite phase was verified for the as-sintered pellet sample, as shown in Figure 1. However, XPS work function measurement and vanadium 2p core level scan on this sample gives a 3.9 ± 0.3 eV work function and a predominantly vanadium 5+ oxidation state on the surface (as shown in Figure 2) rather than the expected 4+ in bulk phase. Given the fact that XRD characterizes bulk crystal structure while XPS measures near-surface (~1 nm) region, this indicates the sample has a likely over-oxidized surface on top of bulk SrVO₃ phase, with a relatively high work function.

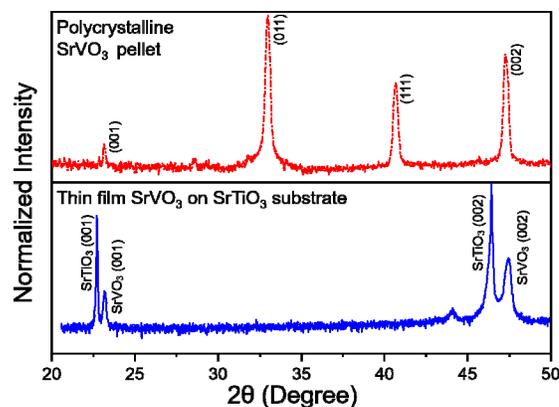


Figure 1. XRD results for both polycrystalline and thin film single crystal SrVO₃ samples. Perovskite SrVO₃ phase can be identified in both cases.

Various surface treatments have been employed to remove the over-oxidized surface layer. One method is to anneal the sample at high temperature in a highly reducing environment (e.g. pure H₂ gas), in order to remove the surface oxide layer. After this treatment, XPS shows a wide spread of work function from 1.8 to 3.1 eV, with the lower bound of this range consistent with DFT calculations (see Figure 2). From Figure 3, the vanadium core level XPS on this H₂-fired sample also suggests increase of the measured surface V(4+) to V(5+) ratio compared to the as-sintered sample.

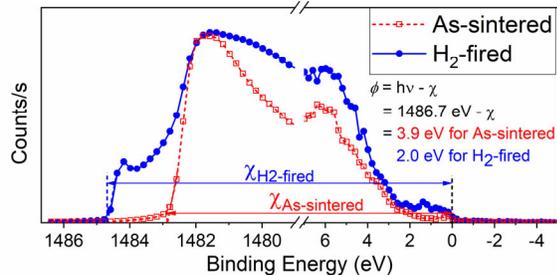


Figure 2. XPS work function measurement for the as-sintered (red) and H₂-fired SrVO₃ pellets (blue), indicating the work function decreases from 3.9 eV to 2.0 eV (this is one work function value within the 1.8 to 3.1 eV range).

Thin Film Sample: Further Verification on a Higher Quality Material Platform

Despite the success of polycrystalline samples showing low work function, there is still a need for better understanding of how to obtain the low work function surface robustly, as well as which surface is responsible for the low work function. The polycrystalline sample is porous with distinct grains, making it hard to measure the exact surface facet orientations. Therefore, a sample with controlled surface orientation would be beneficial in this analysis.

To obtain samples with a well-controlled surface, thin film SrVO₃ was grown via solid-phase epitaxy on a single-crystal SrTiO₃ (001) substrate. Thin film XRD shows SrVO₃ and SrTiO₃ (001) and (002) reflections (see in Figure 1); the missing (011) and (111) reflections indicate the film is aligned with substrate along [001] direction, making it very likely to have (001) surface.

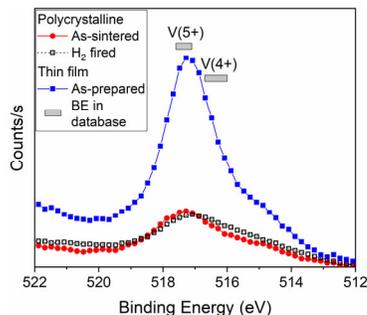


Figure 3. XPS vanadium core level scans for polycrystalline and thin film SrVO₃, showing predominant vanadium 5+ component on the surface prior treatments. H₂ firing help slightly reduce the over-oxidized surface, making V 4+ species intensity slightly stronger.

XPS measurements on epitaxial SrVO₃ give a stronger signal intensity, suggesting a higher sample density than the polycrystalline sample (i.e. low to no porosity). Vanadium core level and work function measurements give similar results as polycrystalline sample, suggesting similar thin over-oxidized surface phase (as shown in Figure 3). Surface treatment gives a similar results as the bulk polycrystalline sample – evidence on surface reduction and a decrease of work function with some sample areas showing a work function consistent with polycrystalline sample and DFT calculation. All these experimental results consistently indicate SrVO₃ is a promising material for thermionic emission applications.

Acknowledgements

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