Searching for Low Work Function Perovskite Oxides using Density Functional Theory

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Abstract: *The work function is a crucial parameter for electron emitters used in vacuum electronic devices as lower function allows higher current density and/or lower operating temperature. Perovskite oxides are a novel class of materials for potential use in electron emission applications due to their tunable work functions, robust stability, and good electronic conductivity. In this work, we performed a high-throughput screening based on Density Functional Theory (DFT) simulations and predicted $BaMoO_3$ to be promising emitter materials with low work function, good stability and high electronic conductivity. Our work also provides a general materials design principle governing the work function of perovskites, which is that perovskites with nearly empty electronic d-bands have the lowest work functions.*

Keywords: work function; vacuum electronic devices; perovskite oxides; Density Functional Theory.

Introduction

The work function is a fundamental property for materials used as thermionic and field electron emitters in vacuum electronic devices such as traveling wave tubes, klystrons, gyrotrons, and magnetrons.[1] In such applications, a low work function is critical for the generation of high current density at low temperature. Currently, the most widely used electron emitters are impregnated W cathodes, where a Ba-O surface dipole layer is required to obtain a low work function. However, this surface layer is volatile and makes these materials suffer from lifetime and performance issues arising from Ba depletion, emission nonuniformity, surface degradation, and device contamination.

Recent computational studies by Jacobs et al.[2] and Zhong et al.[3] have demonstrated from a set of about 20 perovskite compositions that perovskite materials can exhibit low work functions originating from their intrinsic polar surfaces, with the results of Jacobs et al. suggesting $SrVO_3$ is a promising low work function perovskite. In this study we broadened the previous searches by using Density Functional Theory (DFT) to search 2935 perovskite compositions for low work function, stable, and electrically conductive materials for electron emission applications. This screening resulted in a promising new candidate, $BaMoO_3$. In addition, the large amount of data obtained from this computational search also enabled an enhanced understanding of the materials chemistry governing the work function of perovskites.

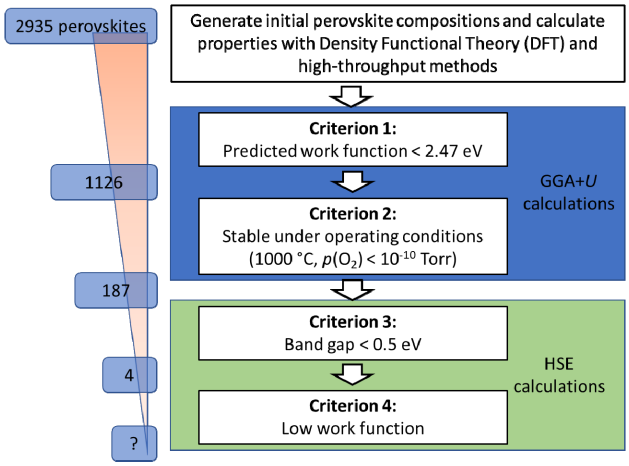

Figure 1. Schematic of the DFT-based high-throughput screening process. At each step, an elimination criterion is invoked to reduce the pool of potentially promising compounds. The numbers on the left indicate the number of materials passing each screening step at the time of this writing.

Results and Discussion

Figure 1 shows a schematic of the screening process and elimination criteria used in this work. The initial pool contains 2935 perovskites. In the first step, the linear correlation between work function and bulk O *p*-band center found by Jacobs et al. is used to screen for low work function.[2] The screening eliminates perovskites with work functions higher than 2.47 eV, the GGA+*U* predicted value of $SrVO_3$, which has been computationally and experimentally shown to be a promising cathode material.[4] After the first screening step, 1126 compounds remained. The second screening step examines the bulk stability based on the energy above the convex hull, E_{hull}, and eliminates perovskites that are unstable under typical thermionic cathode operating conditions (T = 1000 ˚C, $p(O_2) = 10^{-10}$ Torr). 187 candidates remained after this second screening step. In the third screening step, we eliminated materials with predicted band gap > 0.5 eV as these are likely to be poor electrical conductors, even at high temperatures. Band gaps are calculated using high-fidelity Heyd-Scuseria-Ernzerhof (HSE) hybrid functional calculations. Due to

the high computational cost of HSE calculations, we are examining only the top 50 (of 187 materials) based on their predicted work functions, and have currently finished 25 of these top 50 candidates, with 4 of them giving band gaps < 0.5 eV. The fourth and last screening step is to directly calculate the (001) AO-terminated work function at the HSE level to assess whether the perovskite has a low work function surface. Although this step is still in progress, we have already discovered $BaMoO_3$ as a promising candidate with a low work function of 1.06 eV. $BaMoO_3$ has been synthesized experimentally and confirmed to be conductive.[5] The calculated properties of $BaMoO_3$ and also $SrVO_3$ are summarized in **Table 1**.

Table 1. Predicted properties of $BaMoO_3$ comparing with that of $SrVO_3$.

	$SrVO_3$	**$BaMoO_3$**
AO work function	1.86 eV	1.06 eV
HSE band gap	/	0.38 eV
E_{hull}	41.9 meV/atom	26.4 meV/atom
d electron number	1	2

To better understand the physics controlling perovskite work functions we analyzed the predicted work functions of the 2935 perovskites with the data being grouped according to the number of *d*-band electrons. From the distribution of the work functions in different groups, we found trends that for perovskites with empty *d*-band (with 0 *d* electron), the predicted work functions are highest and are distributed around 3.5 eV. For perovskites with low *d*-band filling (between 0 and up to and including 2), the work functions are the lowest, while materials with more *d* electrons (greater than 2 and up to and including 10), the work functions also tend to be high and peak between 3-3.5 eV. Such trends are in agreement with the electronic structure and bonding trends discussed in the work of Jacobs et al.[2], who described the interplay of bonding ionicity, O *p*-band center position, and the resulting work function value for different types of perovskites.

Overall, this work provides recommendations for new perovskite materials to investigate experimentally as potentially novel thermionic emission materials and offers understanding of key electronic properties which set the work function in perovskite materials.

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References

1. S. Gilmour, Principles of Traveling Wave Tubes. Boston: Artech House, 1994.
2. R. Jacobs, J. Booske, and D. Morgan, "Understanding and Controlling the Work Function of Perovskite Oxides Using Density Functional Theory," Adv. Funct. Mater., vol. 26, no. 30, pp. 5471–5482, 2016.
3. Z. Zhong and P. Hansmann, "Tuning the work function in transition metal oxides and their heterostructures," Phys. Rev. B, vol. 93, p. 235116, 2016.
4. R. Jacobs et al., "Perovskite electron emitters: Computational prediction and preliminary experimental assessment of novel low work function cathodes," in 2018 IEEE International Vacuum Electronics Conference, IVEC 2018, 2018, pp. 37–38.
5. K. Kurosaki, T. Oyama, H. Muta, M. Uno, and S. Yamanaka, "Thermoelectric properties of perovskite type barium molybdate," J. Alloys Compd., vol. 372, pp. 65–69, 2004.