First-principles Exploration of Thermodynamically Stable Cs–O Compounds

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Abstract

We performed global structure searches of Cs–O compounds with different stoichiometries (CsO, Cs_2O, and Cs_3O). For each composition, 4~6 (meta)stable structures were identified in the energy range of 100 meV/atom from the lowest energy configurations, which reflects the complicated phases of Cs–O beyond those in the literature. Our first-principles calculations unravel the correlation between the structures' stoichiometries and symmetries and the resulting electronic structures, such as band structure and work functions. In the case of Cs_3O, new structural phases which can be considered as 1D electrides were identified.

Introduction

Cesium oxides have been used as surface coating and interfacial layer substances to improve the performance of photocathodes[1-5], thermionic energy converters[6-7], light-emitting devices[8], and solar cells[9]. The reason why cesium oxides began to attract attention as a surface coating material is due to its low work function and its effect on electronic devices. For example, in the case of semiconductor photocathodes, the cesium oxides coating on the photocathode substrate forms a heterojunction and lowers a work function by deriving band bending even resulting in negative electron affinity[3,10]. However, despite the successful application of cesium oxides coating to multiple devices, experimental characterization of cesium oxides has been limited because cesium oxide compounds (Cs_xO_y) exist in many different stoichiometries with high chemical sensitivity[11-13]. Therefore, it remains a challenge to understand from experimental data their structural properties and resultant electronic properties. In this study, global structure searches of thermodynamically stable structures of Cs-O compound with different stoichiometries (CsO, Cs_2O, and Cs_3O) were performed by applying PSO (particle swarm optimization) algorithm coupled with first-principles total energies. After identifying metastable structures for each composition, first-principles density functional theory calculations were performed to understand underlying electronic structures of identified structures.

Computational Approach

In order to identify not only a globally optimized structure but also locally optimized metastable structures PSO algorithm implemented in CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) software was utilized. After identifying metastable structures, additional first-principles calculations were performed to compare their formation energies and other electronic structures such as band structure and work functions. Superlattice surface slabs were generated to calculate work functions. For all first-principles calculations, the projector augmented wave pseudopotential[15] and the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional[16] implemented in VASP[17] code were employed and non-spin polarized calculations were performed.

Results and discussion

Fig. 1 shows formation energies of identified structures for each composition and their structural symmetry space groups. The formation energy is the change of energy during the formation of a single formula unit of substance from its constituent elements and it can be used to compare relative stability. For cesium oxides, the formation energy per atom was calculated using the following expression:

$$\Delta E_f = \frac{\left[E(\mathrm{Cs}_x\mathrm{O}_y) - \left\{ x \cdot \frac{E(\mathrm{Cs})_{\mathrm{bcc}}}{2} + y \cdot \frac{E(\mathrm{O}_2)}{2} \right\} \right]}{(x+y)}$$

In the case of Cs_3O and Cs_2O, experimentally known structures were found to be the most stable structures, while in CsO, more stable structures ($P2_1/c$ and $C2/m$) were found.

a)

Composition	Formation energy (eV)	Space group
Cs_3O	-0.755	$P2_1/m$
	-0.765	$Pmc2_1$
	-0.772	R-3
	-0.775	$Cmc2_1$
	-0.792	$P6_3/mcm$
Cs_2O	-0.925	Pnnm
	-0.951	Pmmn
	-0.988	Fd-3m
	-0.992	C2/m
	-0.992	R-3m
CsO	-0.939	Amm2
	-0.970	$P2_1/c$
	-1.019	Immm
	-1.021	C2/m
	-1.031	$P2_1/c$

b)

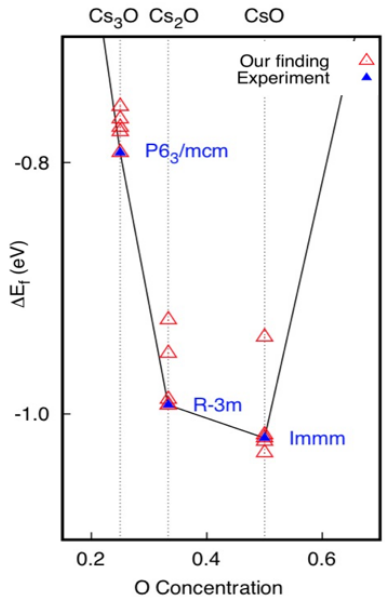

Figure 1. a) Formation energies and space groups of the identified structures. b) Convex-hull phase diagram. Blue color is indicating experimentally synthesized structures and the solid line in the convex-hull diagram was drawn by connecting the structures which were experimentally synthesized in literature.

Fig. 2 shows band structures of the most stable structures for each composition. As oxygen concentration increases, band gap opens and widens, and high band dispersion of conduction band is governed by metallic Cs states.

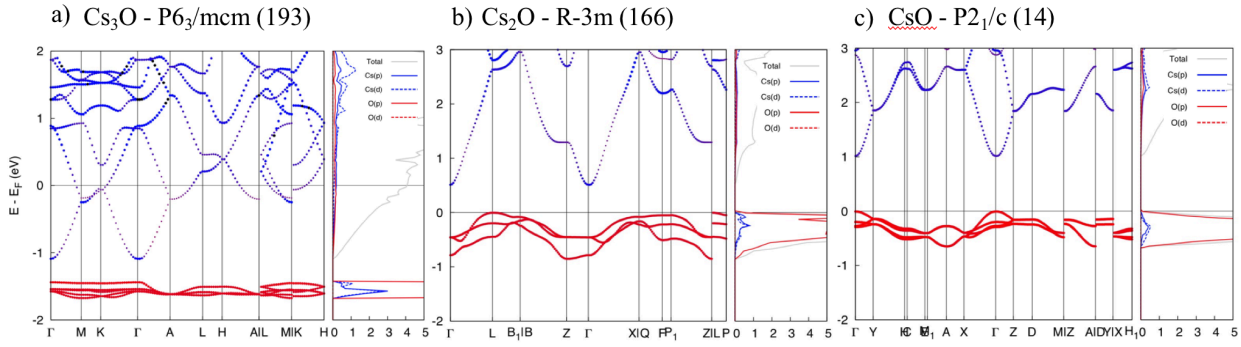

Figure 2. Band structures of the most stable structures of Cs_3O, Cs_2O, and CsO. The contributions from the Cs and O atoms are shown in blue and red, respectively.

Work functions of the identified structures were calculated and plotted in Fig. 3. The work function tends to decrease with increasing oxygen concentration and reaches almost 1.0 eV. This trend is in good agreement with the experimental measurements[18]. It should be noted that the minimum work function that appears in CsO composition corresponds to the newly discovered structure in this study.

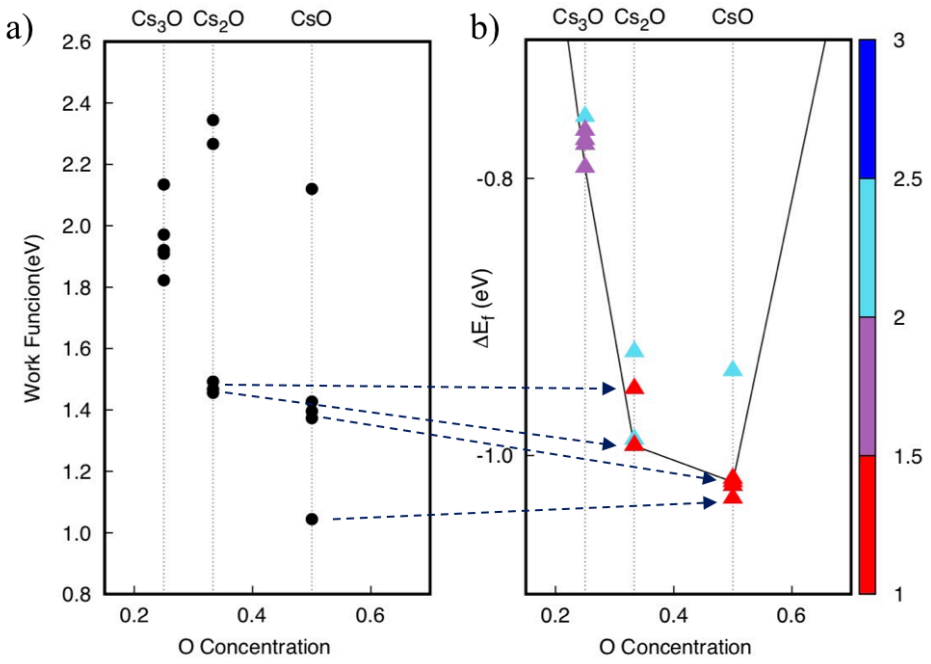

Figure 3. a) Calculated work functions of identified structures. Each point corresponds to each identified structure. b) Convex-hull phase diagram which is coupled with work functions. The color palette represents the work function.

Another interesting finding in this study is that the metastable structures of Cs_3O show similar crystal and electronic structures to the most stable structure which was experimentally reported and recently identified as 1D electride with non-trivial band topology[19]. These 1D electrides show accumulated charge distributions in the vacant space and those charge distributions comes from the anionic electrons in between 1D building blocks.

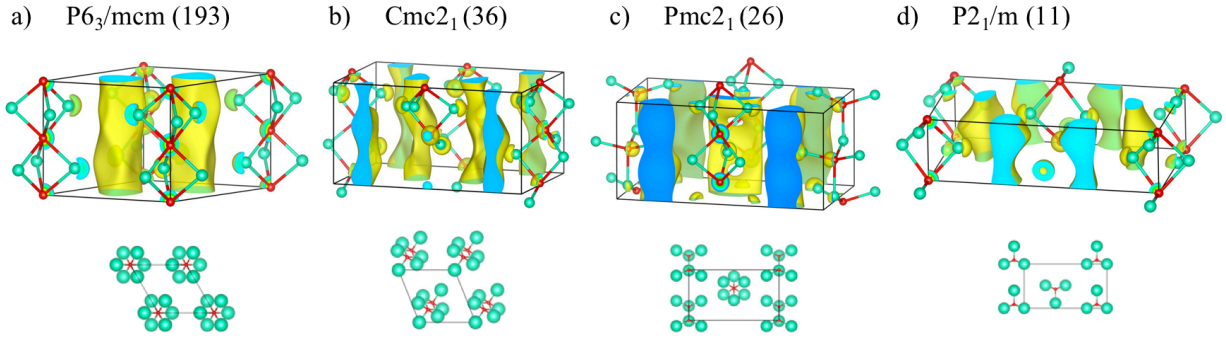

Figure 4. Partial charge density near the fermi-level. This charge density shows distribution of anionic electrons in the vacant space along the z-axis. a) The most stable structure. b-d) Metastable structures.

Conclusion

Four metastable structures were identified near the most stable structure of cesium oxides (CsO, Cs2O, Cs3O) using a global optimization algorithm combined with the first principles energies. More stable structures than experimentally synthesized one were discovered for CsO and it turned out that the newly found structures is crucial for reproducing experimental measurement of work functions. In the case of Cs_3O, new structural phases that can be regarded as 1D electrides were identified from the metastable structures, suggesting a new possibility of electride synthesis.

References

[1] L. R. Koller, *Phys. Rev.* **36**, 1639 (1930).
[2] A. A. Turnbull and G. B. Evans *J. Phys. D: Appl. Phys.* **1**, 155 (1968).
[3] J. J. Uebbing and L. W. James, *J. Appl. Phys.* **41**, 4505 (1970).
[4] M. G. Clark, *J. Phys. D: Appl. Phys.* **8**, 535 (1975).
[5] C. Y. Su, W. E. Spicer, and I. Lindau, *J. Appl. Phys.* **54**, 1413 (1998).
[6] V. Giorgis, F. Morini, T. Zhu, J. F. Robillard, X. Wallart, J. L. Codron, and E. Dubois, *J. Appl. Phys.* **120**, 205108 (2016).
[7] S. Kim, M. Lee, S. Lee, and S. Jhi, *J. Phys.: Condens. Matter* **29**, 315702 (2017).
[8] M.-H. Chen and C.-I. Wu, *J. Appl. Phys.* **104**, 113713 (2008).
[9] A. Hoff, I. Cruz-Cruz, M. C. Siqueira, K. D. Machado, and I. A. Hümmelgen, *Solar Energy Materials and Solar Cells* **171**, 1 (2017).
[10] M. G. Clark, *J. Phys. D: Appl. Phys.* **8**, 535 (1975).
[11] C. Y. Su, I. Lindau, and W. E. Spicer, *Chemical Physics Letters* **87**, 523 (1982).
[12] A. Band, A. Albu-Yaron, T. Livneh, H. Cohen, Y. Feldman, L. Shimon, R. Popovitz-Biro, V. Lyahovitskaya, and R. Tenne, **108**, 12360 (2004).
[13] S. Gemming, G. Seifert, C. Muhle, M. Jansen, A. Albu-Yaron, T. Arad, and R. Tenne, *Journal of Solid State Chemistry* **178**, 1190 (2005).
[14] Y. Wang, J. Lv, L. Zhu, and Y. Ma, *Phys. Rev. B* **82**, 094116 (2010).
[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[16] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
[17] G. Kresse and J. Furthmüller, *Computational Materials Science* **6**, 15 (1996).
[18] B. Woratschek, W. Sesselmann, J. Küppers, G. Ertl, and H. Haberland, *The Journal of Chemical Physics* **86**, 2411 (1987).
[19] C. Park, S. W. Kim, and M. Yoon, *Phys. Rev. Lett.* **120**, 026401 (2018).