Determination of adsorption-controlled growth windows of chalcogenide perovskites

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

Citation
Filippone, Stephen A. et al. "Determination of adsorption-controlled growth windows of chalcogenide perovskites." MRS Communications 8, 1 (March 2018): 145-151 © 2018 Materials Research Society

As Published
http://dx.doi.org/10.1557/mrc.2018.10

Publisher
Cambridge University Press [CUP]

Version
Author’s final manuscript

Citable link
https://hdl.handle.net/1721.1/126213

Terms of Use
Creative Commons Attribution-Noncommercial-Share Alike

Detailed Terms
http://creativecommons.org/licenses/by-nc-sa/4.0/
Determination of Adsorption-Controlled Growth Windows of Chalcogenide Perovskites
Stephen A. Filippone¹, Yi-Yang Sun², R. Jaramillo¹*

1. Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA

2. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China

* rjaramil@mit.edu

ABSTRACT

Ternary sulfides and selenides in the distorted-perovskite structure (“chalcogenide perovskites”) are predicted by theory to be semiconductors with band gap in the visible-to-infrared and may be useful for optical, electronic, and energy conversion technologies. Here we use computational thermodynamics to predict the pressure-temperature phase diagrams for select chalcogenide perovskites. Our calculations incorporate formation energies calculated by density functional theory, and empirical estimates of heat capacities. We highlight the windows of thermodynamic equilibrium between solid chalcogenide perovskites and the vapor phase at high temperature and very low pressure. These results can guide adsorption-limited growth of ternary chalcogenides by molecular beam epitaxy (MBE).

INTRODUCTION

In the long history of research on oxides in the distorted-perovskite (henceforth simply called “perovskite”) structure with corner-sharing BO₆ octahedra, cation alloying and substitution has been a primary means of controlling material properties¹⁻⁶. By contrast, anion alloying and substitution has been little studied. The smaller electronegativity of chalcogen elements such as sulfur or selenium relative to oxygen suggests that substituting chalcogens for oxygen in the perovskite structure may lower the band gap. This expectation is supported out by recent results. For example, experiments show that the band gap for BaZrCh₃ in the perovskite structure decreases from 3.55 eV for Ch = O, to 1.83 eV for Ch = S⁷⁻⁸. Theory predicts that the band gap of ferroelectric PbTiO₃₋ₓSₓ decreases rapidly from 4.1 eV for x = 0, to 2.6 eV for x = 1⁹. With increasing chalcogen content, many AB(O,S,Se)₃ materials in the corner-sharing, perovskite structure become unstable relative to edge- and face-sharing structures with lower symmetry¹⁰⁻¹³. Nevertheless, bulk powder samples of chalcogenide perovskites have been synthesized and studied since the early 1950s¹¹,¹²,¹⁴⁻¹⁶. Recently there has been renewed interest in these materials as semiconductors, stimulated by theoretical predictions of ferroelectricity and promising photovoltaic properties⁹,¹⁷⁻²². An important next step in evaluating chalcogenide perovskites for their usefulness in electronics and energy conversion is to grow single crystal or large-grained thin films.
Molecular beam epitaxy (MBE) offers a high degree of control over phase, morphology, and defects, and for decades has been an indispensable technique for the study of perovskite and other complex-structured oxides. MBE (and its antecedent, the “three-temperature” technique) was originally developed to make films of III-V materials, taking advantage of the existence of thermodynamic equilibrium at high temperature and high vacuum between the desired solid film and the vapor phase. This thermodynamic growth window enables so-called adsorption-limited growth, wherein the growth chamber is supplied with an overpressure of one constituent (e.g. As), and the film grows at a rate determined by the supply of the other constituent (e.g. Ga). There are two primary conditions for adsorption-limited growth: that one constituent have high vapor pressure, and that the desired phase is a line compound. When these conditions are met, then single-phase films can be reliably grown over a range of source rates, greatly simplifying the growth procedure.

Adsorption-limited growth is not possible for most oxide perovskites due to the low vapor pressure of the constituent binary oxides: the thermodynamic growth window is usually located at very high temperature, and at pressure much lower than is achievable by even the best vacuum deposition chambers. As a result, extremely fine source rate control is required to avoid the formation of secondary phases. Stability of atomic fluxes is difficult to control, even with sophisticated monitoring and feedback control loops. Fluctuations in the molecular fluxes lead to off-stoichiometric films, the formation of unwanted secondary phases, and spatial non-uniformity. This challenge stimulated the development of metal-organic oxide MBE, in which one constituent is supplied using a molecular precursor with high vapor pressure. In analyzing the growth of ternary oxides, it is common to use pseudo-binary phase diagrams, as we do here for ternary chalcogenides. This assumes that all metals will spontaneously oxidize, which is a good assumption under conditions of MBE oxide growth.

Here we consider the possibility of adsorption-limited growth of select chalcogenide perovskites by MBE. The thermodynamic growth windows are largely determined by the vapor pressure of binary chalcogenide constituents, and by the thermodynamics of the desired perovskite phase. The vapor pressure of most binary chalcogenide materials is available in thermodynamic databases. Almost no thermodynamic data exists for the chalcogenide perovskites, so we rely on theoretical calculations and assumptions (described below). We find that adsorption-limited growth of chalcogenide perovskites $ABCh_3$ with $A = \text{Ba and Sr}$ and $B = \text{Hf, Zr, and Ti}$ may be possible with very high-performing MBE systems. The situation is more favorable for phases including main-group elements that form binary chalcogenides with high vapor pressure. To demonstrate this, we also calculate the growth window for $\text{ZnSnS}_3$ in the $\text{LiNbO}_3$ structure, which is unstable in the bulk but may be stabilized by epitaxy. We find favorable conditions for adsorption-limited growth on both the Zn- and Sn-rich sides of the quasi-binary phase diagram.

**METHODS**

We used the computational thermodynamics software package FactSage to compute phase diagrams. Thermodynamic data for most binary chalcogenides is available in the databases, but no such information exists for chalcogenide perovskites. In order to model these compounds, the heat capacity and the formation energy must be given. We estimated the heat capacity using the
Neumann-Kopp rule, implemented using the compound module and the mixer function in FactSage. The Neumann-Kopp rule is an empirical method for estimating the heat capacity of a compound\textsuperscript{28}, and has been successfully applied to mixed oxides\textsuperscript{29}. The general form is shown in Equation 1:

\[ C_{pm}(A_xB_{1-x}O_2) = x_AC_{pm}(AO) + x_BC_{pm}(BO) + \Delta C_{dil} \]

\( C_{pm} \) is the molar heat capacity of the compound. When applied to chalcogenide perovskites of the form \( ABO_3 \), the heat capacity is the sum of the heat capacity for the binary compounds: \( ACh \) and \( BCh_2 \). \( \Delta C_{dil} \) is a high temperature correction that we set to zero. The functional form of the heat capacity for each compound is shown in Table I and generally follows the form in Equation 2:

\[ C_p = \sum C_i(T/K)^{P_i} \]

The coefficients \( C_i \) are in units of J/K·mol, and the variables \( (T/K) \) are unitless. The formation energy of the \( ABO_3 \) chalcogenide perovskites relative to decomposition into the binary chalcogenides \( ACh \) and \( BCh_2 \) were calculated by density functional theory (DFT), and are listed in Table I. Of the 18 compounds studied by Sun \textit{et al.}, BaZrS\textsubscript{3}, BaHfS\textsubscript{3}, BaTiS\textsubscript{3}, BaZrSe\textsubscript{3}, SrZrS\textsubscript{3}, SrHfS\textsubscript{3}, and BaHfSe\textsubscript{3} are predicted to be stable relative to decomposition.\textsuperscript{18} Below we present the growth window for these compounds with the exception of BaHfSe\textsubscript{3}, which we cannot calculate because thermodynamic data is not available for HfSe\textsubscript{2}.

**RESULTS AND DISCUSSION**

\textbf{Figure 1} shows the calculated equilibrium phase diagram for the pseudo-binary BaS-ZrS\textsubscript{2} system as a function of temperature and overall composition at a fixed pressure of 7.5x10\textsuperscript{-6} torr. The BaZrS\textsubscript{3} line compound lies at a composition of 50:50 BaS:ZrS\textsubscript{2}. There is a region of two-phase equilibrium between solid BaZrS\textsubscript{3} and a Ba-rich vapor on the Ba-rich side of the phase diagram and in the approximate temperature range 1300 - 1500 °C: this is the thermodynamic growth window. This window is bounded at the bottom by a region of coexistence between BaZrS\textsubscript{3} and BaS solid phases. This is because at lower temperature, solid BaS condenses from the vapor phase, and therefore excess Ba will tend to condense into BaS. The growth window is bounded on the top by a region of coexistence between solid ZrS\textsubscript{2} and a Ba-rich vapor.

Although quasi-binary phase diagrams may better illustrate the materials science, a pressure-temperature phase diagram is often more useful to guide experiment. In \textbf{Figure 2} we show the pressure-temperature equilibrium phase diagrams for those chalcogenide perovskites that are predicted to be stable with respect to decomposition into binary chalcogenides (with the excepcion of BaHfSe\textsubscript{3} as described above).

From this we can determine which compounds have usable growth windows. To start, we look at the maximum pressure required to be just inside the growth window at a particular temperature. This upper pressure limit is determined by the vapor pressure of the more volatile binary compound, which is \( ACh \) for the \( ABO_3 \) materials described here. Using for example 1000 °C, BaZrS\textsubscript{3}, BaHfS\textsubscript{3}, SrHfH\textsubscript{3}, and ZrSrS\textsubscript{3} require a maximum pressure of about 10\textsuperscript{-9} torr for adsorption-limited growth. For BaZrSe\textsubscript{3}, the maximum pressure in the growth window is 10\textsuperscript{-7} torr. BaTiS\textsubscript{3}
does not form until about $10^{-12}$ torr at approximately 800 °C. The case of BaTiS$_3$ can be explained by the existence of a more stable solid phase, TiS. The takeaway from Figure 2 is that, for these materials, adsorption-limited growth may be possible in certain cases, but would require an extraordinary growth chamber with a very high temperature sample stage and an excellent vacuum.

The size of the growth window is another concern. It is difficult to maintain an adsorption-limited process if the window is too small in the pressure or the temperature dimension. The BaZrS$_3$, BaHfS$_3$, BaZrSe$_3$, and SrHfS$_3$ have growth windows that span at least one order of magnitude in pressure. SrZrS$_3$ is more challenging, with a growth window that spans approximately a factor of three in pressure. BaTiS$_3$ has a vanishingly narrow growth window that spans +/- 3% of the pressure range at around $10^{-14}$ torr.

A number of $ABCh_3$ materials are predicted to be thermodynamically unstable with respect to decomposition into binaries. Materials with positive formation energy will not appear on an equilibrium phase diagram. However, it is still interesting to consider adsorption-limited growth for these materials, because it may be possible to make films using kinetic control or epitaxial stabilization. The high-pressure side of the growth window is determined by the binary compound with the higher vapor pressure. Therefore, by plotting the vapor pressure of $ACH$ materials, we anticipate the growth window for $ABCh_3$ materials that are unstable in the bulk. In Figure 3 we plot these binary vapor pressure curves for CaS, BaS, SrS, BaSe, SrSe, and CaSe. The selenides have higher vapor pressure than the sulfides, which means that adsorption-limited growth windows will be easier to achieve for $ABSe_3$ than for $ABS_3$. Figure 3 is also a guide to the growth window for BaHfSe$_3$. This material is predicted to be thermodynamically stable, with a formation energy of -0.447 eV/f.u. Standard thermodynamic data for HfSe$_2$ is not available, so we do not present an equilibrium phase diagram as in Figure 2. However, the high-pressure side of the BaHfSe$_3$ growth window is predicted by the vapor pressure of binary BaSe.

From the above, it is clear the $ABCh_3$ materials with $A =$ alkaline earth and $B =$ refractory transition metal will be challenging to grow in adsorption-limited mode with the capabilities of typical MBE chambers. The situation becomes more favorable when we consider different regions of the periodic table. We take for example ZnSnS$_3$ in the LiNbO$_3$-type structure, which is predicted to be unstable in the bulk, but stable if grown epitaxially on GaN (100)$^{19}$. Due to the relatively high vapor pressures of both ZnS and SnS$_2$, adsorption-limited growth is possible on both the Zn- and Sn-rich side of the quasi-binary phase diagram. In Figure 4 we show the growth windows for Zn-rich conditions (Fig. 4a) and Sn-rich conditions (Fig. 4b). We conclude that growth in Sn-rich conditions is preferable to Zn-rich conditions due to the larger size of its growth window, which results from the fact that the vapor pressure of SnS$_2$ is higher than that of ZnS. In both cases, the pressures and temperatures required for adsorption-limited growth are accessible for typical MBE chambers.

The accuracy of the phase diagrams presented is limited by the available thermodynamic data. We note that the errors introduced by estimating the formation energies and heat capacities of $ABCh_3$ compounds only affect the lower bound of the growth window. While it is important that the lower bound be sufficiently below the upper bound to create an experimentally accessible growth window, its exact position is less important. In general, errors in the formation energies (those that we calculate and those that are contained in the FactSage databases) have impact on the resulting
phase diagrams that is faster than linear, due to the exponential dependence of vapor pressure on formation enthalpy. We estimate that our DFT-calculated formation energies are accurate to within +/- 5%, based on prior comparisons between PBEsol calculations and experimental data\textsuperscript{30}. In Figure 2a we show the effect of a +/- 5% error in the formation energy on the BaZrS\textsubscript{3} phase diagram, see the red lines. The effect on the predicted growth window is negligible, especially for materials like BaZrS\textsubscript{3} which have large growth windows.

The high temperature deviations from of heat capacity from the Neumann-Kopp rule are given by $\Delta C_{dil}$. For the oxides BaZrO\textsubscript{3} and SrZrO\textsubscript{3}, $\Delta C_{dil}/T$ is 1.05x10\textsuperscript{-4} and 6.81x10\textsuperscript{-3}, respectively\textsuperscript{29}. Table 1 shows that the linear heat capacity terms range from approximately 5x10\textsuperscript{-3} to 2x10\textsuperscript{-2}. Assuming that $\Delta C_{dil}$ is comparable for oxide and chalcogenide perovskites allows us to estimate the effect of neglecting $\Delta C_{dil}$ on our calculated phase diagrams. Using $\Delta C_{dil}$ for SrZrO\textsubscript{3} as an upper bound, the max possible error in the linear heat capacity term for materials we investigated is 80% for SrHfS\textsubscript{3}. However, because of the way this error propagates, its effect on the formation enthalpy is much smaller than the +/- 5% uncertainty of our DFT calculations even in the case of SrHfS\textsubscript{3}, for which the error is the greatest. Therefore, conclude that using the Neumann-Kopp rule and neglecting $\Delta C_{dil}$ has a negligible effect on our calculated phase diagrams.

CONCLUSION

We calculate the growth windows for adsorption-limited growth of ternary sulfides and selenides in the distorted-perovskite structure. In many cases, the window for thermodynamic growth of pure-phase $ABCh_3$ solid films lies at high temperature and low pressure (e.g. $T > 1000$ °C and $P < 10^{-9}$ torr) that are challenging for most MBE chambers. The growth window for selenides is more accessible than that for sulfides, and our results suggest that adsorption-limited growth may be achieved for $ABSe_3$ with $A =$ Ca, Sr, and Ba. The growth window becomes much more accessible for materials for which the quasi-binary phase diagram includes including a compound (e.g. $ACh$ or $BCh_2$) with high vapor pressure. We illustrate this case for ZnSnS\textsubscript{3} in the LiNbO\textsubscript{3}-structure\textsuperscript{19}. Other examples may include chalcogenide perovskites with Sn, Ge or Te on the B-site\textsuperscript{22}.

ACKNOWLEDGEMENTS

Stephen A. Filippone acknowledges support from the National Science Foundation Graduate Research Fellowship under Grant No. 1122374. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors(s) and do not necessarily reflect the views of the National Science Foundation. Y.-Y. S. acknowledges support from National Natural Science Foundation of China under Grant No. 11774365. This project was funded in part by the MIT Skoltech Seed Fund, as part of the MIT Skoltech Program.
REFERENCES

1. Nechache, R., Harnagea, C., Li, S., Cardenas, L., Huang, W., Chakrabartty, J. & Rosei, F. Bandgap tuning of multiferroic oxide solar cells. *Nat. Photonics* **9**, 61–67 (2015).

2. Grinberg, I., West, D. V., Torres, M., Gou, G., Stein, D. M., Wu, L., Chen, G., Gallo, E. M., Akbashev, A. R., Davies, P. K., Spanier, J. E. & Rappe, A. M. Perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials. *Nature* **503**, 509–512 (2013).

3. Berger, R. F. & Neaton, J. B. Computational design of low-band-gap double perovskites. *Phys. Rev. B* **86**, 165211 (2012).

4. Choi, W. S., Chisholm, M. F., Singh, D. J., Choi, T., Jr, G. E. J. & Lee, H. N. Wide bandgap tunability in complex transition metal oxides by site-specific substitution. *Nat. Commun.* **3**, ncomms1690 (2012).

5. Gou, G. Y., Bennett, J. W., Takenaka, H. & Rappe, A. M. Post density functional theoretical studies of highly polar semiconductive Pb(Ti$\{1-x\}$Ni$_x$O$_3$ solid solutions: Effects of cation arrangement on band gap. *Phys. Rev. B* **83**, 205115 (2011).

6. Xu, X. S., Ihlefeld, J. F., Lee, J. H., Ezekoye, O. K., Vlahos, E., Ramesh, R., Gopalan, V., Pan, X. Q., Schlom, D. G. & Musfeldt, J. L. Tunable band gap in Bi(Fe$_{1-x}$Mn$_x$)O$_3$ films. *Appl. Phys. Lett.* **96**, 192901 (2010).

7. Parida, S., Satapathy, A., Sinha, E., Bison, A. & Rout, S. K. Effect of Neodymium on Optical Bandgap and Microwave Dielectric Properties of Barium Zirconate Ceramic. *Metall. Mater. Trans. A* **46**, 1277–1286 (2015).
8. Niu, S., Huyan, H., Liu, Y., Yeung, M., Ye, K., Blankemeier, L., Orvis, T., Sarkar, D., Singh, D. J., Kapadia, R. & Ravichandran, J. Bandgap Control via Structural and Chemical Tuning of Transition Metal Perovskite Chalcogenides. *Adv. Mater.* **29**, 1604733 (2017).

9. Brehm, J. A., Takenaka, H., Lee, C.-W., Grinberg, I., Bennett, J. W., Schoenberg, M. R. & Rappe, A. M. Density functional theory study of hypothetical PbTiO3-based oxysulfides. *Phys. Rev. B* **89**, 195202 (2014).

10. Perera, S., Hui, H., Zhao, C., Xue, H., Sun, F., Deng, C., Gross, N., Milleville, C., Xu, X., Watson, D. F., Weinstein, B., Sun, Y.-Y., Zhang, S. & Zeng, H. Chalcogenide perovskites – an emerging class of ionic semiconductors. *Nano Energy* **22**, 129–135 (2016).

11. Meetsma, A., Wiegers, G. A. & de Boer, J. L. Structure determination of SnZrS3. *Acta Crystallogr.* **C 49**, 2060–2062 (1993).

12. Clearfield, A. The synthesis and crystal structures of some alkaline earth titanium and zirconium sulfides. *Acta Crystallogr.* **16**, 135–142 (1963).

13. Lee, C.-S., Kleinke, K. M. & Kleinke, H. Synthesis, structure, and electronic and physical properties of the two SrZrS3 modifications. *Solid State Sci.* **7**, 1049–1054 (2005).

14. Hahn, H. & Mutschke, U. Untersuchungen über ternäre Chalkogenide. XI. Versuche zur Darstellung von Thioperowskiten. *Z. Für Anorg. Allg. Chem.* **288**, 269–278 (1957).

15. Schmidt, L. Superconductivity in PbNbS3 and PbTaS3. *Phys. Lett. A* **31**, 551–552 (1970).

16. Lelieveld, R. & IJdo, D. J. W. Sulphides with the GdFeO3 structure. *Acta Crystallogr. Sect. B* **36**, 2223–2226 (1980).

17. Bennett, J. W., Grinberg, I. & Rappe, A. M. Effect of substituting of S for O: The sulfide perovskite BaZrS3 investigated with density functional theory. *Phys. Rev. B* **79**, 235115 (2009).
18. Sun, Y.-Y., Agiorgousis, M. L., Zhang, P. & Zhang, S. Chalcogenide Perovskites for Photovoltaics. *Nano Lett.* **15**, 581–585 (2015).

19. Kolb, B. & Kolpak, A. M. First-Principles Design and Analysis of an Efficient, Pb-Free Ferroelectric Photovoltaic Absorber Derived from ZnSnO3. *Chem. Mater.* **27**, 5899–5906 (2015).

20. Meng, W., Saparov, B., Hong, F., Wang, J., Mitzi, D. B. & Yan, Y. Alloying and Defect Control within Chalcogenide Perovskites for Optimized Photovoltaic Application. *Chem. Mater.* **28**, 821–829 (2016).

21. Wang, H., Gou, G. & Li, J. Ruddlesden–Popper perovskite sulfides A3B2S7: A new family of ferroelectric photovoltaic materials for the visible spectrum. *Nano Energy* **22**, 507–513 (2016).

22. Ju, M.-G., Dai, J., Ma, L. & Zeng, X. C. Perovskite Chalcogenides with Optimal Bandgap and Desired Optical Absorption for Photovoltaic Devices. *Adv. Energy Mater.* **7**, 1700216 (2017).

23. Tsao, J. Y. *Materials fundamentals of molecular beam epitaxy*. (Boston : Academic Press, c1993., 1993).

24. Henini, M. *Molecular beam epitaxy : from research to mass production*. (Amsterdam : Elsevier, [2013], 2013).

25. Theis, C. D., Yeh, J., Schlom, D. G., Hawley, M. E. & Brown, G. W. Adsorption-controlled growth of PbTiO3 by reactive molecular beam epitaxy. *Thin Solid Films* **325**, 107–114 (1998).

26. Haislmaier, R. C., Stone, G., Alem, N. & Engel-Herbert, R. Creating Ruddlesden-Popper phases by hybrid molecular beam epitaxy. *Appl. Phys. Lett.* **109**, 043102 (2016).
27. Bale, C. W., Bélisle, E., Chartrand, P., Decterov, S. A., Eriksson, G., Gheribi, A. E., Hack, K., Jung, I.-H., Kang, Y.-B., Melançon, J., Pelton, A. D., Petersen, S., Robelin, C., Sangster, J. & Van Ende, M.-A. FactSage Thermochemical Software and Databases. (2010).

28. Kopp, H. Investigations of the Specific Heat of Solid Bodies. *Philos. Trans. R. Soc. Lond.* **155**, 71–202 (1865).

29. Leitner, J., Voňka, P., Sedmidubský, D. & Svoboda, P. Application of Neumann–Kopp rule for the estimation of heat capacity of mixed oxides. *Thermochim. Acta* **497**, 7–13 (2010).

30. Csonka, G. I., Perdew, J. P., Ruzsinszky, A., Philipsen, P. H. T., Lebègue, S., Paier, J., Vydrov, O. A. & Ángyán, J. G. Assessing the performance of recent density functionals for bulk solids. *Phys. Rev. B* **79**, 155107 (2009).
**FIG. 1:** Composition-temperature equilibrium phase diagram for the pseudo-binary BaS - ZrS$_2$ system at a pressure of 7.5x10$^{-6}$ torr. The thermodynamic growth window for BaZrS$_3$ is the Ba-rich side of the phase diagram.

**FIG. 2:** Temperature-pressure phase diagrams for six of chalcogenide perovskites that are calculated to be thermodynamically stable relative to decomposition into binary chalcogenides. The fixed composition in each case is a mole fraction of 0.6 of the ACh component. In each case, the thermodynamic growth window is labeled “ABCh$_3$ + vapor”, for variable elements A, B, and Ch. Plots are ordered by the formation energy of the ternary phase from the binaries, from most to least stable. a) BaS-ZrS$_2$, b) BaS-HfS$_2$, c) BaS-TiS$_2$, d) BaSe-ZrSe$_2$, e) SrS-HfS$_2$, f) SrS-ZrS$_2$. The additional red lines in a) show how the phase diagram would be changed by a +/-5% error in the formation energy of BaZrS$_3$.

**FIG. 3:** Vapor pressure of the ACh binaries associated with ABCh$_3$ compounds of interest. These curves can be used to estimate the upper bound of the growth window for compounds which are not thermodynamically stable.

**FIG. 4:** Pressure-temperature equilibrium phase diagrams for the ZnS-SnS$_2$ system. Growth windows are available on both Zn-rich and Sn-rich sides of the phase diagram. a) Zn-rich side of the phase diagram with SnS$_2$ mole fraction of 0.4. b) Sn-rich side of the phase diagram with SnS$_2$ mole fraction of 0.6.
Table I. Heat capacity (J/mol K) and formation energy for each chalcogenide perovskite material. The heat capacity values are presented using the functional form in Equation 2, and the table entries are the coefficients $C_i$. The formation energy from the binary chalcogenides in units of eV/formula unit is listed below each compound formula (blue fields).

| Compound | $T=298$ | $T=300-1823K$ | $T=1823-3000K$ |
|----------|---------|----------------|-----------------|
| BaZrS$_3$ | $P=0$ | 1.42E+02 | 1.69E+02 |
|          | $P=0.5$ | -6.24E-01 | -6.24E-01 |
|          | $P=1$ | 2.75E-02 | 1.24E-02 |
|          | $P=-0.5$ | -4.38E+02 | -4.38E+02 |
|          | $P=-1$ | 1.26E+03 | 1.26E+03 |
| BaHfS$_3$ | $P=0$ | 1.52E+02 | |
|          | $P=0.5$ | -6.24E-01 | |
|          | $P=1$ | 1.24E-02 | |
|          | $P=-0.5$ | -4.38E+02 | |
|          | $P=-1$ | 1.26E+03 | |
| BaTiS$_3$ | $P=0$ | 1.11E+02 | 1.40E+02 | 1.62E+02 |
|          | $P=0.5$ | -6.24E-01 | -6.24E-01 | -6.24E-01 |
|          | $P=1$ | 1.27E-01 | 3.99E-02 | 1.24E-02 |
|          | $P=-0.5$ | -4.38E+02 | -4.38E+02 | -4.38E+02 |
|          | $P=-1$ | 1.26E+03 | 1.26E+03 | 1.26E+03 |
| BaZrSe$_3$ | $P=0$ | 1.31E+02 | |
|          | $P=0.5$ | |
|          | $P=1$ | |
|          | $P=-0.5$ | |
|          | $P=-1$ | |
| SrZnS$_3$ | $P=0$ | 1.39E+02 | 1.14E+02 | 1.42E+02 |
|          | $P=1$ | 6.77E-03 | 2.05E-02 | 5.40E-03 |
|          | $P=-1$ | -1.25E+04 | 2.21E+03 | 2.21E+03 |
|          | $P=-2$ | 1.66E+06 | -1.37E+06 | -1.37E+06 |
| SrHfS$_3$ | $P=0$ | 1.49E+02 | 1.49E+02 | 1.24E+02 |
|          | $P=1$ | 8.29E-03 | 8.29E-03 | 5.40E-03 |
|          | $P=-1$ | -1.25E+04 | -1.25E+04 | 2.21E+03 |
|          | $P=-2$ | 1.66E+06 | 1.66E+06 | -1.37E+06 |
| SnZnS$_3$ | $P=0$ | 1.14E+02 | 1.23E+02 | |
|          | $P=1$ | 2.20E-02 | 1.76E-02 | |
|          | $P=-2$ | -4.35E+05 | |