Determination of Adsorption-Controlled Growth Windows of Chalcogenide Perovskites

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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 BO_6 octahedra, cation alloying and substitution has been a primary means of controlling material properties[1–6]. 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 $BaZrCh_3$ in the perovskite structure decreases from 3.55 eV for Ch = O, to 1.83 eV for Ch = S[7,8]. Theory predicts that the band gap of ferroelectric $PbTiO_{3-x}S_x$ decreases rapidly from 4.1 eV for $x = 0$, to 2.6 eV for $x = 1$[9]. 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 symmetry[10–13]. Nevertheless, bulk powder samples of chalcogenide perovskites have been synthesized and studied since the early 1950s[11,12,14–16]. Recently there has been renewed interest in these materials as semiconductors, stimulated by theoretical predictions of ferroelectricity and promising photovoltaic properties[9,17–22]. 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[23]. 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[24–26]. 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 = Ba and Sr and B = 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 $ZnSnS_3$ in the $LiNbO_3$ structure, which is unstable in the bulk but may be stabilized by epitaxy[19]. 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[27] 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[28], and has been successfully applied to mixed oxides[29]. The general form is shown in **Equation 1**:

[1] $C_{pm}(A_{x_A}B_{x_B}O_z) = x_A C_{pm}(\mathrm{A}O_a) + x_B C_{pm}(\mathrm{B}O_b) + \Delta C_{dil}$

C_{pm} is the molar heat capacity of the compound. When applied to chalcogenide perovskites of the form $ABCh_3$, the heat capacity is the sum of the heat capacity for the binary compounds: ACh and BCh_2. ΔC_{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**:

[2] $C_p = \sum_i C_i (T/K)^{P_i}$

The coefficients C_i are in units of J/K·mol, and the variables (T/K) are unitless. The formation energy of the $ABCh_3$ 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 *et al.*, $BaZrS_3$, $BaHfS_3$, $BaTiS_3$, $BaZrSe_3$, $SrZrS_3$, $SrHfS_3$, and $BaHfSe_3$ are predicted to be stable relative to decomposition.[18] Below we present the growth window for these compounds with the exception of $BaHfSe_3$, which we cannot calculate because thermodynamic data is not available for $HfSe_2$.

RESULTS AND DISCUSSION

Figure 1 shows the calculated equilibrium phase diagram for the pseudo-binary BaS-ZrS_2 system as a function of temperature and overall composition at a fixed pressure of 7.5×10^{-6} torr. The $BaZrS_3$ line compound lies at a composition of 50:50 BaS:ZrS_2. There is a region of two-phase equilibrium between solid $BaZrS_3$ 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 $BaZrS_3$ 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 Zr_2S_3 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 **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 excepetion of $BaHfSe_3$ 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 $ABCh_3$ materials described here. Using for example 1000 °C, $BaZrS_3$, $BaHfS_3$, $SrHfH_3$, and $ZrSrS_3$ require a maximum pressure of about 10^{-9} torr for adsorption-limited growth. For $BaZrSe_3$, the maximum pressure in the growth window is 10^{-7} torr. $BaTiS_3$

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 -0.447eV/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[30]. In **Figure 2a** we show the effect of a +/- 5% error in the formation energy on the $BaZrS_3$ phase diagram, see the red lines. The effect on the predicted growth window is negligible, especially for materials like $BaZrS_3$ which have large growth windows.

The high temperature deviations from of heat capacity from the Neumann-Kopp rule are given by ΔC_{dil}. For the oxides $BaZrO_3$ and $SrZrO_3$, $\Delta C_{dil}/T$ is 1.05×10^{-4} and 6.81×10^{-3}, respectively[29]. **Table 1** shows that the linear heat capacity terms range from approximately 5×10^{-3} to 2×10^{-2}. Assuming that ΔC_{dil} is comparable for oxide and chalcogenide perovskites allows us to estimate the effect of neglecting ΔC_{dil} on our calculated phase diagrams. Using ΔC_{dil} for $SrZrO_3$ as an upper bound, the max possible error in the linear heat capacity term for materials we investigated is 80% for $SrHfS_3$. 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 $SrHfS_3$, for which the error is the greatest. Therefore, conclude that using the Neumann-Kopp rule and neglecting ΔC_{dil} has a negligible effect on our calculated phase diagrams.

Commented [RJ1]: Is this accurate?

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 $ZnSnS_3$ in the $LiNbO_3$-structure[19]. Other examples may include chalcogenide perovskites with Sn, Ge or Te on the B-site[22].

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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).

$BaZrS_3$		***T*=298- 1823K**	***T*=1823-3000K**	
-1.786	***P*$_i$=0**	1.42E+02	1.69E+02	
	***P*$_i$=0.5**	-6.24E-01	-6.24E-01	
	***P*$_i$=1**	2.75E-02	1.24E-02	
	***P*$_i$=-0.5**	-4.38E+02	-4.38E+02	
	***P*$_i$=-1**	1.26E+03	1.26E+03	
$BaHfS_3$		***T*=298-3000K**		
-1.756	***P*$_i$=0**	1.52E+02		
	***P*$_i$=0.5**	-6.24E-01		
	***P*$_i$=1**	1.24E-02		
	***P*$_i$=-0.5**	-4.38E+02		
	***P*$_i$=-1**	1.26E+03		
$BaTiS_3$		***T*=298- 420K**	***T*=420-1000K**	***T*=1000-3000K**
-0.691	***P*$_i$=0**	1.11E+02	1.40E+02	1.62E+02
	***P*$_i$=0.5**	-6.24E-01	-6.24E-01	-6.24E-01
	***P*$_i$=1**	1.27E-01	3.39E-02	1.24E-02
	***P*$_i$=-0.5**	-4.38E+02	-4.38E+02	-4.38E+02
	***P*$_i$=-1**	1.26E+03	1.26E+03	1.26E+03
$BaZrSe_3$		***T*=298- 310K**		
-0.513	***P*$_i$=0**	1.31E+02		
$SrZrS_3$		***T*=298-700K**	***T*=700-1823K**	***T*=1823-3000K**
-0.509	***P*$_i$=0**	1.39E+02	1.14E+02	1.42E+02
	***P*$_i$=1**	6.77E-03	2.05E-02	5.40E-03
	***P*$_i$=-1**	-1.25E+04	2.21E+03	2.21E+03
	***P*$_i$=-2**	1.66E+06	-1.37E+06	-1.37E+06
$SrHfS_3$		***T*=298-310K**	***T*=310-700K**	***T*=700-3000K**
-0.503	***P*$_i$=0**	1.49E+02	1.49E+02	1.24E+02
	***P*$_i$=1**	-8.29E-03	-8.29E-03	5.40E-03
	***P*$_i$=-1**	-1.25E+04	-1.25E+04	2.21E+03
	***P*$_i$=-2**	1.66E+06	1.66E+06	-1.37E+06
$SnZnS_3$		***T*=298-1995K**	***T*=1995-2000K**	
-2.18	***P*$_i$=0**	1.14E+02	1.23E+02	
	***P*$_i$=1**	2.20E-02	1.76E-02	
	***P*$_i$=-2**	-4.35E+05		