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Automated procedure to determine the thermodynamic stability of a material and the range of chemical potentials necessary for its formation relative to competing phases and compounds

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Abstract

We present a simple and fast algorithm to test the thermodynamic stability and determine the necessary chemical environment for the production of a multiterinary material, relative to competing phases and compounds formed from the constituent elements. If the material is found to be stable, the region of stability, in terms of the constituent elemental chemical potentials, is determined from the intersection points of hypersurfaces in an $(n - 1)$ -dimensional chemical potential space, where n is the number of atomic species in the material. The input required is the free energy of formation of the material itself, and that of all competing phases. Output consists of the result of the test of stability, the intersection points in the chemical potential space and the competing phase to which they relate, and, for two- and three-dimensional spaces, a file which may be used for visualization of the stability region. We specify the use of the program by applying it to a ternary and quaternary system. The algorithm automates essential analysis of the thermodynamic stability of a material. This analysis consists of a process which is lengthy for ternary materials, and becomes much more complicated when studying

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materials of four or more constituent elements, which are of increased interest in recent years for technological applications such as energy harvesting and optoelectronics. The algorithm will therefore be of great benefit to the theoretical and computational study of such materials.

Keywords: Thermodynamic stability, Chemical potential, Materials design, Defect formation analysis

PROGRAM SUMMARY

Manuscript Title: Automated procedure to determine the thermodynamic stability of a material and the range of chemical potentials necessary for its formation relative to competing phases and compounds

Authors: J. Buckeridge, D. O. Scanlon, A. Walsh, C. R. A. Catlow

Program Title: CPLAP

Journal Reference:

Catalogue identifier:

Licensing provisions: none

Programming language: FORTRAN 90

Computer: Any computer with a FORTRAN 90 compiler

Operating system: Any OS with a FORTRAN 90 compiler

RAM: 2 megabytes

Number of processors used: one

Keywords: Thermodynamic stability, chemical potential, materials design, defect formation analysis

Classification: 16.1 Structure and properties, 23 Statistical Physics and Thermodynamics

Nature of problem:

To test the thermodynamic stability of a material with respect to competing phases and standard states of the constituent atomic species and, if stable, determine the range of chemical potentials consistent with its synthesis.

Solution method:

Assume that the formation of the material of interest occurs, rather than that of competing phases and standard states of the constituent elemental species. From this assumption derive a series of conditions on the elemental chemical potentials. Convert these conditions to a system of m linear equations with n unknowns, where $m > n$. Solve all combinations of n linear equations, and test which solutions are compatible with the conditions on the chemical potentials. If none are, the system is unstable. Otherwise, the compatible results define boundary points of the stability region within the space spanned by the chemical potentials.

Restrictions:

33 The material growth environment is assumed to be in thermal and diffusive equi-
34 librium.

35 *Additional comments:*

36 For two- and three-dimensional spaces spanned by the chemical potentials, files
37 are produced for visualization of the stability region (if it exists).

38 *Running time:* Less than one second.

39

40 1. Introduction

41 Over the past few decades, there has been considerable growth in the
42 development of advanced materials for energy harvesting and transparent
43 electronics applications. [1, 2, 3, 4] At present, two of the greatest challenges
44 facing the optoelectronics industry are the production of stable and economi-
45 cally viable p -type materials, [5, 6] and the replacement of rare or inaccessible
46 components such as indium with more earth-abundant elements. [7, 8, 9, 10]
47 This has led to increased interest in more exotic materials, consisting of
48 ternary, [11, 12, 13] quaternary, [14, 15, 16] and quinary [17, 18, 19]
49 systems. These materials are also of increased interest for applications in
50 batteries [20] and solid state electrochemistry. [21] Having a large number of
51 elements in a compound offers a greater degree in chemical freedom, where
52 the tuning of properties of interest, such as band gaps, can be performed by
53 varying the composition.

54 Instrumental in this research is the theoretical prediction of material prop-
55 erties, using various computational approaches, *e.g.* density functional theory
56 (DFT) and methods based on interatomic potentials. [22] A key considera-
57 tion when predicting materials appropriate for particular applications is the
58 thermodynamical stability of the system, as stable materials present far fewer
59 technological challenges when incorporated into devices. [23, 24] It is of great
60 interest to predict the range of chemical potentials of the component elemen-
61 tal species over which the target phase is stable, rather than the elemental
62 species themselves or competing phases, as this gives an indication the chem-
63 ical environment necessary for the synthesis of that phase. Indeed, in order
64 to predict the stability of a material, one needs to compare its free energy
65 with that of all competing phases, including those consisting of subsets of
66 the elemental species in the material. [25] The standard procedure [25, 26]
67 is to calculate all relevant free energies at the athermal limit, under the
68 assumption of thermodynamic equilibrium. Assuming that the material is

thermodynamically stable, rather than the competing phases, leads to a set of conditions on the elemental chemical potentials, from which one can work out the stability range (if it exists). For binary systems, where the number of independent variables is one, the procedure is trivial. For ternary systems, though the calculation is still straightforward, if there are many competing phases, the exercise can become tedious. For quaternary or higher order systems, the calculation of the stability region becomes quite involved, as there are typically a large number of competing phases to consider, and three or more independent variables. It is evident that an automated process to perform these tasks would be of great benefit to theoreticians working on these problems.

Consideration of the chemical potential landscape within which a material forms is also crucial when predicting the nature and concentration of defects. The synthesis of a material in different conditions can mean that the formation of different defects becomes favorable. Calculations of defect formation energies, which depend on the chemical potentials, provide useful information to experimentalists wishing to produce a material with a particular defect-related property. For example, to produce a material with significant concentrations of a p -type donor incorporated during the growth process, it is necessary to know which chemical environment favors the formation of that particular donor defect. Knowledge of the full range of elemental chemical potentials within which the material is stable is required, in order to predict where in that range the formation of the p -type donor defect is favored. It is therefore necessary to work out accurately the stability region in the chemical potential space — not carrying out this procedure correctly can lead to unphysical predictions of defect formation energies. [27, 28] We stress that this type of analysis is limited to growth conditions where the assumption of thermodynamic equilibrium is reasonable.

In this paper, we present a simple, fast and effective algorithm to determine the range of the elemental chemical potentials within which the formation of a stoichiometric material will be favorable, in comparison to the formation of competing phases. If there is no range, then the material is not thermodynamically stable within the specified environment. The algorithm works by first reading in the free energy of formation of the material itself and that of the competing phases, which must be provided by the user. Setting the condition that the material is, in principle, stable constrains the values of the elemental chemical potentials, effectively reducing the number of independent variables by one, meaning that the space spanned by the elemental

107 chemical potentials is $(n - 1)$ -dimensional, where n is the total number of
 108 elements in the material. The condition that the competing phases do not
 109 form provides further conditional relations among the independent variables.
 110 A set of linear equations, corresponding to the set of all conditions on the
 111 independent variables, is constructed. All possible combinations of the linear
 112 equations in the set are solved in order to find their intersection points. The
 113 intersection points are then checked to determine which ones satisfy every
 114 condition (if none do the system is not thermodynamically stable). Those
 115 that do form the corner points of the region of stability in the chemical
 116 potential space. The algorithm is based on the fact that each competing
 117 phase and standard state effectively defines a hypersurface in the elemental
 118 chemical potential space, and the region bounded by these hypersurfaces cor-
 119 responds to the region of values of chemical potentials in which the material
 120 will be stable. The elemental chemical potentials are given with respect to
 121 their standard states, i.e. we set the energy that the element has (per atom)
 122 in its standard state as the zero of chemical potential for that element. The
 123 algorithm requires that the energy of formation of the material and each
 124 competing phase is calculated (or measured) prior to execution. For an *in*
 125 *silico* study, it is therefore of great importance that the user searches the
 126 chemical databases (such as the Inorganic Crystal Structure Database [29])
 127 extensively, and calculates the energy of all phases and limiting compounds
 128 using the same level of theory. [30, 31, 26, 25, 1] We have incorporated the
 129 algorithm in a FORTRAN program called ‘Chemical Potential Limits Analysis
 130 Program’ (CPLAP) which we have made available online. [32, 33] For con-
 131 venience, if the chemical potential space is two-dimensional (2D) or three-
 132 dimensional (3D), the program produces files that can be used as input to
 133 GNUPLOT [34] and MATHEMATICA, [35] to visualize the region of stability. An
 134 option to fix the value of a particular chemical potential is available, which
 135 effectively reduces the dimensionality by one.

136 The rest of the paper is structured as follows: In Sec. 2 we discuss the
 137 relevant theory on which the algorithm is based; in Sec. 3 we present the
 138 algorithm; in Sec. 4 we demonstrate how the program works using a ternary
 139 and quaternary system as examples; and in Sec. 5 we summarize our work.
 140 All the figures in this work, apart from the flowcharts, have been produced
 141 using GNUPLOT, from the output from CPLAP.

142 2. Theory

143 The fundamental assumption, upon which analysis of the chemical po-
 144 tential landscape in which a material forms is based, is that the combined
 145 system in the growth environment is in thermodynamic equilibrium. To illus-
 146 trate the necessary theory, we consider a binary system A_mB_n , which forms
 147 via the reaction:



148 at constant pressure and temperature. The formation of A_mB_n competes
 149 with the phase A_pB_q . The procedure is then to assume that A_mB_n forms,
 150 rather than A_pB_q or the standard states of A and B , and see if this leads to
 151 a contradiction.

152 We recall that the chemical potential μ_α of species or compound α is
 153 defined as

$$\mu_\alpha = \left(\frac{\partial G}{\partial N_\alpha} \right)_{p,T}, \quad (2)$$

154 where G is the Gibbs free energy of the system ($G = U - TS + pV$, U is the
 155 internal energy, T is the temperature, S is the entropy, p is the pressure, and
 156 V is the volume) and N_α is the number of particles of species or compound
 157 α .

158 We first consider the chemical potential of individual species in the com-
 159 pound A_mB_n (i.e. A and B). We denote the chemical potential of species α
 160 in its standard state as μ_α^S . We would now like to refer the elemental chemical
 161 potentials μ_α to their respective μ_α^S , i.e. we set

$$\mu_\alpha = \mu_\alpha^T - \mu_\alpha^S, \quad (3)$$

162 where μ_α^T is the chemical potential of species α that shares a common ref-
 163 erence with μ_α^S . We do this for convenience; by determining the μ_α^S in a
 164 consistent manner, we will automatically obtain a common reference for all
 165 elemental chemical potentials. We note that, when calculating formation en-
 166 ergies that depend on the chemical potentials, $\mu_\alpha^T = \mu_\alpha^S + \mu_\alpha$ should be used.
 167 In order to avoid formation of the standard states of A and B , we must have

$$\mu_\alpha \leq 0, \quad (4)$$

168 placing an upper bound on each elemental chemical potential.

169 We now consider all species involved in the reaction given in Eqn. 1, so
 170 that $\alpha = A, B, A_mB_n$, and follow the analysis given in Ref. [36]. Under the

assumption of constant p and T , the differential dG in the Gibbs free energy is given by:

$$dG = \sum_{\alpha} \mu_{\alpha}^T dN_{\alpha}. \quad (5)$$

As dN_{α} is proportional to the coefficient i_{α} in the reaction given by Eqn. 1 ($i_{\alpha} = m$ for $\alpha = A$, $i_{\alpha} = n$ for $\alpha = B$, $i_{\alpha} = -1$ for $\alpha = A_mB_n$), it can be written as $dN_{\alpha} = i_{\alpha}dN$, where dN is the number of occurrences of the reaction in Eqn. 1. We can therefore write

$$dG = \left(\sum_{\alpha} i_{\alpha} \mu_{\alpha}^T \right) dN. \quad (6)$$

At equilibrium,¹ $dG = 0$, implying that

$$\sum_{\alpha} i_{\alpha} \mu_{\alpha}^T = 0, \quad (7)$$

from which we obtain (remembering $i_{A_mB_n} = -1$):

$$m\mu_A + n\mu_B = \mu_{A_mB_n} = \Delta G_f[A_mB_n]; \quad (8)$$

here $\Delta G_f[X] = \Delta H_f[X] - T\Delta S$ is the Gibbs free energy of formation of compound X with respect to the standard states of its constituent elements, $H_f[X]$ is the enthalpy of formation of X , and ΔS is the change in entropy. For crystalline systems with low levels of disorder, a good approximation is to set $\Delta S = 0$, so that $\Delta G_f[X] = \Delta H_f[X]$. Under this approximation we can set the chemical potentials of A and B in their standard states equal to the total energy (per atom) of the standard states. Calculating all total energies, including those required to determine $\Delta H_f[X]$, in a consistent manner ensures all chemical potentials have a common reference. Although it is possible to include vibrational entropic effects using, for example, the quasi-harmonic approximation, and configurational entropic effects for disordered systems, in the remainder of this paper we assume that the approximation $\Delta G_f[X] = \Delta H_f[X]$ applies. Eqn. 8 now becomes:

$$m\mu_A + n\mu_B = \mu_{A_mB_n} = \Delta H_f[A_mB_n], \quad (9)$$

¹Once equilibrium is reached, the reaction will not proceed further; therefore there will not be any further change in the thermal average values of the concentrations. This implies that, given the volume at equilibrium, Eqn. 7 will be valid when V and T are specified instead of p and T , as was our initial assumption. See Ref. [36]

effectively constraining our mathematical problem, so that one chemical potential can be written in terms of the other, i.e. the number of independent variables is one. For a binary system, therefore, the chemical potential space is one-dimensional (1D), spanned by the one independent variable.

Combining Eqns. 4 and 9 and taking μ_A to be the independent variable, we find that:

$$\frac{\Delta H_f[A_m B_n]}{m} \leq \mu_A \leq 0, \quad (10)$$

with μ_B being determined for each value of μ_A from Eqn. 9. It follows then that the boundary $\mu_A = 0$ corresponds to A -rich/ B -poor growth conditions, and the boundary $\mu_A = \Delta H_f[A_m B_n]/m$ corresponds to B -rich/ A -poor growth conditions. Eqn. 10 defines the stability region (a line segment) in the 1D chemical potential space spanned by μ_A .

We now include in our calculation the competing phase $A_p B_q$. The assumption that $A_p B_q$ does not form leads to the following condition:

$$p\mu_A + q\mu_B \leq \mu_{A_p B_q} = \Delta H_f[A_p B_q]. \quad (11)$$

Combining this with Eqn. 9 provides the following limits:

$$\begin{aligned} \left(p - \frac{qm}{n}\right) \mu_A &\leq \Delta H_f[A_p B_q] - \frac{q}{n} \Delta H_f[A_m B_n]; \\ \left(q - \frac{pn}{m}\right) \mu_B &\leq \Delta H_f[A_p B_q] - \frac{p}{m} \Delta H_f[A_m B_n]. \end{aligned} \quad (12)$$

If these limits are inconsistent with Eqn. 4 then $A_m B_n$ is unstable with respect to the formation of $A_p B_q$. If they are consistent, then they effectively reduce the range given in Eqn. 10, i.e. they reduce the extent of the stability region. The addition of more competing phases will further restrict the stability region, which will (if it exists) consist of a line segment in the 1D space spanned by μ_A , with corresponding values of μ_B derived from Eqn. 9. This solves the case of a binary system.

We now consider a ternary system, to demonstrate the generalization of the process as one increases the dimensionality of the chemical potential space. We consider the system $A_m B_n C_p$, whose formation competes with the phases $A_q B_r$ and $A_s B_t C_v$.

Corresponding to Eqn. 9, the assumption that $A_m B_n C_p$ forms in an equilibrium reaction with the constituent elements' standard phases provides the constraint:

$$m\mu_A + n\mu_B + p\mu_C = \mu_{A_m B_n C_p} = \Delta H_f[A_m B_n C_p], \quad (13)$$

allowing us to express one of the chemical potentials, say μ_C , in terms of the other two, leaving two independent variables μ_A and μ_B spanning a 2D chemical potential space. Allowing μ_C to adopt its maximum bounded value of zero (see Eqn. 4) gives the following condition on μ_A and μ_B :

$$m\mu_A + n\mu_B \geq \Delta H_f[A_m B_n C_p]. \quad (14)$$

Combining Eqns. 4 and 13 gives the following conditions on the chemical potentials:

$$\mu_i \geq \Delta H_f[A_m B_n C_p]/i_\alpha, \quad (15)$$

where i_α stands for either m , n , or p , whichever is appropriate.

Assuming the competing phases do not form leads to the conditions:

$$q\mu_A + r\mu_B \leq \mu_{A_q B_r} = \Delta H_f[A_q B_r]; \quad (16)$$

$$s\mu_A + t\mu_B + v\mu_C \leq \mu_{A_s B_t C_v} = \Delta H_f[A_s B_t C_v]. \quad (17)$$

Using Eqn. 13 to eliminate μ_C from Eqn. 17, we see that Eqns. 4, 14, 15, 16, and 17 define conditional relations on a 2D plane formed by μ_A and μ_B . If there does not exist a region in the 2D plane that conforms to every condition, then the system is not thermodynamically stable. Otherwise, we have a region of stability. One method of determining if this is the case is to set the inequality signs in Eqns. 4, 14, 15, 16, and 17 to equality signs, giving a series of linear equations with two unknowns. These linear equations define lines on the 2D plane formed by μ_A and μ_B . Their intersection points can be determined by solving the appropriate combinations of the linear equations. Those that then simultaneously satisfy the conditions given by Eqns. 4, 14, 15, 16 and 17 (if any) will bound the region of stability. The result will be a 2D stability region in the plane defined by μ_A and μ_B , with the corresponding value of μ_C at each point in the stability region determined from Eqn. 13. Graphically, one can display this solution as a 2D plot in the space spanned by μ_A and μ_B , with the corresponding values of μ_C given at points of interest.

The generalization of this procedure to systems with larger number of constituent elements is as follows. For a system with n constituent elements, we will have $n - 1$ independent variables. The higher dimensional analogues of Eqns. 4, 14, and 15 provide $2n - 1$ linear equations (which correspond to hypersurfaces in the $(n - 1)$ -dimensional space), and each competing phase provides an additional linear equation. We therefore have a minimum of

250 $2n - 1$ linear equations with $n - 1$ unknowns. Mathematically, the solution is
 251 trivial, as it only involves solving different combinations of the linear equa-
 252 tions and checking which solutions are compatible with a series of conditional
 253 statements. In practice, however, if we have m competing phases there are
 254 $2^{n+m-1}C_{n-1}$ combinations to consider, and carrying out the procedure can be
 255 quite time consuming and error-prone. This is the reason we have developed
 256 a program to automate it.

257 3. Algorithm

258 Input to the program consists of the number of species in the compound
 259 of interest, the names and stoichiometry of the species, and the free energy of
 260 formation of the compound. One must also input the total number (if any)
 261 of competing phases, and, for each one, the number of species, the names
 262 and stoichiometry of each species, and the free energy of formation of that
 263 competing phase. The input can be provided via a file, or interactively while
 264 running the program.

265 The user must specify which elemental chemical potential is to be set as
 266 the dependent variable. We note here that the procedure carried out by the
 267 program can, in principle, be performed without any dependent variable set.
 268 If this is done, however, only the intersection points with the hypersurface
 269 corresponding to the compound of interest are viable solutions, since, by
 270 not setting a dependent variable, the constraint given by Eqns. 9 or 13 (or
 271 the higher-dimensional analogue) is assumed no longer to apply, and instead
 272 effectively the equality sign is replaced by a ‘greater than or equals to’ sign
 273 (i.e. the assumption that the reaction in Eqn. 1 is in equilibrium no longer
 274 holds). Only those results that are consistent with the constraint are actual
 275 solutions of the problem at hand. So, though more intersection points may
 276 be found when no dependent variable is set, only those that intersect the
 277 hypersurface corresponding to the compound of interest are actual solutions.
 278 If no dependent variable is set, the program warns the user of this fact,
 279 and how to interpret the results. It is always preferable to set a dependent
 280 variable.

281 After reading in the input, the main algorithm begins (see Fig. 1). If the
 282 system is binary, the solution is relatively trivial. The program carries out
 283 the procedure as described in Sec. 2 for binary systems, which is to check
 284 that the limits imposed by the competing phases (Eqns. 12) are consistent
 285 with Eqn. 4 and the constraint (Eqn. 9), and, if they are, to return the line

segment that defines the region of stability. The constraint is also returned as output. Note that this is a separate procedure from that used when the number of species is greater than two.

For ternary and higher-order systems a more complex algorithm is used. From the input, the program constructs a matrix of linear equations with $n-1$ unknowns, where n is the number of species in the system. The compound of interest itself provides one linear equation (Eqn. 14, or its higher-dimensional analogue). Each independent variable then contributes two linear equations; one given by Eqn. 4, the other given by Eqn. 15, which means that there are, at a minimum, $2n-1$ linear equations in the matrix. Additional equations are provided by the competing phases: one per phase. If there are m competing phases, we therefore have, in total, $2n+m-1$ linear equations. Once the matrix has been constructed, it is passed to a sorting routine which extracts every possible combination of $n-1$ equations from the $2n+m-1$ total. This sorting routine is described in Appendix A. For each combination, the $n-1$ equations are solved using a standard *LU* decomposition and back-substitution method, [37] if a solution exists. In this way a series of intersection points are found (redundancies are checked for, and removed). Each intersection point is tested to see if it obeys simultaneously all the conditions on the elemental chemical potentials (Eqns. 4, 14, 15, 16, and 17 or higher-dimensional analogues). If none do, the system is not thermodynamically stable. Otherwise, those that do correspond to corner points in the stability region. The output is then sent to file, consisting of the limiting conditions applied, the resulting intersection points (with, for each one, the corresponding value of the dependent variable), and a list composed of each competing phase, with its corresponding linear equation and intersection points (if any).

An option is provided to print to file a grid of points within the stability region, with the grid density provided by the user. Such a grid of values may be useful for demonstrating the variation of the formation energy of a particular defect as the elemental chemical potentials are varied; for this the user would be required to calculate the formation energy at each grid point. If the chemical potential space is 2D or 3D, the program outputs a file which may be loaded directly into **GNU**PLOT, and text which may be pasted into a notebook in **MATHEMATICA**, to produce a plot of the stability region, which will be useful for visualization of results. In addition, for 2D chemical potential spaces, a text file is produced which contains the necessary data to plot the lines in the chemical potential space corresponding to the material

324 of interest and its competing phases.

325 It is possible to restart a run from a previous calculation. Options are
326 then available to set a different chemical potential as the dependent variable,
327 to provide additional competing phases not considered in the original run,
328 or to set a chemical potential to a particular value (effectively reducing the
329 dimensionality of the chemical potential space by one). The latter option is
330 not available for binary systems, as the solution is trivial.

331 We note that, in principle, the procedure could be extended to arbitrary
332 pressure and temperature ranges by including thermodynamic potentials ei-
333 ther from computations (using phonon frequency calculations and/or statis-
334 tical mechanics) or thermochemical data. Such an extension is beyond the
335 immediate scope of the present work.

336 Our approach should be compared with that of the **CALPHAD** code, [38, 39,
337 40] which is widely used in modelling phase diagrams of alloys over a range
338 of temperature, pressure and composition. **CALPHAD** uses a model with ad-
339 justable parameters to describe the thermodynamic properties of each phase
340 of a material, fitting the parameters to results from thermochemical and ther-
341 mophysical studies stored in databases, and determines a consistent phase
342 diagram using a wide range of data. The aim of our approach is different;
343 it identifies the range of elemental chemical potentials over which a specified
344 phase is stable.

345 4. Examples

346 4.1. Ternary system

347 As our first example of the application of our program, we consider the
348 system BaSnO_3 , [41] an indium-free transparent conducting oxide (TCO).
349 The formation of BaSnO_3 (in the cubic perovskite structure) occurs in com-
350 petition with the phases BaO , SnO , SnO_2 , and Ba_2SnO_4 , as determined by
351 searching the Inorganic Crystal Structure Database [29] for systems con-
352 sisting of combinations of the elements Ba, Sn, and O. Our aim here is to
353 determine the ranges of chemical potentials in which stoichiometric BaSnO_3
354 will form, using our program. The enthalpies of formation of the compet-
355 ing phases and the material itself have been calculated previously, [41] using
356 DFT with the PBE0 [42, 43] hybrid functional (at the athermal limit). The
357 values are presented in Table 1. These, and the stoichiometries of the rel-
358 evant compounds, form the input to our program. The constraint on the

359 elemental chemical potentials is (see Eqn. 13):

$$\mu_{\text{Ba}} + \mu_{\text{Sn}} + 3\mu_{\text{O}} = \mu_{\text{BaSnO}_3} = -11.46 \text{ eV}. \quad (18)$$

360 We set the chemical potential of O, μ_{O} , as the dependent variable.

Table 1: Enthalpies of formation (ΔH_f) of BaSnO_3 and its relevant competing phases. The values, which are taken from Ref. [41], were determined using DFT with the PBE0 hybrid functional.

System	ΔH_f (eV)	System	ΔH_f (eV)
BaSnO_3	-11.46	Ba_2SnO_4	-17.13
BaO	-5.14	SnO	-2.54
SnO_2	-5.29		

361 After running the program, we find that the system is thermodynamically
 362 stable. Given that BaSnO_3 forms, the limiting conditions that apply to the
 363 two independent variables μ_{Ba} and μ_{Sn} are (energies in eV):

$$\begin{aligned}
 \mu_{\text{Ba}} + \mu_{\text{Sn}} &\geq -11.46, \\
 2\mu_{\text{Ba}} - \mu_{\text{Sn}} &\leq -5.52, \\
 2\mu_{\text{Ba}} - \mu_{\text{Sn}} &\leq -3.95, \\
 -\mu_{\text{Ba}} + 2\mu_{\text{Sn}} &\leq 3.85, \\
 \mu_{\text{Ba}} &\leq 0, \\
 \mu_{\text{Sn}} &\leq 0, \\
 \mu_{\text{Ba}} &\geq -11.46, \\
 \mu_{\text{Sn}} &\geq -11.46.
 \end{aligned} \quad (19)$$

364 We present the resulting intersection points bounding the stability region in
 365 Table 2, where we give the corresponding value of the dependent variable
 366 μ_{O} , and the competing phases to which the intersection points correspond.
 367 The stability region is plotted in Fig. 2. We note that, if we change which
 368 chemical potential is set as the dependent variable, we obtain the same results
 369 (as we must). The only difference will be in the appearance of the figure, as
 370 one of the axes will be changed to that of the new independent variable.

371 It is worth noting that if one of the competing phases, say Ba_2SnO_4
 372 (which could easily be overlooked), is not included in the calculation, the

Table 2: Intersection points bounding the stability region in the 2D chemical potential space spanned by the independent variables μ_{Ba} and μ_{Sn} . The corresponding values of the dependent variable μ_{O} , and the relevant competing phases, are also given. All energies are in eV.

	μ_{Ba}	μ_{Sn}	μ_{O}	Competing phases
A	-5.66	-5.80	0.00	Ba ₂ SnO ₄ , BaSnO ₃
B	-6.18	-5.29	0.00	SnO ₂ , BaSnO ₃
C	-2.76	0.00	-2.90	Ba ₂ SnO ₄
D	-3.53	0.00	-2.64	SnO ₂

373 resulting stability region (see Fig. 3) is approximately twice as extensive
374 as that shown in Fig. 2, indicating the importance of taking into account
375 all relevant competing phases. If one or more is left out, the analysis may
376 be incorrect. Similarly, when calculating the total energies of the standard
377 phases of the constituent elements, the correct ground-state of O₂ (triplet
378 spin configuration) must be used, as well as sufficient k -point sampling for
379 the metallic standard phases.

380 As is discussed in Ref. [41], the most stable n -type intrinsic defect in
381 BaSnO₃ is the O vacancy (V_O). The formation enthalpy $\Delta H_f[\text{V}_\text{O}]$ of the
382 (neutral) defect is determined from the reaction



383 according to:

$$\Delta H_f[\text{V}_\text{O}] = (E^D - E^H) + E_{\text{O}_2} + \mu_{\text{O}}, \quad (21)$$

384 where E^H is the energy of the stoichiometric host supercell, E^D is the energy
385 of a supercell containing the defect, and E_{O_2} is the energy per atom of O in
386 its elemental (O₂ gas) form, which we have set as the chemical potential of
387 O in its standard state, μ_{O}^S (see Sec. 2). As can be seen, $\Delta H_f[\text{V}_\text{O}]$ depends
388 on μ_{O} . By printing a grid of points contained within the stability region,
389 one obtains a list of points at which $\Delta H_f[\text{V}_\text{O}]$ can be determined, which
390 in turn can be used to demonstrate how the defect formation energy varies
391 at the different possible growth conditions. We show the results of such a
392 calculation in Fig. 4, where the variation in $\Delta H_f[\text{V}_\text{O}]$ is shown within the
393 stability region in the chemical potential space. We see that, unsurprisingly,
394 Ba- and Sn-rich conditions favor its formation. It should be remembered
395 that the defect concentration depends exponentially on this quantity.

396 *4.2. Quaternary system*

397 We now discuss the application of CPLAP to the quaternary system LaCu-
 398 OSe. This layered oxyselenide is a promising degenerate *p*-type wide band-
 399 gap semiconductor. [44, 45, 46, 15] With four species in the compound, we
 400 have a 3D chemical potential space. There are a large number of compet-
 401 ing phases (22) to be taken into consideration, as determined by searching
 402 the Inorganic Crystal Structure Database [29] for systems consisting of com-
 403 binations of the elements La, Cu, O, and Se. We therefore have a much
 404 more complicated problem than for the ternary system BaSnO₃, discussed
 405 in Sec. 4.1. This example demonstrates well the power of our program in
 406 analyzing the chemical potential ranges.

407 We have calculated the enthalpy of formation of the compound and its
 408 competing phases using DFT with the HSE06 [47] hybrid functional. Our
 409 purpose here is to discuss the ranges of chemical potentials consistent with
 410 the growth of the material, which can support future studies of its defect and
 411 materials physics. The calculated enthalpies of formation are shown in Table
 412 3. These, along with the stoichiometries of the compounds, form the input
 413 to CPLAP.

Table 3: Enthalpies of formation (ΔH_f) of LaCuOSe and its relevant competing phases. The values were determined using DFT with the HSE06 hybrid functional.

System	ΔH_f (eV)	System	ΔH_f (eV)
LaCuOSe	-9.55	CuSe ₂	-1.16
La ₂ CuO ₄	-19.94	CuSe ₂ O ₅	-6.54
CuLaO ₂	-10.60	La ₂ SeO ₂	-16.27
La ₂ O ₃	-17.70	La ₂ (SeO ₃) ₃	-27.94
La ₃ Se ₄	-15.77	La ₄ Se ₃ O ₄	-33.16
LaCuSe ₂	-6.96	LaCu ₂	-2.13
LaSe ₂	-5.64	LaCu ₅	-4.52
LaSe	-4.41	La(CuO ₂) ₂	-13.07
Ce ₂ Se	-1.95	LaCuO ₃	-10.61
CuSe	-1.17	Se ₂ O ₅	-3.37
Cu ₃ Se ₂	-3.55	SeO ₂	-1.95
La ₂ Cu(SeO ₃) ₄	-32.78		

414 The constraint on the chemical potentials is:

$$\mu_{\text{La}} + \mu_{\text{Cu}} + \mu_{\text{O}} + \mu_{\text{Se}} = \mu_{\text{LaCuOSe}} = -9.55 \text{ eV.} \quad (22)$$

415 We choose μ_{Se} as the dependent variable. Running the program, we find that
 416 the system is thermodynamically stable. As there are 29 limiting conditions
 417 on the independent variables, we do not list them here. We find 20 inter-
 418 section points in the 3D chemical potential space spanned by μ_{La} , μ_{Cu} , and
 419 μ_{O} . They are presented, along with the corresponding values of μ_{Se} and the
 420 relevant competing phases, in Table 4. The 3D stability region is shown in
 421 Fig. 5. The relevant competing phases describe 2D surfaces in the 3D space,
 422 which are shown using colors in Fig. 5 (we note that, because GNUPLOT can-
 423 not plot surfaces parallel to the z -axis, we must represent such surfaces by
 424 placing a cross at their mid-point, as we do for the competing phase LaCu_5).

Table 4: Intersection points bounding the stability region in the 3D chemical potential space spanned by the independent variables μ_{La} , μ_{Cu} and μ_{O} . The corresponding values of the dependent variable μ_{Se} , and the relevant competing phases, are also given. All energies are in eV.

	μ_{La}	μ_{Cu}	μ_{O}	μ_{Se}	Competing phases
A	-5.78	-1.18	-2.59	0.00	LaCuSe_2 , Cu_3Se_2 , LaCuOSe
B	-5.70	-1.26	-2.59	0.00	LaCuSe_2 , $\text{La}_4\text{Se}_3\text{O}_4$, LaCuOSe
C	-6.77	-1.18	-1.60	0.00	Cu_3Se_2 , $\text{La}_2(\text{SeO}_3)_3$, LaCuOSe
D	-6.67	-1.26	-1.62	0.00	$\text{La}_2(\text{SeO}_3)_3$, $\text{La}_4\text{Se}_3\text{O}_4$, LaCuOSe
E	-6.62	-1.00	-1.49	-0.44	CuLaO_2 , La_2O_3 , $\text{La}_2(\text{SeO}_3)_3$
F	-3.95	-0.11	-3.27	-2.22	CuLaO_2 , La_2O_3 , LaCu_5
G	-5.67	-0.36	-2.28	-1.24	CuLaO_2 , Cu_2Se , Cu_3Se_2
H	-4.60	0.00	-3.00	-1.95	CuLaO_2 , Cu_2Se
I	-6.77	-0.91	-1.46	-0.42	CuLaO_2 , Cu_3Se_2 , $\text{La}_2(\text{SeO}_3)_3$
J	-4.52	0.00	-3.04	-1.99	CuLaO_2 , LaCu_5
K	-5.77	-1.11	-2.05	-0.62	La_2O_3 , La_2SeO_2 , $\text{La}_4\text{Se}_3\text{O}_4$
L	-3.23	-0.26	-3.75	-2.32	La_2O_3 , La_2SeO_2 , LaCu_5
M	-6.51	-1.19	-1.56	-0.29	La_2O_3 , $\text{La}_2(\text{SeO}_3)_3$, $\text{La}_4\text{Se}_3\text{O}_4$
N	-2.96	-0.56	-4.31	-1.72	La_3Se_4 , LaCuSe_2 , La_2SeO_2
O	-2.61	-0.38	-4.57	-1.98	La_3Se_4 , LaCuSe_2 , LaCu_5
P	-2.54	-0.40	-4.58	-2.04	La_3Se_4 , La_2SeO_2 , LaCu_5
Q	-4.12	-0.36	-3.83	-1.24	LaCuSe_2 , Cu_2Se , Cu_3Se_2
R	-3.60	-0.18	-4.18	-1.59	LaCuSe_2 , Cu_2Se , LaCu_5
S	-4.61	-1.11	-3.21	-0.62	LaCuSe_2 , La_2SeO_2 , $\text{La}_4\text{Se}_3\text{O}_4$
T	-4.52	0.00	-3.08	-1.95	Cu_2Se , LaCu_5

425 If we are interested in, *e.g.*, O-poor conditions, we can set μ_{O} to a low

value, say -4 eV (which is close to, but a little above its minimum value of -4.58 eV — see Table 4). Doing this reduces the dimensionality of the problem by one. The resulting stability region is a 2D ‘slice’ taken from the 3D stability region shown in Fig. 5. We present this 2D stability region in Fig. 6, along with the relevant competing phases, which describe lines in the 2D chemical potential space.

Other sections of the stability region that may be of interest can be extracted easily by setting chemical potentials to particular values. The visualization of the resulting regions can be further modified by changing the dependent variable. This demonstrates the versatility of **CPLAP** in exploring the region of stability in the chemical potential space. To carry out these types of manipulations, in particular for a quaternary system such as LaCuOSe, ‘by hand’ can be quite time-consuming and error-prone. Once the calculation is set up, the region of stability can be explored easily and accurately, with visualization possible when the system is 2D or 3D. For quinary (or higher order) systems, one has to set a chemical potential to a particular value before the stability region can be visualized (in 3D). The ease with which one can systematically explore the stability region using **CPLAP** will be of great benefit to the theoretical and computational study of systems consisting of 4 or more species.

5. Conclusion

In summary, we have described a simple and effective algorithm to determine the thermodynamical stability and range of chemical potentials consistent with the formation of a particular compound of interest, in comparison with the formation of competing phases and elemental forms of the constituent species. By assuming that the compound of interest forms in equilibrium, rather than competing phases and standard states, a set of conditions on the chemical potentials can be derived. These conditions can be interpreted as defining a region bounded by hyper-surfaces in an $(n - 1)$ -dimensional chemical potential space, where n is the number of species in the system. Determining this region of stability gives the chemical potential landscape consistent with the production of the compound of interest. The algorithm works by reading in the energies of formation of the compound itself, and all competing phases, then constructing a matrix of linear equations, solving all possible combinations of the equations, and finding which solutions (if any) obey the conditions on the chemical potentials. We have

462 incorporated the algorithm in a FORTRAN program (CPLAP). Options are avail-
 463 able to set a chemical potential to a particular value, and to print a grid of
 464 points within the stability region. For 2D and 3D systems, files are produced
 465 to allow visualization of the results. We have demonstrated the effective-
 466 ness of the program using a ternary and quaternary system. We have also
 467 demonstrated the flexibility with which the program may be used to explore
 468 a region of stability in the chemical potential space.

469 This program will be of benefit to the theoretical and computational
 470 study of materials with 3 or more constituent species, particularly for the
 471 design of novel functional materials that are thermodynamically stable, and
 472 the generality of the present approach has clear advantages.

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483 Appendix A. Sorting routine

484 In this appendix we describe the sorting algorithm used to extract all
 485 appropriate combinations from the set of linear equations derived from the
 486 conditions on the chemical potentials (see Sec. 3). We assume that there
 487 are n unknowns, and m linear equations, where $m \geq n$. The aim of the
 488 sorting algorithm is to extract all combinations of n equations from the total
 489 m (there will be mC_n combinations).

490 The input to the routine is the matrix M_{ij} , which is $m \times (n + 1)$ dimen-
 491 sional. Each row corresponds to a linear equation; the first n columns are
 492 the coefficients of the n unknowns, and the $n + 1$ -column is the right-hand-
 493 side of the linear equation. The output from the routine will be the mC_n
 494 matrices S_{ij} , which are the $n \times n$ dimensional matrices of coefficients, and
 495 the vectors v_i , which are the n -dimensional corresponding vectors consisting

of the right-hand-sides of the appropriate equations. S and v can then be used in a standard LU decomposition and back-substitution approach [37] to determine the unknowns (i.e. to find the intersection points of the linear equations, if they exist).

The routine works by creating an array *ival*, which is n -dimensional. The elements in the array are initially set as the integers $1, 2, \dots, n$. The array is then used to construct S and v . By sequentially changing the arrangement of the elements of the array (and allowing the array elements to adopt values up to m), all mC_n combinations are extracted from the matrix M . The algorithm is shown in detail in Fig. A.7.

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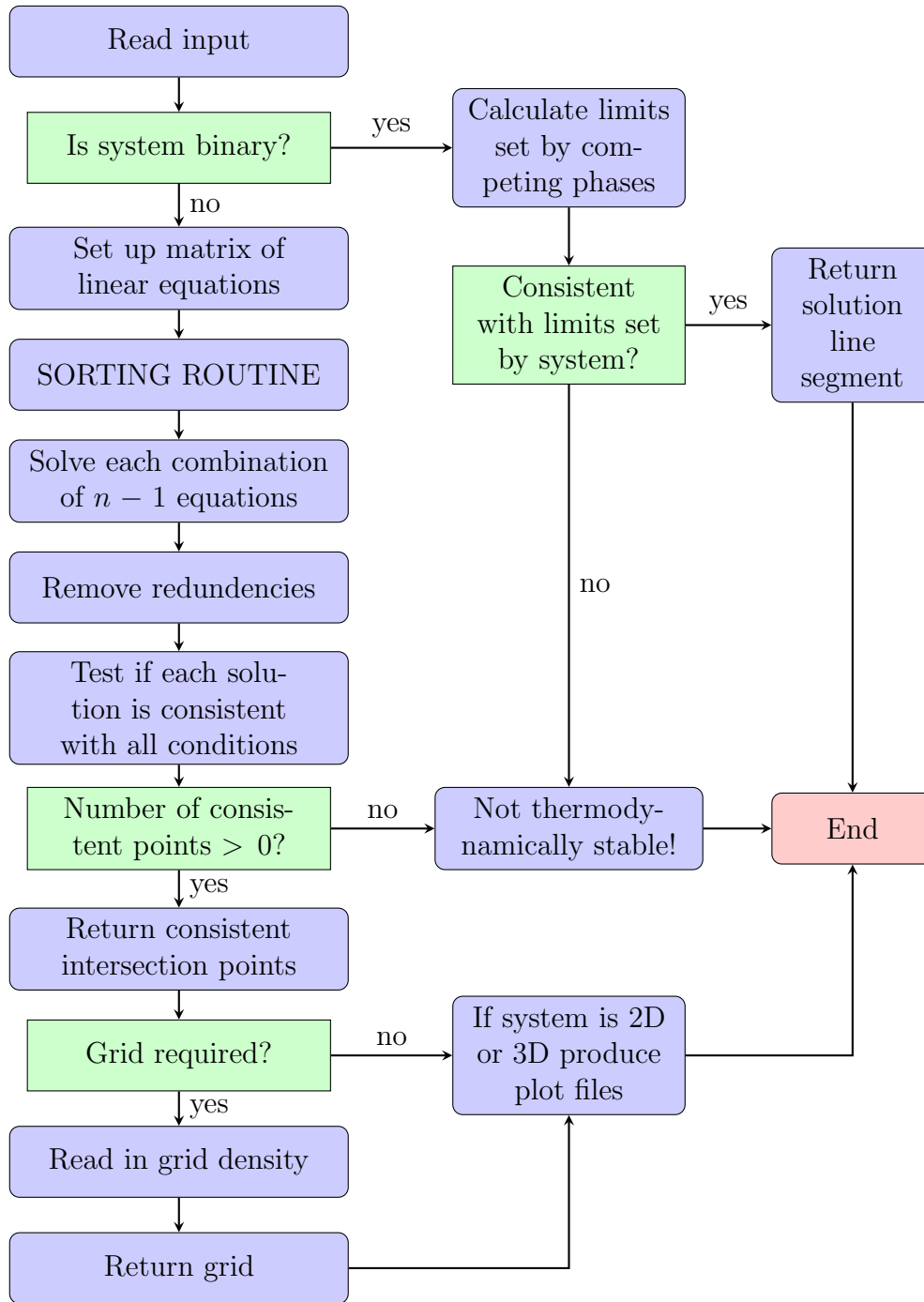


Figure 1: Flowchart of main algorithm.

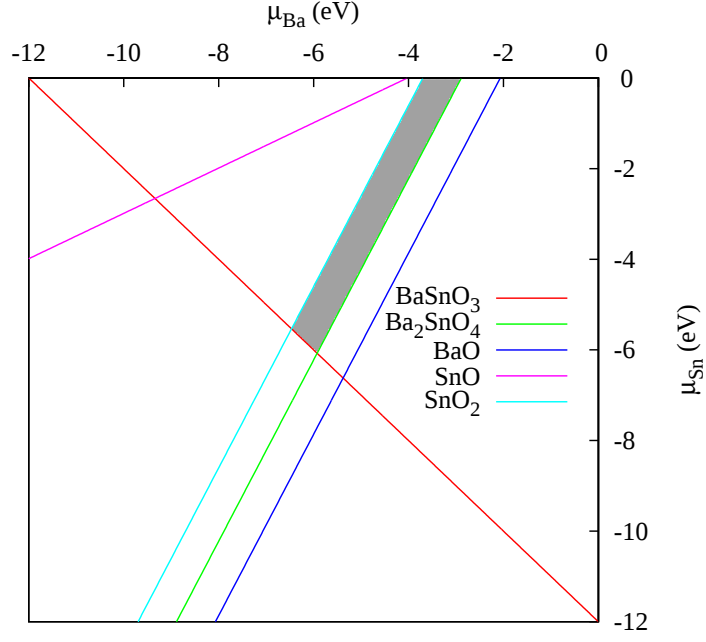


Figure 2: (Color online) Region of stability (shaded) for BaSnO_3 in the 2D space spanned by μ_{Ba} and μ_{Sn} . The (colored) lines indicate the limits imposed by the competing phases and the compound of interest.

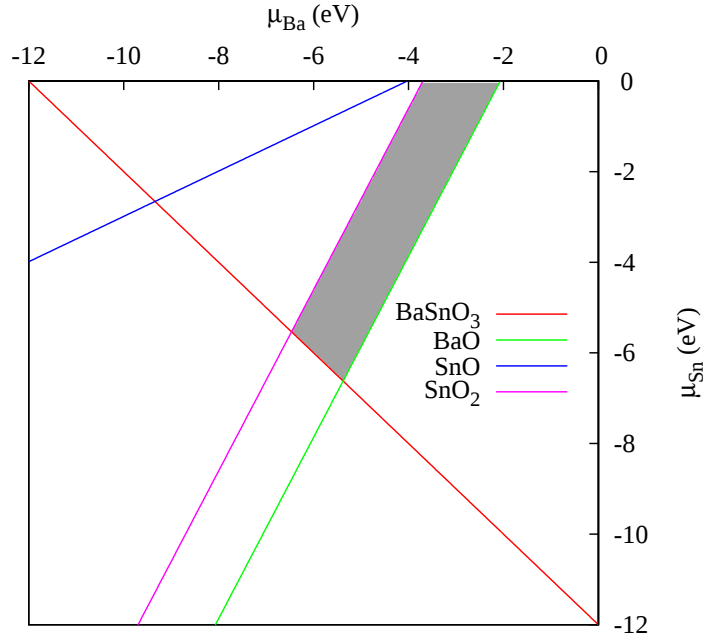


Figure 3: (Color online) Region of stability (shaded) for BaSnO_3 in the 2D space spanned by μ_{Ba} and μ_{Sn} when the competing phase Ba_2SnO_4 is not taken into account.

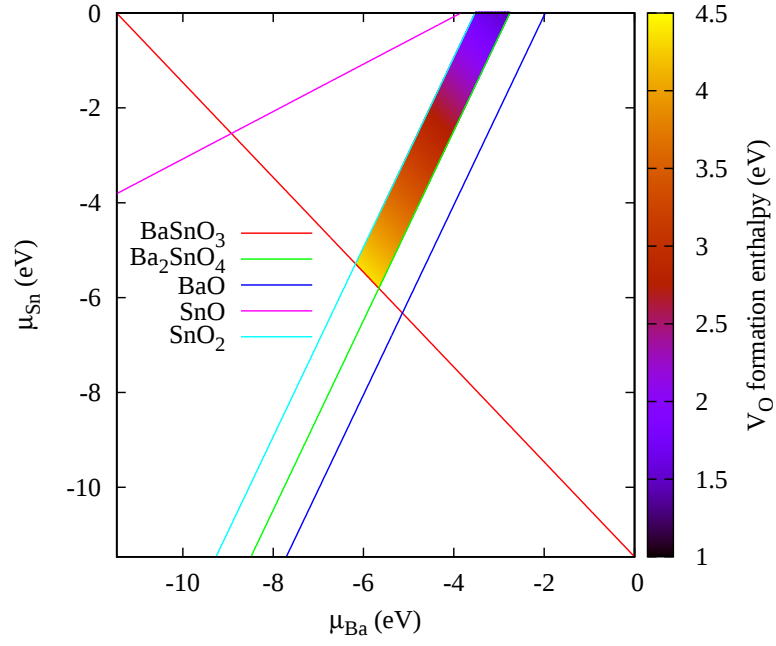


Figure 4: (Color online) Variation in V_{O} formation enthalpy as a function of chemical potential, shown within the stability region for the formation of BaSnO_3 . The (colored) lines indicate the limits imposed by competing phases.

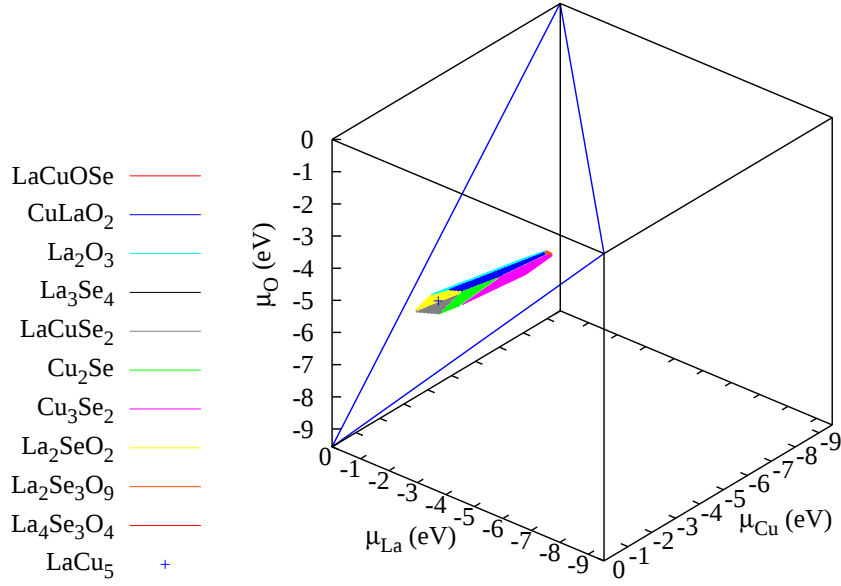


Figure 5: (Color online) Region of stability for LaCuOSe in the 3D space spanned by μ_{La} , μ_{Cu} and μ_{O} . The thick (blue) lines indicate the boundary provided by the compound of interest (LaCuOSe). The (colored) surfaces indicate the limits imposed by the competing phases and the compound of interest. Surfaces parallel to the z -axis are represented by a cross at their mid-point.

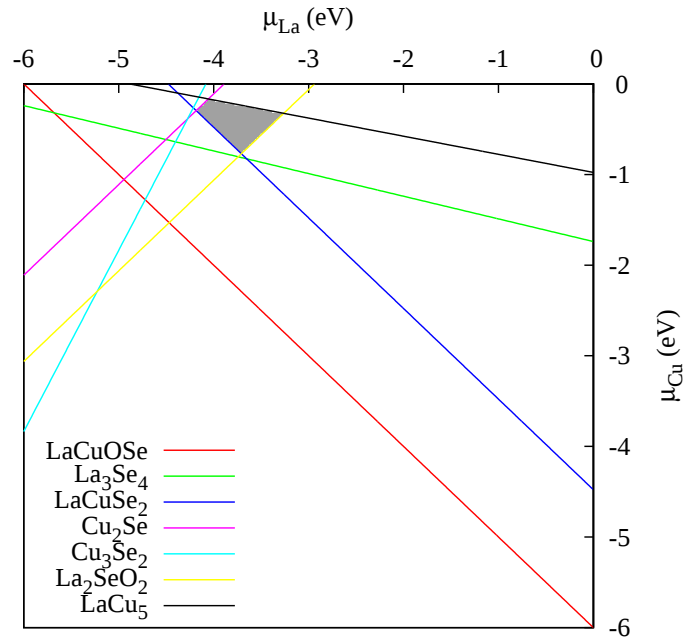


Figure 6: (Color online) Region of stability for LaCuOSe in O-poor growth conditions ($\mu_{\text{O}} = -4$ eV). The chemical potential space is 2D, spanned by μ_{La} and μ_{Cu} . The region is effectively a ‘slice’ taken from the 3D stability region shown in Fig. 5. The (colored) lines indicate the limits imposed by the relevant competing phases and the compound of interest.

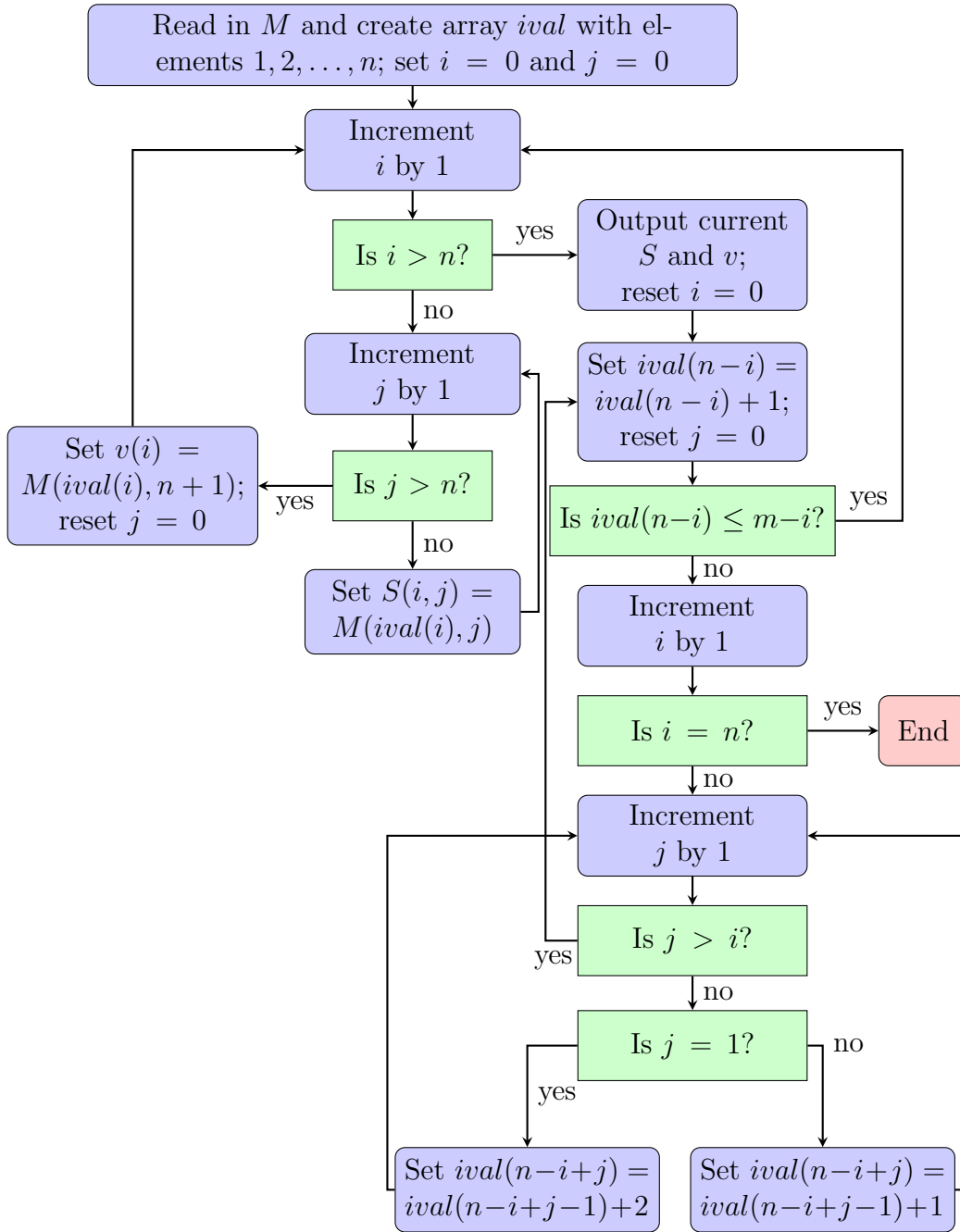


Figure A.7: Flowchart of sorting routine.