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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☆

J. Buckeridge [a,*], D.O. Scanlon [a,b], A. Walsh [c], C.R.A. Catlow [a]

[a] University College London, Kathleen Lonsdale Materials Chemistry, Department of Chemistry, 20 Gordon Street, London WC1H 0AJ, United Kingdom
[b] Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom
[c] Centre for Sustainable Chemical Technologies and Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom

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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 multiternary 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 both to a ternary system and to a 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 materials of four or more constituent elements, which have become 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.

**Program summary**

*Program title:* CPLAP

*Catalogue identifier:* AEQO_v1_0

*Program summary URL:* http://cpc.cs.qub.ac.uk/summaries/AEQO_v1_0.html

*Program obtainable from:* CPC Program Library, Queen's University, Belfast, N. Ireland

*Licensing provisions:* Standard CPC licence, http://cpc.cs.qub.ac.uk/licence/licence.html

*No. of lines in distributed program, including test data, etc.:* 4301

*No. of bytes in distributed program, including test data, etc.:* 28851

*Distribution format:* tar.gz

*Programming language:* FORTRAN 90.

*Computer:* Any computer with a FORTRAN 90 compiler.

*Operating system:* Any OS with a FORTRAN 90 compiler.

*RAM:* 2 megabytes

*Classification:* 16.1, 23.

☆ This paper and its associated computer program are available via the Computer Physics Communication homepage on ScienceDirect (http://www.sciencedirect.com/science/journal/00104655).

* Corresponding author. Tel.: +44 2076790486.
*E-mail address:* j.buckeridge@ucl.ac.uk (J. Buckeridge).

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*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:*
The material growth environment is assumed to be in thermal and diffusive equilibrium.

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

*Running time:*
Less than one second.



## 1. Introduction

Over the past few decades, there has been considerable growth in the development of advanced materials for energy harvesting and transparent electronics applications [1–5]. At present, two of the greatest challenges facing the optoelectronics industry are the production of stable and economically viable p-type materials [6,7], and the replacement of rare or inaccessible components such as indium with more earth-abundant elements [8–11]. This has led to increased interest in more exotic materials, consisting of ternary [12–14], quaternary [15–17], and quinternary [18–20] systems. These materials are also of increased interest for applications in batteries [21] and solid-state electrochemistry [22]. Having a large number of elements in a compound offers a greater degree of chemical freedom, where the tuning of properties of interest, such as band gaps, can be performed by varying the composition.

Instrumental in this research is the theoretical prediction of material properties, using various computational approaches, for example, density functional theory (DFT) and methods based on interatomic potentials [23]. A key consideration when predicting materials appropriate for particular applications is the thermodynamical stability of the system, as stable materials present far fewer technological challenges when incorporated into devices [24,25]. It is of great interest to predict the range of chemical potentials of the component elemental species over which the target phase is stable, rather than the elemental species themselves or competing phases, as this gives an indication the chemical environment necessary for the synthesis of that phase. Indeed, in order to predict the stability of a material, one needs to compare its free energy with that of all competing phases, including those consisting of subsets of the elemental species in the material [26]. The standard procedure [26,27] is to calculate all relevant free energies at the athermal limit, under the 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 [28,29]. 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 are 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 chemical potentials is $(n - 1)$-dimensional, where $n$ is the total number of elements in the material. The condition that the competing phases do not form provides further conditional relations among the independent variables. A set of linear equations, corresponding to the set of all conditions on the independent variables, is constructed. All possible combinations of the linear equations in the set are solved in