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How to cite

DEPMEIER, Wulf et al. An application of the flux function method to a five-component system: the chemical vapour transport of Ni-Cl boracite. In: Journal of crystal growth, 1979, vol. 46, n° 5, p. 718–721. doi: 10.1016/0022-0248(79)90193-3

This publication URL: https://archive-ouverte.unige.ch/unige:33300

Publication DOI: 10.1016/0022-0248(79)90193-3

Journal of Crystal Growth 46 (1979) 718–721
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LETTER TO THE EDITORS

AN APPLICATION OF THE FLUX FUNCTION METHOD TO A FIVE-COMPONENT SYSTEM: THE CHEMICAL VAPOUR TRANSPORT OF Ni–Cl BORACITE

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Received 2 February 1979

The flux function method has been applied to the five-component Ni/BO/Cl/H system to find promising conditions for the growth of Ni–Cl boracite crystals by chemical vapour transport.

The boracite structural family (general formula $M_3B_7O_{13}X$, with M being a divalent metal, e.g. Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and X being, e.g. OH, F, Cl, Br, I) exhibits interesting crystal physical properties, such as ferromagnetoelectricity [1], etc. Boracites are to date the only compounds for which both ferroelectricity and ferromagnetism (weak) have been rigorously shown to be present [1–4] in one and the same phase. For most physical measurements (e.g. measurements of tensorial properties) it is necessary to grow crystals of sufficient size and perfection so that single domains of known orientation can be cut out. In 1965 a method for the growth of single crystals of boracites by chemical vapour transport was published [5]. This so-called "three-crucible method" was based on thermodynamic considerations as well as numerous experiments, and the growth conditions were essentially found empirically. A modification of the method was later used to transport prereacted Ni–Cl and Cr–Cl boracites to produce epitaxial layers on boracite substrates [6].

Recently, a project was started to synthesize new boracites and to study their structures, phase transitions and physical properties. Because of the multitude of factors that influence the crystal growth process, considerable time and effort could be saved if conditions for a high transport rate could be predicted theoretically from thermochemical data. A new approach to the solution of such a problem has recently been given by Noläng and Richardson [7–10], involving the introduction of the transport flux function Φ. This is directly related to the transport rate of the solid under consideration, since

$$J = \bar{D}^0 (\mathrm{d}T/\mathrm{d}x)\, \Phi \,,$$

where J is the flux, $\bar{D}^0$ is an average diffusion coefficient for the vapour species at a standard temperature and pressure and $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient. The flux function is defined by the same set of independent variables as is the equilibrium state between the vapour phase and the condensed phases. Free energy minimization techniques are used to compute values of the flux function, and the phase rule is used to guide the choice of variables for which the analysis is carried out.

As is always the case when dealing with a large number of independent variables, an appropriate method of graphical representation is crucial. In refs. [9] and [10] it was stated that only chemical vapour transport systems with a maximum of four degrees of freedom easily lend themselves to graphical representations. In this paper, it is shown how the flux function/predominance diagram approach can be extended to the analysis of transport of $Ni_3B_7O_{13}Cl$ in the Ni/B/O/Cl/H system, for which there are five degrees of freedom. We believe that the graphical methods described will be useful in other cases of similar complexity.

In contrast to the three-crucible method, the general strategy was to find out the conditions for which the boracite was the only condensed phase in equilibrium with the vapour. These conditions are desirable for crystal growth, since only the boracite would be expected to condense in the growth zone. With the boracite and vapour as the only phases, and with the elements Ni, B, O, Cl and H (the latter is the transporting component) as components, the equilibrium model system for the flux function [10] has five degrees of freedom (phase rule). The five independent variables can, for instance, be chosen as the total pressure P, the temperature T, and three concentration related quantities. The latter were chosen to be $\log a_{Ni}$, $\log a_{Cl_2}$ and $\log a_{O_2}$ (decadic logarithms of component activities referred to pure solid nickel, and gases at one atmosphere as standard states, respectively). Two-dimensional sections can be drawn through the resulting five-dimensional variable space, and fig. 1 shows such a section for fixed values of P and T and with $\log a_{Cl_2}$ as ordinate, $\log a_{O_2}$ as abscissa and $\log a_{Ni}$ as parameter. Boracite, $(NiO)_5(B_2O_3)_7(NiCl_2)$, is the only ternary compound in the condensed $NiO/NiCl_2/B_2O_3$ system. Accordingly, there are three phase stability domains, each of them corresponding to three condensed phases: (i) $NiO + NiCl_2$ + boracite, (ii) $NiO + B_2O_3$ + boracite (disregarding possible boracites), and (iii) $NiCl_2 + B_2O_3$ + boracite. For each of these domains, there are three degrees of freedom. However, three of these variables have been fixed in fig. 1 (the inclusion of a new component, viz hydrogen, also gives rise to an additional phase, and the number of degrees of freedom is unchanged), so that the above phase stability domains are points. Similarly, conditions for the phase stability of two condensed phases are represented by lines, e.g. for $NiCl_2$ + boracite, which bound the area on the diagram corresponding to the range of stability for boracite + vapour alone.

The choice of log (component activity) axes

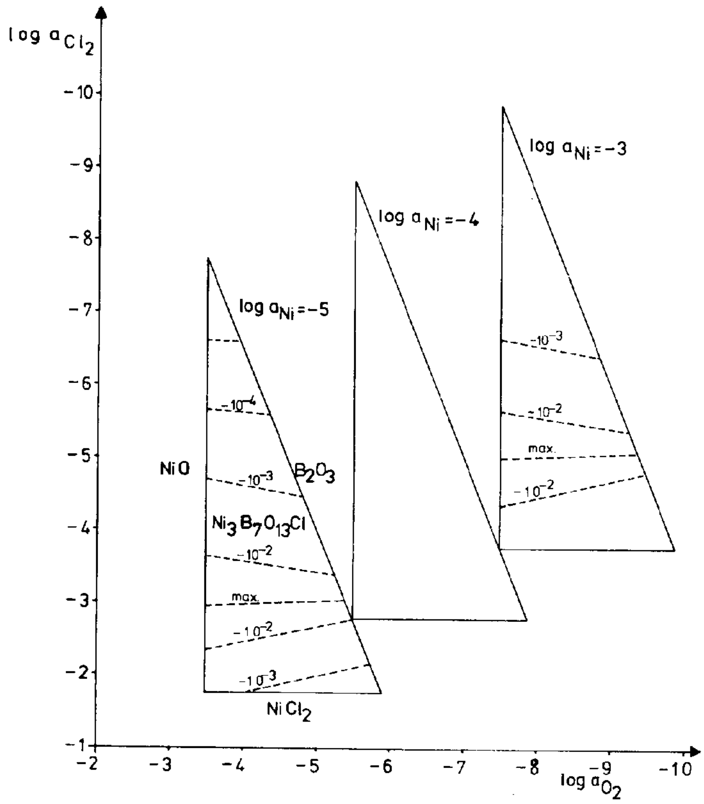

Fig. 1. Predominance/flux function diagram for phase equilibrium conditions and rate of chemical transport of Ni–Cl boracite in the five-component Ni/B/O/Cl/H system. The values for the temperature and the pressure are fixed to T = 1100 K and P = 1 atm. The contour lines within two of the triangles are the flux function of the boracite (units of mol m^{-3} K^{-1}). The transport direction is from hot to cold.

results in a simple rectilinear geometry for the boundaries of the phase stability domains in a predominance diagram such as fig. 1. Equations for the vertices, edges, and boundary planes of the polyhedron bounding the stability domain of boracite + vapour in $\log a_{Cl_2}$, $\log a_{O_2}$, $\log a_{Ni}$ (constant P and T) variable space are readily obtained from the thermochemical data for the condensed phases involved, and for O_2 and Cl_2 (see appendix for an example). Any point in the predominance diagram corresponds to a completely specified set of values for all the chosen independent variables, and therefore values of any dependent variable such as Φ or the vapour concentrations of the components of the equilibrium model system can be drawn in as contour lines. This has been done in fig. 1 for flux function values computed using the free energy minimization program FREEMIN (current version of earlier program EPCBN [7]) and the flux function program EPPBN [7].

Thermodynamic data for the chemical species were taken from the data bank FREDACS [7,11]. Values for the boracite were estimated. Negative values of Φ indicate transport from hot to cold. The ridge formed by the Φ values almost parallel to the $\log a_{O_2}$ axis shows that the transport rate will not be very sensitive to the oxygen activity, in contrast to the effect of the chlorine activity. As the nickel activity is changed, the ridge is displaced with respect to $\log a_{Cl_2}$ and $\log a_{O_2}$. Its absolute shape and height are nevertheless almost the same, so that a number of combinations of experimental variables could be used to give practically the same rate of transport. The maximum absolute value of the flux function for the boracite is about 0.02 mol K^{-1} m^{-3}, which corresponds to a reasonable transport rate in the usual configuration for chemical transport. Corresponding calculations and plots can (and should) be done for other values of the temperature and pressure. In addition, to aid the planning of experiments, contours of the vapour concentrations of Ni, B, O, Cl, and H should be plotted in the diagrams to give information needed for setting up an experiment according to the predictions (see also refs. [7–10]). An interesting possibility would be to plot all of these contours on the faces of the stability domain polyhedron folded out flat to give a two-dimensional figure.

Additional calculations have been done that show that for $T = 900$ K, the flux function is too small in absolute value to allow for a sufficient yield in a realistic experiment. This result is in good agreement with experimental observations reported previously [5]. A calculation with a total pressure of 5 atm and varying a_{Cl_2} showed no significant change in the flux function, and therefore it was concluded as a first approximation that increasing the total pressure would not give rise to a significant improvement.

The flux function/predominance diagram approach gives information on phase stability conditions and transport rates, and can be used as a guide to the setting up of experiments where the effects of nucleation, kinetics and the possible involvement of convective transport can be investigated. Such experimental work is planned.

Partial support of this work by the Fonds National Suisse de la Recherche Scientifique is gratefully acknowledged.

Appendix

The geometry of the predominance diagram

At equilibrium,

$$\mu_{Ni_3B_7O_{13}Cl} = 3\mu_{Ni} + 7\mu_B + \tfrac{13}{2}\mu_{O_2} + \tfrac{1}{2}\mu_{Cl_2} , \tag{1}$$

$$\mu_{B_2O_3} = 2\mu_B + \tfrac{3}{2}\mu_{O_2} , \tag{2}$$

$$\mu_{NiO} = \mu_{Ni} + \tfrac{1}{2}\mu_{O_2} , \tag{3}$$

$$\mu_{NiCl_2} = \mu_{Ni} + \mu_{Cl_2} , \tag{4}$$

where the chemical potentials μ are related to standard chemical potentials μ° and activities a by

$$\mu = \mu^\circ + RT \ln a . \tag{5}$$

When a condensed phase is present in its standard state at equilibrium,

$$a = 1 \quad \text{and} \quad \mu = \mu^\circ .$$

For instance, when $Ni_3B_7O_{13}Cl$ and B_2O_3 are both present at equilibrium, μ_B can be eliminated from eqs. (1) and (2) to give

$$\log a_{Cl_2} = -\tfrac{5}{2} \log a_{O_2} - 6 \log a_{Ni} - \Delta G^\circ / RT \ln 10 , \tag{6}$$

where

$$\Delta G^\circ = 6\mu^\circ_{Ni} + \tfrac{5}{2}\mu^\circ_{O_2} + \mu^\circ_{Cl_2} + 7\mu^\circ_{B_2O_3} - 2\mu^\circ_{Ni_3B_7O_{13}Cl} . \tag{7}$$

Eq. (6) represents a plane in $\log a_{Cl_2}$, $\log a_{O_2}$, $\log a_{Ni}$ variable space (constant temperature), and becomes a line of slope $-5/2$ in fig. 1 where $\log a_{Ni}$ is the parameter. Equations for other planes can be derived in a similar manner, each of them for the presence of a different condensed phase in addition to the boracite. They form the surfaces of a polyhedron defining the stability domain for the equilibrium of boracite + vapour alone. The edges and vertices of this polyhedron give the conditions for the stability of boracite plus two or three additional condensed phases, respectively.

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