Gas phase synthesis of epitaxial layers of nickel-chlorine boracite on chromium-chlorine boracite

SCHMID, Hans, TIPPMANN, Heinz

Abstract

Layers of Ni boracite were epitaxially grown on Cr-Cl boracite at 900 Deg. At the reaction temperature both substrate and layer had the cubic 43m symmetry whereas at room temperature the layer is ferroelectric (symmetry mm2) and the substrate is still cubic. The layers were produced both by (1) CVT reactions in closed quartz ampules and by 2 variants of a CVD process by using either the reactants BCl3(g) + H2O(g), or B2O3(g) for the formation of the intermediate gaseous (BOCl)3 and the B2O3 hydrates. The reactant NiCl2(g) was obtained by reaction Ni(s) + Cl2(g) = NiCl2(g) at .apprx.1000 Deg inside the reactor. Layer thicknesses of 1-100 mm were achieved. The growth rate was .apprx.1 mm/min. The best substrates were those with smooth, as-grown surfaces; these layers were characterized after cooldown by a pattern of ferroelectric 180 Deg domains with the spontaneous polarization oriented perpendicularly to the surface, an average domain size of 1-10 mm and good contrast (at l = 546 nm) between antiparallel domains placed between crossed polarizers and a retarder. The ferroelectric poling fields were >107 V/m.

Reference


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GAS PHASE SYNTHESIS OF EPITAXIAL LAYERS OF NICKEL–CHLORINE BORACITE ON CHROMIUM–CHLORINE BORACITE

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Layers of Ni–Cl boracite have been epitaxially grown on Cr–Cl boracite at 900°C. At the reaction temperature both substrate and layer had the cubic 43m symmetry whereas at room temperature the layer is ferroelectric (symmetry mm2) and the substrate is still cubic. The layers have been produced both by (i) CVT reactions in closed quartz ampoules and by (ii) two variants of a CVD process using either the reactants \( \text{BCl}_3(g) + \text{H}_2\text{O}(g) \), or \( \text{B}_2\text{O}_3(l) + \text{H}_2\text{O}(g) \) for the formation of the intermediate gaseous \( \text{BOCl} \) and the \( \text{B}_2\text{O}_3 \) hydrates. The reactant \( \text{NiCl}_2(g) \) has been obtained by the reaction \( \text{Ni}(s) + \text{Cl}_2(g) = \text{NiCl}_2(g) \) at about 1000°C inside the reactor. Layer thicknesses from 1 up to 100 \( \mu \text{m} \) have been achieved. The growth rate was of the order of 1 \( \mu \text{m}/\text{min} \). The best substrates were found to be those with smooth, as-grown surfaces; these layers were characterized after cool-down by a pattern of ferroelectric 180° domains with the spontaneous polarization oriented perpendicularly to the surface, an average domain size between 1 and 10 \( \mu \text{m} \) and by good contrast (at \( \lambda = 546 \text{ nm} \)) between antiparallel domains placed between crossed polarizers and a retarder. The ferroelectric poling fields were \( >10^7 \text{ V m}^{-1} \).

1. Introduction

1.1. Motivation

Orthorhombic boracites are ferroelectric and are characterized by the symmetry species [1] \( \bar{4}3m \)Fmm2. Hence a jumping of the optical indicatrix of the orthorhombic phase by 90° around the orthorhombic c-axis (which is parallel to the spontaneous polarization and to the pseudo-cubic (100) direction) can take place upon 180° reversal of the spontaneous polarization [2–5]. This can be achieved by applying a voltage to the electrodes (e.g. transparent Au on Cr [3]) deposited on the facets of wafers cut parallel to pseudocubic (100). This behaviour is similar to that of \( \text{Gd}_2(\text{MoO}_4)_3 \), which is characterized by species \( \bar{4}2m \)Fmm2 [6,7]. The switchable spontaneous birefringence at room temperature is about 10–15 times higher in orthorhombic boracites (\( \Delta n: 0.004 \) to 0.022) [4] than in \( \text{Gd}_2(\text{MoO}_4)_3 \) (\( \Delta n: 0.0004 \)).

This means that at equal switching field strength the switching voltage can in principle be made much smaller in the case of boracites, provided they can be produced in the form of relatively thin layers or wafers. Such sheets would be interesting, because applications like light gates, passive display, page composers, etc. can be envisaged [3,5]. Whereas compositions with relatively small birefringence (e.g. Fe–I boracite with \( \Delta n=0.004 \)) can be used in the form of self-supporting single crystalline wafers, compositions with higher \( \Delta n \) necessitate the fabrication of epitaxial, substrate-supported layers with a thickness of a few microns if a quarter wave device is desired.

The objective of the work described in this paper was to demonstrate the practical feasibility of making such layers by a chemical process.

1.2. Approach

The fabrication of epitaxial boracite layers seemed possible by modifying one of the two previously known methods of obtaining single crystalline boracite, namely: the hydrothermal or hydrothermal-like
method [8–18], or the chemical vapour transport (CVT) method [19–23].

The gas phase approach was finally chosen, because of easier control of the experimental parameters and because it entails less risk of partial replacement of the halogen by OH than the hydrothermal method. Because of the well-known tendency of increase of the Curie temperature in the series I → Br → Cl → F → OH boracite, the partial incorporation of OH was expected to lead to an undesirable increase of switching field strength of hydrothermal halogen boracites.

Table 1
Potential point groups and crystallographic cuts of substrates appropriate for switchable layers of orthorhombic boracite

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Point group</th>
<th>Possible cuts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>m3m</td>
<td>(001)</td>
</tr>
<tr>
<td></td>
<td>43m</td>
<td>(h00)</td>
</tr>
<tr>
<td></td>
<td>m3</td>
<td>(010)</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>(100)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4</td>
<td>(001)</td>
</tr>
<tr>
<td></td>
<td>42m</td>
<td>(001)</td>
</tr>
</tbody>
</table>

Table 2
Estimated data of enthalpy and entropy of formation of some boracites, $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$ (units in kcal mole$^{-1}$ and cal deg$^{-1}$ mole$^{-1}$, respectively)

<table>
<thead>
<tr>
<th>M</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_2^{298}$</td>
<td>$\Delta H_2^{298}$</td>
<td>$S_2^{298}$</td>
</tr>
<tr>
<td>Mg</td>
<td>71.9</td>
<td>-1494</td>
<td>74.7</td>
</tr>
<tr>
<td>(Ti)</td>
<td>78.0</td>
<td>-1361</td>
<td>80.3</td>
</tr>
<tr>
<td>Cr</td>
<td>-1297</td>
<td>97.9</td>
<td>-1333</td>
</tr>
<tr>
<td>Mn</td>
<td>95.2</td>
<td>-1238</td>
<td>92.9</td>
</tr>
<tr>
<td>Fe</td>
<td>84.2</td>
<td>-1239</td>
<td>87.5</td>
</tr>
<tr>
<td>Co</td>
<td>81.2</td>
<td>-1237</td>
<td>82.3</td>
</tr>
<tr>
<td>Ni</td>
<td>94.1</td>
<td>-1174</td>
<td>87.2</td>
</tr>
<tr>
<td>Cu</td>
<td>84.4</td>
<td>-1315</td>
<td>87.9</td>
</tr>
<tr>
<td>Zn</td>
<td>92.1</td>
<td>-1258</td>
<td>93.9</td>
</tr>
</tbody>
</table>

a) Boracite unknown.

Remark: Entropy data obtained by Kelley’s “sum method” (see e.g. ref. [38]); the $\Delta H^o$ data given in the table are based on the assumption that the enthalpy of formation from the components MO(s), $\text{B}_2\text{O}_3(s)$ and $\text{MX}_2(s)$ was approximately zero. The real values are probably 5–6% more negative as can be estimated from a comparison of the method applied to Cd and Ca borates [31] of similar metaloxide/$\text{B}_2\text{O}_3$ ratio as occurring in boracite. The data for the entropies and enthalpies of the components were taken from ref. [42], those of VO(s) from ref. [19] and $S_2^{298}$ of CrO from ref. [43].
both up and down polarity of the applied field. The same is true for a random orientation of crystallites having \((100)_{\text{cub}}\) parallel to an isotropic substrate surface, and equally for a polycrystalline ceramic material with prototypic symmetry \(43m\).

2.2. The thermal expansion condition

Because the composition of the boracite layer is cubic at the deposition temperature and remains cubic for several hundred degrees during cooling, it is necessary that the thermal expansion coefficient of the substrate is isotropic in the contact plane. This requirement reduces very much the possibilities of choice of the substrate. As shown on table 1, it can be fulfilled for substrates with one of the five cubic point groups or with one of the tetragonal groups \(4\) or \(42m\).

The orthorhombic groups \(mmm\) and \(222\) and the monoclinic group \(2/m\) necessitate special cuts for achieving isotropy of the expansion coefficient. Therefore they are inconvenient. Consideration of the various limitations suggested therefore that a boracite having cubic \(43m\) symmetry at room temperature should be used as substrate.

2.3. Optical and chemical conditions

There exist only a few halogen boracites which are with certainty cubic (43m) at room temperature: Cr–Cl, Cr–Br, Cr–I, Co–I and Ni–I. Cr–Cl boracite was chosen for two reasons: (i) greatest chemical stability (see table 2) and (ii) good transmission at wavelengths smaller than about 590 nm [24]; this behaviour matches the maxima of transmission of Ni–Cl boracite centring at about 500 and 580 nm [25].

3. Choice of the layer material

For the choice of the composition of the ferroelectrically active boracite layer the following criteria have to be taken into account:

(i) In order to avoid decomposition of the substrate by the reactive atmosphere, the free energy of formation of the substrate should be more negative than that of the layer (see table 2).
(ii) For reasons of easy control of the synthesis, only the bivalent oxidation state of the metal of the layer boracite should be stable.
(iii) Experience with epitaxy of garnets on garnet shows [26] that (a) the difference in lattice parameters of substrate/layer should be less than about 1% (cf. table 3) and (b) the difference in thermal expansion should be negligible in order to avoid dislocations in the layer and cracking.
(iv) To avoid ferroelastic clamping of the domains and concomitant high coercive field, the orthorhombic shear angle of the layer material should be \(<1\) min of arc or preferably zero [3,5].

Ni–Cl boracite was chosen as the layer material because conditions (i), (ii) and (iii) are well fulfilled. Although criterion (iv) is not fulfilled (the shear angle of Ni–Cl boracite is \(2.4 \pm 1\) min of arc [14]) that latter point has no impact on the chemical problem. The experiments suggest that the first criterion is met.

4. Experimental

4.1. Synthesis of single crystal substrates from \(\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}\)

Step I: In a first stage Cr–Cl boracite has been synthesized by the previously described “three crucible
Table 4
Thermochemical data of some hypothetical transport reactions and equilibria of importance in the gas phase synthesis of Ni–Cl boracite

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction (Transport)</th>
<th>(Transport) reaction equilibrium</th>
<th>((\Delta H^\circ_{298} R)^{\text{Ref.}}) kcal mol(^{-1})</th>
<th>((\Delta S^\circ_{298} R)) cal mol(^{-1}) deg(^{-1})</th>
<th>((\Delta G^\circ_{298} R)^{\text{Ref.}}) kcal mol(^{-1})</th>
<th>(\text{lg} K_p)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{Ni}_3\text{B}_5\text{O}_9\text{Cl}(s) + 5 \text{HCl}(g) + \text{H}_2\text{O}(g) \rightleftharpoons 7 \text{HBO}_2(g) + 3 \text{NiCl}_2(g))</td>
<td>+436.2</td>
<td>+271.0</td>
<td>+125.4</td>
<td>-23.9</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(\text{Ni}_3\text{B}_5\text{O}_9\text{Cl}(s) + 5 \text{HCl}(g) + 8 \text{H}_2\text{O}(g) \rightleftharpoons 7 \text{HBO}_2(g) + 3 \text{NiCl}_2(g))</td>
<td>+118.7</td>
<td>+48.1</td>
<td>+61.5</td>
<td>-12.1</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(\text{Ni}_3\text{B}_5\text{O}_9\text{Cl}(g) + 5 \text{HCl}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \frac{7}{3} (\text{HBO}_2(g) + 3 \text{NiCl}_2(g))</td>
<td>+107.2</td>
<td>+63.8</td>
<td>+34.0</td>
<td>-6.49</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(\text{Ni}_3\text{B}_5\text{O}_9\text{Cl}(g) + 12 \text{HCl}(g) = \frac{7}{3} (\text{BOCl}_3(g) + 3 \text{NiCl}_2(g) + 6 \text{H}_2\text{O}(g))</td>
<td>+214.1</td>
<td>+86.5</td>
<td>+114.0</td>
<td>-21.9</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(\text{B}_2\text{O}_3(g) + \text{H}_2\text{O}(g) = 2 \text{HBO}_2(g))</td>
<td>+89.1</td>
<td>+50.7</td>
<td>+30.9</td>
<td>-5.9</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(\text{B}_2\text{O}_3(g) + \text{H}_2\text{O}(g) = \frac{2}{3} (\text{HBO}_2(g))</td>
<td>-4.92</td>
<td>-8.48</td>
<td>+4.81</td>
<td>-0.92</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(\text{B}_2\text{O}_3(g) + 3 \text{H}_2\text{O}(g) = 2 \text{H}_2\text{BO}_3(g))</td>
<td>-1.65</td>
<td>-12.98</td>
<td>+13.24</td>
<td>-2.52</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(\text{B}_2\text{O}_3(g) + 2 \text{HCl}(g) = \frac{2}{3} (\text{BOCl}_3(g) + \text{H}_2\text{O}(g))</td>
<td>+25.61</td>
<td>-2.01</td>
<td>+27.92</td>
<td>-5.32</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(\text{NiCl}_2(g) = \text{NiCl}_2(g))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.855</td>
<td>(13)</td>
</tr>
<tr>
<td>10</td>
<td>(\text{NiO}(s) + 2 \text{HCl}(g) = \text{NiCl}_2(g) + \text{H}_2\text{O}(g))</td>
<td>+30.4</td>
<td>+19.8</td>
<td>+7.69</td>
<td>-1.47</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>(\text{NiO}(s) + 6 \text{HCl}(g) = \text{NiCl}_2(g) + 2 \text{H}_2\text{O}(g))</td>
<td>+187.9</td>
<td>+115.9</td>
<td>+54.96</td>
<td>-10.48</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>(\text{NiO}(s) + 6 \text{HCl}(g) = 2 \text{NiCl}_2(g) + 3 \text{H}_2\text{O}(g))</td>
<td>+97.2</td>
<td>+52.2</td>
<td>+37.33</td>
<td>-7.11</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>(\text{NiO}(s) + 6 \text{HCl}(g) = \frac{2}{3} (\text{HBO}_2(g) + 3 \text{NiCl}_2(g) + 2 \text{H}_2\text{O}(g))</td>
<td>+93.9</td>
<td>+56.7</td>
<td>+26.87</td>
<td>-5.5</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>(\text{NiO}(s) + 8 \text{HCl}(g) = \frac{2}{3} (\text{BOCl}_3(g) + 3 \text{NiCl}_2(g) + \text{H}_2\text{O}(g))</td>
<td>+297.8</td>
<td>-72.1</td>
<td>+380.5</td>
<td>-72.5</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>(\text{B}_2\text{O}_3(g) + 6 \text{HCl}(g) = 2 \text{Cl}_2\text{O}(g) + 3 \text{H}_2\text{O}(g))</td>
<td>+65.6</td>
<td>-12.6</td>
<td>+80.1</td>
<td>-15.26</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>(\text{BOCl}_3(g) + 6 \text{HCl}(g) = 3 \text{Cl}_2\text{O}(g) + 3 \text{H}_2\text{O}(g))</td>
<td>+60.1</td>
<td>-15.9</td>
<td>+78.34</td>
<td>-14.93</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>(\text{B}_2\text{O}_3(g) + 3 \text{HCl}(g) = 2 \text{Cl}_2\text{O}(g) + 2 \text{H}_2\text{O}(g))</td>
<td>-11.72</td>
<td>-31.67</td>
<td>+24.61</td>
<td>-4.69</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>(\text{HBO}_2(g) + 9 \text{HCl}(g) = 3 \text{Cl}_2\text{O}(g) + 6 \text{H}_2\text{O}(g))</td>
<td>+105.8</td>
<td>-6.23</td>
<td>+112.9</td>
<td>-21.53</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>(\text{HBO}_2(g) + 3 \text{HCl}(g) = 2 \text{Cl}_2\text{O}(g) + 3 \text{H}_2\text{O}(g))</td>
<td>+33.6</td>
<td>+0.17</td>
<td>+33.41</td>
<td>-6.37</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>(\text{Ni}_3\text{B}_5\text{O}_9\text{Cl}(s) + 26 \text{HCl}(g) = 7 \text{Cl}_2\text{O}(g) + 13 \text{NiCl}_2(g) + 13 \text{H}_2\text{O}(g))</td>
<td>+354.2</td>
<td>+49.3</td>
<td>+297.65</td>
<td>-56.7</td>
<td>(a)</td>
<td></td>
</tr>
</tbody>
</table>

Legend: (a) calculated from Table 7 data
(b) schematic balance of OVD/BOl^3 process, however kinetically and thermodynamically improbable
(c) from ref. obtained with first approximation for T = 1163°K

*) Remark: for the transport reactions (i.e. one solid reactant): positive \(\Delta H^\circ_{298}\) means transport from T_2 - T_1 (T_2 > T_1)

Method" [19] working in closed quartz ampoules. In that method the overall reaction

\[\text{MX}_2(s or l) + 7 \text{B}_2\text{O}_3(l) + 5 \text{MO}(s) \rightarrow 2 \text{M}_3\text{B}_7\text{O}_{13}X(s)\]

(M = metal, X = halogen), is carried out by placing the three condensed reactants in three different crucibles (see fig. 1) and transporting them to the
Table 5
(a)-(g) Growth conditions of Cr–Cl and Ni–Cl boracite

<table>
<thead>
<tr>
<th>Nr.</th>
<th>B_2O_3 (gr)</th>
<th>CrO Cr_2O_3 Cr (gr)</th>
<th>CrCl_2 (gr)</th>
<th>H_2BO_3 (gr)</th>
<th>temp. (°C)</th>
<th>time (hrs)</th>
<th>yield (gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>2.8</td>
<td>1.6</td>
<td>1.5</td>
<td>0.1</td>
<td>1038</td>
<td>8</td>
<td>132</td>
</tr>
</tbody>
</table>

b) Cr_3B_2O_7Cl, ampoule-method/pure transport → single crystals

<table>
<thead>
<tr>
<th>Nr.</th>
<th>B_2O_3 (gr)</th>
<th>Cr_3B_2O_6Cl (gr)</th>
<th>CrCl_2 (gr)</th>
<th>H_2BO_3 (gr)</th>
<th>temp. (°C)</th>
<th>time (hrs)</th>
<th>yield (gr)</th>
<th>crystal size</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>1.0</td>
<td>1.5</td>
<td>0.1</td>
<td>1040</td>
<td>8</td>
<td>264</td>
<td>0.95</td>
<td>3.5 mm</td>
</tr>
</tbody>
</table>

c) Ni_3B_2O_5Cl-layer deposition on Zn_3B_2O_5Cl - substrate: ampoule method

<table>
<thead>
<tr>
<th>Nr.</th>
<th>B_2O_3 (gr)</th>
<th>NiO (gr)</th>
<th>NiCl_2 (gr)</th>
<th>NiCl_2.6H_2O</th>
<th>temp. (°C)</th>
<th>time (hrs)</th>
<th>layer thickness (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>1.5</td>
<td>2.6</td>
<td>0.1</td>
<td>900</td>
<td>1</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>

d) Ni_3B_2O_5Cl-layer deposition on Cr_3B_2O_7Cl; ampoule method

<table>
<thead>
<tr>
<th>Nr.</th>
<th>B_2O_3 (gr)</th>
<th>NiO (gr)</th>
<th>NiCl_2 (gr)</th>
<th>H_2BO_3 (gr)</th>
<th>temp. (°C)</th>
<th>time (hrs)</th>
<th>layer thickness (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>1.5</td>
<td>2.6</td>
<td>0.1</td>
<td>900</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

e) Ni_3B_2O_5Cl-pure transport: ampoule method → single crystals

<table>
<thead>
<tr>
<th>Nr.</th>
<th>B_2O_3 (gr)</th>
<th>Ni_3B_2O_5Cl (gr)</th>
<th>NiCl_2 (gr)</th>
<th>NiCl_2.6H_2O</th>
<th>temp. (°C)</th>
<th>time (hrs)</th>
<th>single crystal size</th>
<th>crystal size</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>1.1</td>
<td>2.6</td>
<td>0.1</td>
<td>900</td>
<td>1</td>
<td>1</td>
<td>60</td>
<td>5 mm</td>
</tr>
</tbody>
</table>

f) Ni_3B_2O_5Cl-layer deposition on Cr_3B_2O_7Cl; BCl_3/H_2O-process; (Fig. 3)

<table>
<thead>
<tr>
<th>Cl_2</th>
<th>N_2</th>
<th>BCl_3</th>
<th>N_2</th>
<th>N_2</th>
<th>H_2O</th>
<th>HCl</th>
<th>P_total (Torr)</th>
<th>temp. (°C)</th>
<th>time (hrs)</th>
<th>layer thickness (um)</th>
<th>substrate final</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>20</td>
<td>0.7</td>
<td>20</td>
<td>283</td>
<td>7</td>
<td>70</td>
<td>500</td>
<td>900</td>
<td>0.5</td>
<td>&lt; 0.5</td>
<td>80</td>
</tr>
</tbody>
</table>

g) Ni_3B_2O_5Cl-layer deposition on Cr_3B_2O_7Cl; B_2O_3(g)/H_2O (g)-process (Fig. 3, inset 2) [experiment TMA59]

<table>
<thead>
<tr>
<th>Cl_2</th>
<th>N_2</th>
<th>BCl_3</th>
<th>N_2</th>
<th>N_2</th>
<th>H_2O</th>
<th>HCl</th>
<th>P_total (Torr)</th>
<th>temp. (°C)</th>
<th>time (hrs)</th>
<th>layer thickness (um)</th>
<th>substrate final</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>20</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<td>85</td>
<td>2.2</td>
<td>20</td>
<td>500</td>
<td>900</td>
</tr>
</tbody>
</table>

*) valid for bottom of ampoule
growing nuclei by means of gas phase reactions (cf. table 4). In the particular case of Cr boracites, the oxide CrO is not known but can be replaced by a mixture of Cr + Cr2O3. A small amount of H3BO3 is used to provide the H2O necessary for the vapour transport. The experimental parameters are given in table 5a.

In the case of Cr boracite this method yields mostly polycrystalline boracite cakes inside the crucible containing B2O3, and thick crusts of boracite on the outside wall of the crucible. The outside crusts are typical of Cr boracites only and they give the impression of having "crept" over the edge.

Step II: In a second stage Cr—Cl boracite single crystalline platelets and cubes having (100) facets of 3—4 mm² have been obtained by chemical vapour transport using the preformed polycrystalline Cr—Cl boracite, obtained in step I, as source material instead of the mixture Cr2O3 + Cr. Otherwise the three crucible arrangement has been maintained (for experimental parameters cf. table 5b).

This new CVT version of obtaining good boracite crystals by means of a two step process has also proved successful for growing manganese boracites [4]. In that case the two step process is particularly helpful because during step I the presence of free MnO leads to heavy attack of the quartz (risk of explosion!) and to many nuclei leading to polycrystalline material only, whereas the preformed Mn boracite does in no way attack the quartz and the smaller number of nuclei formed in step II lead to larger crystals.

4.2. Epitaxial growth of Ni3B7O13Cl

The epitaxial growth of Ni—Cl boracite has been carried out by (i) chemical vapour transport (CVT) in closed quartz ampoules and by means of (ii) chemical vapour deposition (CVD) type reactions using an open flow system.

4.2.1. Chemical vapour transport (CVT)

The three-crucible method described previously [19] has been adapted for the production of layers of

![Fig. 1. Transport of boracite in a temperature gradient (three crucible method).]
Ni–Cl boracite by placing a quartz substrate holder in between the crucibles containing B$_2$O$_3$ and NiO, respectively (cf. fig. 1).

4.2.1.1. Deposition of Ni$_3$B$_7$O$_{13}$Cl on Zn$_3$B$_7$O$_{13}$Cl. In a preliminary test run, as-grown Zn–Cl boracite crystals of little value have been used as a substrate. During a one hour run at 900°C a layer of about 100 μm thickness has been obtained (figs. 2a and 2b, table 5c). Zn–Cl boracite is a chemically resistant but not optically acceptable (trigonal at room temperature) substrate for Ni–Cl boracite. The experiment showed, however, the feasibility of the layer production and gave the order of magnitude of the growth rate (about 100 μm/h).

4.2.1.2. Deposition of Ni$_3$B$_7$O$_{13}$Cl on Cr$_3$B$_7$O$_{13}$Cl. By using the same experimental arrangement and experimental parameters as described for the deposition on Zn–Cl boracite (section 4.2.1.1), Ni–Cl boracite has been deposited on Cr–Cl boracite (cf. table 5d). The growth rate at 900°C ranged between 40 and 100 μm/h) for the ten experiments carried out.

4.2.1.3. Synthesis of single crystals and layers of Ni$_3$B$_7$O$_{13}$Cl by transport of a preformed charge in a temperature gradient. In the case of the original three-crucible method the system is strongly off equilibrium during the growth of boracite owing to the presence of the starting material NiO in the ampoule. In that case the reaction can take place isothermally [19].

In an attempt at creating quasi-equilibrium conditions during the deposition of the layers and to regulate the deposition rate by changes of the three parameters: (i) mean temperature, (ii) temperature gradient, and (iii) quantity of the initial transport agent H$_2$O, attempts were made to transport a charge of Ni$_3$B$_7$O$_{13}$Cl, in contrast to the original method [19] where only some of the components need to migrate through the vapour phase.

In a first stage it was possible to demonstrate the transportability of Ni$_3$B$_7$O$_{13}$Cl in a temperature gradient by keeping an excess of liquid B$_2$O$_3$ and solid NiCl$_2$ in the ampoule. In this way good and fairly large single crystals have been obtained (cf. table 5e) in a way analogous to the transport of Cr–Cl boracite (cf. table 5b).

In a second stage Ni$_3$B$_7$O$_{13}$Cl layers have been produced on Cr$_3$B$_7$O$_{13}$Cl under identical conditions. The properties of these layers were similar to those described in section 4.2.1.2.

4.2.1.4. Synthesis of Ni$_3$B$_7$O$_{13}$Cl from the starting materials B$_2$O$_3$(l), NiCl$_2$(s) and H$_3$BO$_3$(s). During the different variations of the synthesis of boracite with the ampoule method it has been found out – for Ni–Cl boracite and other boracite compositions as well – that boracite single crystals and layers can also be produced in the ampoule when the source material NiO, or Ni$_3$B$_7$O$_{13}$Cl, is entirely absent. In that case the NiO necessary for boracite formation is generated by hydrolysis of NiCl$_2$ by means of the water contained in the added H$_3$BO$_3$. The reaction proceeds until practically all the original H$_2$O of H$_3$BO$_3$ has
been consumed by the formation of hydrogen halide on the one hand and boracite on the other hand. Weighing of the boracite crystals formed in this way showed that the reaction proceeds nearly quantitatively. This result is in excellent accord with preliminary computer based calculations (cf. mode 6) showing that in the equilibrium state the vapour pressure of HCl exceeds by two orders of magnitude the next frequent species of the vapour phase, namely H$_2$O! These facts lead to the following conclusions:

(i) Independently of the particular method used (NiO source, Ni−Cl boracite source, absence of a NiO or Ni−Cl boracite reservoir) the initial stages of crystallization will proceed under continuously changing supersaturation of the various gas species until equilibrium is attained. This will be the case when practically the whole initially available H$_2$O quantity will be transformed to HCl and boracite.

(ii) It follows from point (i) that a reservoir containing NiO or Ni−Cl boracite is superfluous if thin layers are to be produced, because in that case the supersaturations will not appreciably change.

4.2.2. Chemical vapour deposition (CVD)

4.2.2.1. CVD apparatus and operation. The reactions tentatively postulated for the transport of preformed Ni−Cl boracite (cf. table 4, reaction numbers 1−4) can in principle also be used for the open-tube CVD synthesis of boracite if operated from right to left (table 4). An apparatus was therefore constructed (fig. 3), allowing the introduction, generation and mixing of the following reactants: NiCl$_2$(g), BCl$_3$(g), H$_2$O(g), HCl(g), H$_3$BO$_3$(g), (HBO$_2$)$_3$(g), HBO$_2$(g) and (BOCl)$_3$(g).

The reaction chamber is a quartz tube placed in a tubular resistance heated furnace (fig. 3). The gaseous reactants are produced in the reaction zone behind the nozzle by one of the following two methods:

(i) The gaseous B$_2$O$_3$ hydrates and (BOCl)$_3$ are generated by passing H$_2$O vapour and HCl gas over a quartz boat containing liquid B$_2$O$_3$ (reactions 5 to 8). The substrate is placed above or right after the boat.

(ii) The gaseous B$_2$O$_3$ hydrates and (BOCl)$_3$ are generated by hydrolysing BCl$_3$ gas (reactions 16 to 19, table 3) in a HCl/H$_2$O stream. The substrate is placed
Remarks concerning the reactants

NiCl₂(g) vapour has been generated by passing chlorine at \( \sim 1000^\circ C \) through a plug of nickel-wool placed in the inner tube (fig. 3). At that temperature and at the flow rates used (cf. table 4), the reaction \( \text{Ni} + \text{Cl}_2 \rightarrow \text{NiCl}_2 \) is practically quantitative. Thus the flow of Cl₂ may be equated to that of NiCl₂(g). In order to avoid condensation of solid NiCl₂, the partial pressure of NiCl₂ was always kept well below the saturation pressure, i.e. the flow rate of Cl₂ was always chosen in such a way that the partial pressure of NiCl₂ was \(-20 \text{ Torr at } 900^\circ C\).

H₂O(g): In both kinds of experiment (a and b) of the process H₂O(g) is led into the reactor by means of N₂ carrier gas bubbled through water of room temperature (fig. 3). The flowmeter measuring the rate of N₂ is placed before the entrance to the bubbler.

HCl(g) is taken from a cylinder and after having passed through a flowmeter, the HCl stream is admixed (valve R) to the N₂/H₂O stream. Hereafter the mixed gases enter the reaction zone via the outer tube, surrounding the inner, NiCl₂ generating tube.

Note: When HCl gas of room temperature is admixed to the N₂ stream having been saturated with H₂O vapour at room temperature, a H₂O/HCl condensate forms inside the mixing valve and its vicinity. This effect occurs because of the azeotropic nature of the liquid–vapour phase diagram of the HCl/H₂O system [27]. The system is schematically shown on inset 3 of fig. 3 for 50 and 750 Torr. As can be seen from the phase diagram, this condensation problem can be easily solved by placing an auxiliary heater (A) over the zone in question (fig. 3).

BCl₃(g): The development of the BCl₃ variant (b) of the CVD process was motivated by the results of Deiss and Blum [28] who unexpectedly obtained Mg–Cl, Fe–Cl and Cr–Cl boracite by passing a BCl₃/H₂ mixture over the corresponding oxides. In the case of nickel they obtained, however, only boride and possibly borate.

For operation of the BCl₃ hydrolysis process, BCl₃ gas is taken from a bottle, passed through a flowmeter and admixed to the Cl₂ stream. However, in order to keep the partial pressures of the boron oxide hydrates below their saturation pressures above B₂O₃(l), reactions 5 to 8 leading to the condensation of a growth blocking layer of B₂O₃(l), very small flow rates of BCl₃, smaller than the range of available flowometers, had to be controlled. This has been achieved by diluting the primary BCl₃ stream by means of a N₂ stream and by subsequent control of the diluted stream by a flowmeter (fig. 3).

B₂O₃(l): In the hypothetical reaction equilibria (table 3) and in the overall discussion in this paper the liquid boron oxide phase, B₂O₃(l), is considered as pure. This is in fact an over-simplification and it is necessary to point out the following deliberately neglected facts:

(i) Liquid B₂O₃ dissolves SiO₂ of the SiO₂ crucible (etc.) to a considerable extent, e.g. about 65 mole% SiO₂ dissolves in B₂O₃ at 900°C. Although the SiO₂–B₂O₃ phase diagram is known [29], the time necessary for attaining the equilibrium is not.

(ii) The various species of the gas phase will be more or less soluble in the liquid, glassy B₂O₃/SiO₂ phase. These solubilities as a function of temperature, pressure and the concentration of the co-solvents are not known.

(iii) From (ii) it follows that for a given quantity of transport agent (e.g. initial H₂O) the total and partial pressures in the ampoule will depend upon the amount of the liquid phase present. Moreover, owing to the consumption of B₂O₃ during some of the synthesis modes (cf. table 6), these pressures will vary with time.

(iv) Probably there exist also silicon hydroxides (e.g. Si₂O(OH)₆, SiO(OH)₂ [30,31], and hydroxychlorides in the gas phase as well as in dissolved form in the B₂O₃/SiO₂ phase. Although the silicon compounds do not seem to participate in the boracite synthesis, they may influence the solubilities of their co-solutes in the B₂O₃/SiO₂ phase, some partial pressures and the total pressures.

The enumerated problems (certainly a not exhaustive list) show that at the present state of knowledge only a semiempirical approach can lead to experimental success.

4.2.2.3. The mixing of the reactant gases. The mixing of the reactant gases in the CVD reactor caused some difficulties. Owing to density differences
between the gases entering through the inner and those entering through the outer tube (fig. 3), the gases separated into layers and advanced by laminar flow. This has been monitored by means of a long rectangular platinum foil which has been placed vertically into the reactor tube right behind the nozzle (see fig. 3) and which worked as a "photographic plate". It showed the deposition of boracite crystals \((111)_{\text{cub}}\) parallel to sheet) in a zone about 6 mm high and 10 cm long. Above and below this zone, similar zones of \(3\text{NiO} \cdot \text{B}_2\text{O}_3\) were observed. Both boracite and borate occurred below the centre of the tube only. There was nearly no deposition in the upper half. This method first described by Stein [26] for CVD of garnet layers proved invaluable for determining the optimal location of the substrate. Only after such a study it was possible to obtain boracite layers free of spurious borate.

In an attempt to improve the mixing of the gases, simulation experiments at room temperature have been performed by means of the reaction \(\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})\) which produces a \(\text{NH}_4\text{Cl}(\text{s})\) fog in the reaction zone. These experiments showed that best mixing was obtained with a slit-like nozzle, which creates turbulence.

4.3.2. Classification of the CVT and CVD growth experiments for layers and single crystals of \(\text{Ni}_3\text{B}_7\text{O}_{13}\text{Cl}\) by means of the phase rule

As has been shown in the preceding paragraphs, the synthesis of layers and single crystals of \(\text{Ni}_3\text{B}_7\text{O}_{13}\text{Cl}\) (and other boracite compositions) can be realized in a variety of ways. These differ in particular by the kinds of condensed phases present, the reaction equilibria involved and by the number of degrees of freedom available. The phase rule has been used in the form

\[ I_c - R_i + 2 - \phi = F \]

where \(I_c\) = number of chemical species, \(R_i\) = number of independent reactions, \(\phi\) = number of phases and \(F\) =
degrees of freedom. This approach allows to understand reasonably well, on the basis of hypothetical reactions (see table 4), the various experimental situations encountered, and for example, the effects of a changing supersaturation on the quality of the crystals (cf. CVT mode 2).

In the philosophy of a more modern approach [39] the elements are considered as the components of the system and the auxiliary concept of “hypothetical reactions” can be dropped:

\[(\text{Ni} + \text{B} + \text{O} + \text{Cl} + \text{H} = 5) + 2 - \phi = F .\]

This approach is of more general utility for the quantitative treatment, but because the chemical system is considered as a “black box” it may spring less to the eye at first sight.

The various situations are collected in table 6 and will be commented upon in the following section.

4.2.3.1. CVT in closed ampoules

CVT mode 1: This is the situation encountered in the three-crucible method [19] in which the reactants NiO, NiCl₂ and B₂O₃ are provided in three separately arranged crucibles, and where H₂O in the form e.g. of H₃BO₃ is introduced as the initial transport agent. The quantities of the reactants are chosen in such a way that during the conversion period of NiO to boracite, a surplus of solid NiCl₂ and liquid B₂O₃ is maintained. During that period there is only one degree of freedom, e.g. temperature. In practice this means that the system is off equilibrium until the last rest of NiO is consumed. This period is, however, characterized by a stationary kind of dynamic equilibrium which comes to an end with the disappearance of the last traces of NiO. At that point the system gains one more degree of freedom.

CVT mode 2 is identical with mode 1 except for the vapour pressure of NiCl₂ which lies below its saturation pressure, i.e. there is no condensed phase of NiCl₂ present. Because NiCl₂ is consumed during the boracite synthesis, the NiCl₂ pressure will decrease continuously. This means monotonic change of supersaturation with time and may lead to slight changes of the physical and chemical properties of the crystallized boracite (formation of growth layers [2]). In the case of iodine boracites the difficulty arises that owing to a high equilibrium pressure of iodine of the transition metal iodides very high iodine pressures would have to be maintained in the ampoule, in order to compel the system into mode 1 (double ampoule or autoclave necessary). Therefore, the so far grown Ni—I boracites [19] are carried out by mode 2.

CVT mode 3 describes the situation of transport of preformed Cr—Cl boracite (see section 4.1., step II) and Ni—Cl boracite (see section 4.2.1.3) where only the metal halide, B₂O₃(l) and boracite are present as condensed phases.

CVT mode 4 occurs if one attempts to transport Ni—Cl boracite in a temperature gradient with a pressure of NiCl₂ below its saturation pressure and a reservoir of B₂O₃(l) so as to avoid partial decomposition of the boracite during the transport.

CVT mode 5: This saturation occurs when only NiCl₂(s) and B₂O₃(l), together with some H₃BO₃ are introduced into the ampoule in such quantities that NiCl₂(s) and B₂O₃(l) are present at the reaction temperature. Then practically all the H₂O contained initially in H₃BO₃ is transformed to boracite on the one hand and to HCl on the other.

CVT mode 6 is exemplified when one starts with B₂O₃(l) and some unsaturated vapour of NiCl₂ in the ampoule. Then the H₂O of the initial H₃BO₃ may be transformed to boracite as in mode 5.

4.3.1. CVD

CVD mode 1 corresponds to the situation where the gaseous boron oxide hydrates and (BOCl)₃ are obtained by reaction of H₂O/HCl gas with B₂O₃(l) (reactions 5 to 8). In the presence of a carrier gas, the number of degrees of freedom is four (for example: total pressure, temperature, H₂O/HCl pressure ratio, and NiCl₂ partial pressure).

CVD mode 2 applies if the gaseous boron oxide hydrates and (BOCl)₃ are produced by means of hydrolysis of BC₁₃ in such a way as to avoid the condensation of B₂O₃(l) (see section 4.2.2.2). As can be seen from table 6 the CVD mode 2 offers the largest number of degrees of freedom (five, if a carrier gas is used). Therefore it is the most versatile but also the most difficult experimental situation because all these parameters have to be rigorously controlled.

5. Properties of the Ni₃B₇O₁₃Cl layers

5.1. CVT layers

The quality of the CVT layers was very much superior to those obtained by CVD. The properties
of the CVT layers will therefore be discussed in some
detail in this paragraph.

5.1.1. Nucleation of the layers

In an attempt to obtain a glimpse of the initial
stages of growth, a Cr–Cl boracite substrate with
growth steps (step height 0.1 μm) and very smooth
intermediate terraces (fig. 4a) has been inserted dur­
ing 5 min into the furnace. This resulted in a maximal
temperature of 825°C inside the ampoule (test on
dummy). As can be seen from the photograph in
reflected light and Nomarski contrast, small islands of
about 550 Å thickness have been formed on the ter­
races (fig. 4b). Along the steps the islands have
already collapsed, showing easier nucleation along
these lines. The domains were too thin for the deter­
mination of the orientation of the spontaneous polar­
ization by optical means.

5.1.2. The thickness of the produced layers

The thickness of the produced layers ranged
between <1 and 100 μm. The measurement of the
thickness was done by one or both of the following
two methods:

(i) If the ferroelectric domains of Ni–Cl boracite are
oriented with their spontaneous polarization perpen­
dicular to the surface, the birefringence Δnγα = 0.022 [2] corresponds to that orientation. By mea­
suring the retardation by means of a compensator,
the thickness d is obtained by the relation

\[ d = \frac{T}{\Delta n_{\gamma\alpha}} \]

where T is the path difference. The method
is not applicable if spurious domains of other orienta­
tions interfere.

(ii) By preparing a polished orthogonal section
through the sandwich substrate + layer, the layer
thickness can be measured directly by means of a
measuring ocular.

Both methods have an accuracy of about ±0.8 μm
for an objective 40X and an ocular 20X.

5.1.3. The smoothness or roughness of the layer sur­
face

The smoothness or roughness of the layer surface
is essentially ruled by the quality of the substrate sur­
face. The smoothest layer surface was obtained on
substrates on which no growth centre and no growth
step could be seen (fig. 5). The next best layers were
those obtained on as-grown substrates with a single
growth centre and flat vicinal facets showing no
growth steps (fig. 6a). By means of Nomarski inter­
fERENCE contrast (fig. 6b) many tiny growth hillocks
indicate a very homogeneous distribution of nuclei.
The very homogeneous extinction in transmission
(fig. 6c) indicates a very uniform thickness (about
1 μm).

Polished surfaces (fig. 7a) often resulted in layers
with uneven growth hillocks (figs. 7b and 7c).

5.1.4. Domain properties

5.1.4.1. Static properties. The as-grown CVT layers of
a thickness equal or smaller than about 10 μm were
characterized by ferroelectric domains with the
spontaneous polarization oriented up and down (fig. 8) only. With a magnification of 800X, domains with a diameter below 1 \( \mu \text{m} \) can be seen. The domain walls appear as dark lines, if viewed with crossed polarizers (fig. 8a), with an apparent width of about 0.3 \( \mu \text{m} \).

Fig. 6. Layer of Ni–Cl boracite (1 \( \mu \text{m} \) thick) on Cr–Cl boracite (70 \( \mu \text{m} \) thick) prepared in a sealed ampoule. Up-down domains only. (a) Virgin surface of substrate, one growth centre, vicinal facets without visible growth steps. (b) Surface of layer in reflected light, Nomarski contrast. (c) Layer in transmitted light, crossed polarizers, path difference compensated for one domain orientation.
Fig. 7. Growth of a Ni–Cl boracite layer on a polished substrate; (a) polished substrate, interference fringes; (b) growth hillocks on layer, Nomarski contrast; (c) interference fringes corresponding to (b).

Fig. 8. Ferroelectric domains with antiparallel spontaneous polarization (perpendicular to surface) of a 2 μm thick layer of Ni–Cl boracite on Cr–Cl boracite (70 μm thick); ampoule CVT method; filter: λ = 546 nm; transmitted light: (a) crossed polarizers, vibration direction parallel (100)_{cub}; (b) ditto, but compensation of path difference for domains of one of the polarities; (c) schematic.
However, since the resolving power $\lambda/2A$ was 0.32 $\mu$m (wavelength $\lambda = 0.55 \mu$m, aperture $A = 0.85$) the real thickness is probably much smaller.

The two kinds of thickness measurement (see section 5.1.2) gave the same result showing that the domains penetrated the entire thickness of the layer.

Layers with a thickness above about 10 $\mu$m usually showed also domains having their spontaneous polarization oriented within the plane of the layer. This shows that for thin layers there exists a mechanical interaction with the substrate, whereas thick layers behave like free bulk crystals.

In some samples the regions (domains) with equal orientation of polarization were much larger (fig. 9). In that case fine lines were observed which were surrounded on either side by domains of equal orientation of polarization. These lines are supposed to be micro-fissures.

5.1.4.2. Quasistatic switching. The testing of the switching of the samples was done in three different ways:

(i) Sample without electrodes, transparent In$_2$O$_3$

Fig. 9. Large ferroelectric up-down domains of a Ni–Cl boracite layer (thickness 5–6 $\mu$m). (a) and (b) correspond to compensation of the path difference of the opposite domains; the net of lines is probably caused by microfissures.
electrodes of switching device (fig. 10) in direct contact with sample.

(ii) Test as under (i) but layer covered with transparent In$_2$O$_3$ electrode.

(iii) Test as under (i) but after removal of In$_2$O$_3$ layer of (ii) by means of HCl.

For a particular sample (fig. 11) the poling of the ferroelectric layer started at about 100 kV cm$^{-1}$ and saturation was achieved at $\sim$500 kV cm$^{-1}$ for one polarity (fig. 11c), with nearly 100% remanence (fig. 11d). For the opposite polarity only about one third of the surface was saturable (fig. 11a) and the remanence of that part was less than 100% (fig. 11b). The same sample under condition (ii) could not be switched at all, whereas after removal of the In$_2$O$_3$ electrode, the initial behaviour has been reestablished. This showed that the In$_2$O$_3$ electrode blocked the switching entirely by mechanical interaction (blocked ferroelasticity). The substrate-layer interaction seems to block only partially.

5.2. Properties of CVD layers

The quality of the layers achieved with the CVD experiments was much less satisfactory than that

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Fig. 11. Switching properties of a 2 µm thick layer of Ni–Cl boracite on a 50 µm thick substrate of Cr–Cl boracite: transparent gold electrodes; (a) +500 kV cm$^{-1}$; (b) remanence of (a); (c) −500 kV cm$^{-1}$; (d) remanence of (c).
obtained by the CVT process. A typical surface state is shown in fig. 12 (scanning electron microscope photograph) which shows a strong influence of the gas flow. The layers did not show the up-down patterns. The switching behaviour has not been studied.

6. Some thermodynamic considerations

In table 4 some plausible reactions have been written down concerning CVT and CVD of Ni$_3$B$_7$O$_5$Cl, B$_2$O$_3$, NiCl$_2$, (3 NiO) ÷ B$_2$O$_3$ and NiO (reactions 1 to 14). The convention used by Schäfer [32] for transport reactions of writing the condensed phase on the left hand side of the equation, has been respected. If the equations are read from right to left, they describe CVD synthesis reactions. The reaction enthalpy ($\Delta H^R_{298}$), the reaction entropy ($\Delta S^R_{298}$), the free energy of reaction at 1147 K, ($\Delta G^R_{1147}$) and the logarithm of the equilibrium constant $K_p$ have also been indicated in table 4.

The free energy of reaction and the equilibrium constant have been calculated by means of the so-called “First Approximation”:

$$\Delta H^R_{298} - T\Delta S^R_{298} = \Delta G^R_T$$

$$= -RT \log K_p \ .$$

Table 7

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^R_{298}$ (kcal mol$^{-1}$)</th>
<th>$\Delta S^R_{298}$ (cal deg$^{-1}$ mol$^{-1}$)</th>
<th>Ref.</th>
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<td>HCl(g)</td>
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<td>[41]</td>
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<td>NiCl$_2$(g)</td>
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<td>NiO(s)</td>
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<td>(3NiO)B$_2$O$_3$(s)</td>
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</tr>
<tr>
<td>B$_2$O$_3$(l)</td>
<td>-299.28 ± 0.4</td>
<td>18.739</td>
<td>[41]</td>
</tr>
<tr>
<td>H$_3$BO$_3$(g)</td>
<td>-237.16 ± 0.6</td>
<td>[70.539]</td>
<td>[41]</td>
</tr>
<tr>
<td>HBO$_2$(g)</td>
<td>-134.0 ± 1</td>
<td>[57.273]</td>
<td>[41]</td>
</tr>
<tr>
<td>(HBO$_2$)$_3$(g)</td>
<td>-543 ± 3</td>
<td>[83.047]</td>
<td>[41]</td>
</tr>
<tr>
<td>(BO$_2$CO$_3$)(g)</td>
<td>-390 ± 2</td>
<td>[91.367]</td>
<td>[41]</td>
</tr>
<tr>
<td>BCl$_3$(g)</td>
<td>-96.31 ± 0.5</td>
<td>69.328</td>
<td>[41]</td>
</tr>
</tbody>
</table>

a) $\Delta H^R_{298}$, reaction from 3NiO + B$_2$O$_3$, and $\frac{3}{2}$NiO + $\frac{5}{2}$B$_2$O$_3$ + NiCl$_2$, increased negatively by 1%, real value probably still more negative.

b) $\Delta S^R_{298}$: by using “Kelley’s sum rule”, see e.g. ref. [38], this paper.

The positive sign of ($\Delta H^R_{298}$) of the CVT reactions of Ni$_3$B$_7$O$_5$Cl (reactions 1 to 4), (3 NiO) ÷ B$_2$O$_3$ (reactions 11 to 14), NiO (reaction 10) and B$_2$O$_3$ (reactions 5 and 8) indicates [32] that transport should occur from the higher to the lower temperature. This expectation has repeatedly been confirmed for Ni$_3$B$_7$O$_5$Cl (see section 4). The negative sign of ($\Delta H^R_{298}$) of reactions 6 and 7 shows their tendency to transport B$_2$O$_3$ also in the opposite sense.

The negative sign of log $K_p$ shows that all the equilibria listed are shifted to the left hand side. However, the relatively small absolute value of log $K_p$ of reactions 3 and 6 would suggest that the boracite and B$_2$O$_3$ transport essentially proceeds via (HBO$_2$)$_3$. Because log $K_p$ of reactions 5, 7, 8, 17 and 19 is rather small, too, the participation of HBO$_2$, H$_3$BO$_3$, (BO$_2$CO$_3$, BCl$_3$ cannot be excluded. At this stage no statement can be made concerning the reaction mechanisms at the surface of the crystals.

As can be seen from fig. 13, the partial pressure of HBO$_2$ dominates below about 120 Torr (at 874°C) H$_2$O pressure and the pressures of H$_3$BO$_3$ and (HBO$_2$)$_3$ dominate above about 120 Torr H$_2$O if
liquid $\text{B}_2\text{O}_3$ is present. The boracite syntheses were all carried out below $10^2$ Torr $\text{H}_2\text{O}$ where HBO$_2$ is the dominating boron/oxide hydrate. The curves of fig. 13 have been calculated using the $K_p$ data of Blauer and Farber [33] for reactions 5, 6 and 7. Because no error limits had been given for the experimentally determined $K_p$ of reaction 7, the curve corresponding to H$_3$BO$_3$ may in reality be shifted parallel to itself to an appreciable extent.

With a view to the great number of gaseous species present in the CVD and CVT synthesis of boracites, future studies of the chemistry of boracite synthesis will require computer based equilibrium (etc.) calculations using a free energy minimization approach. In a preliminary trial Diehl [34] has calculated the partial pressures of the gaseous species for the case of CVT of Ni$_3$B$_7$O$_{13}$Cl using the approach and program of Nolang and Richardson [35–37]. The results are shown in table 8.

The interesting features of Diehl’s computation are the following:

(i) the only condensed phases occurring are Ni$_3$B$_7$O$_{13}$Cl and $\text{B}_2\text{O}_3$(l). This means that partial decomposition of boracite occurs under the chosen conditions. As has been shown by experiment (see section 4.2.1.3), the decomposition of Ni–Cl boracite to $\text{B}_2\text{O}_3$ is entirely suppressed if $\text{B}_2\text{O}_3$(l) and NiCl$_2$(s) are charged into the ampoule right from the beginning.

(ii) The total pressure is nearly entirely made up of HCl gas, a result which agrees well with experiment (see section 4.2.1.4).

(iii) Beside the initially proposed gaseous species (see table 4) it is interesting to note that also H$_2$, Cl$_2$, Cl, NiCl and BCl have to be considered, if about $10^{-7}$ atm is taken as a lower limit of importance for the partial pressure.

(iv) The case where the total pressure equals 1 atm (table 8), comes close to the conditions for CVD which was nearly always run at about 1 atm total pressure (see section 4.2.2). The case where the total pressure equals 5 atm comes close to the CVT conditions realized in the closed ampoules [19] and which were sometimes run even up to a total pressure of about 15 atm.

(v) Table 8 shows well how the relative importance of (BOCl)$_3$, BCl$_3$, H$_3$BO$_3$ and (HBO$_2$)$_3$ increases as expected in passing from a total pressure of 1 to 5 atm.

More detailed work on the thermodynamic basis of boracite synthesis is underway.

Table 8

<table>
<thead>
<tr>
<th>Vapour species</th>
<th>Partial pressure (atm)</th>
<th>Partial pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 atm</td>
<td>5 atm</td>
</tr>
<tr>
<td>HCl</td>
<td>0.983</td>
<td>0.493 x 10^-1</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>0.920 x 10^-2</td>
<td>0.396 x 10^-1</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.769 x 10^-2</td>
<td>0.335 x 10^-1</td>
</tr>
<tr>
<td>(BOCl)$_3$</td>
<td>0.240 x 10^-4</td>
<td>0.331 x 10^-3</td>
</tr>
<tr>
<td>HBO$_2$</td>
<td>0.490 x 10^-4</td>
<td>0.102 x 10^-3</td>
</tr>
<tr>
<td>H$_3$BO$_3$</td>
<td>0.311 x 10^-4</td>
<td>0.150 x 10^-3</td>
</tr>
<tr>
<td>BCl$_3$</td>
<td>0.166 x 10^-4</td>
<td>0.230 x 10^-3</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>0.264 x 10^-4</td>
<td>0.137 x 10^-3</td>
</tr>
<tr>
<td>Cl</td>
<td>0.186 x 10^-4</td>
<td>0.423 x 10^-4</td>
</tr>
<tr>
<td>H$_3$BO$_3$</td>
<td>0.101 x 10^-4</td>
<td>0.925 x 10^-4</td>
</tr>
<tr>
<td>NiCl</td>
<td>0.923 x 10^-5</td>
<td>0.174 x 10^-4</td>
</tr>
<tr>
<td>(HBO$_2$)$_3$</td>
<td>0.750 x 10^-5</td>
<td>0.683 x 10^-4</td>
</tr>
<tr>
<td>BOCl</td>
<td>0.515 x 10^-6</td>
<td>0.124 x 10^-5</td>
</tr>
</tbody>
</table>
7. Conclusions

The synthesis of epitaxial boracite layers by means of CVT and CVD has proved feasible. So far the best layers have been obtained by CVT. The CVD methods also appear promising for making single crystals and mixed crystals. Further improvement of the methods will require studies of thermodynamic parameters, phase diagrams, reaction kinetics, reaction mechanisms and gas dynamics (mixing). For the technical application (electro-optics) of the layers, the development of shear free compositions and conducting transparent substrates would be mandatory.

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References


[34] R. Diehl, Institut für Angewandte Festkörperforschung Freiburg i. Br., private communication.


