Flux growth of ZnGa2O4 single crystals

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FLUX GROWTH OF ZnGa₂O₄ SINGLE CRYSTALS

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Single crystals of ZnGa₂O₄ have been grown from a PbO—PbF₂—B₂O₃ flux. By addition of SiO₂ to this flux, inclusion free crystals of maximum dimensions of 10 mm along the edge have been obtained. We have also studied the growth of ZnGa₂O₄ from less volatile melts, such as the Na₂O—ZnO—Ga₂O₃ system and a Pb₂P₂O₇ flux. From the Na₂O—ZnO—Ga₂O₃ system only very small ZnGa₂O₄ crystals could be grown. From the Pb₂P₂O₇ flux, inclusion free crystals, the largest about 7 mm along an edge, have been obtained using a ZnO/Ga₂O₃ molar ratio equal to 4. Lattice constants are reported for the temperature range from 20°C to 1200°C.

In view of the increasing interest [1—4] for single crystal films of magnetic spinel ferrites, the need is felt for suitable non-magnetic substrates. In a recent article [2] we have pointed out that gallates are suited in this respect. In this study we discuss the growth of ZnGa₂O₄ single crystals as a possible substrate material.

The crystals obtained in this study were in general octahedrally shaped, optically clear and free of inclusions. Flux residues were leached away in a mixture of hot dilute acetic acid and nitric acid.

Crystals of ZnGa₂O₄ have been grown by Chase and Osmer [5] from a PbO—PbF₂—B₂O₃ flux containing ZnO and Ga₂O₃ in a 1 : 1 molar ratio. We have used this melt composition (cf. table 1) for the growth of ZnGa₂O₄ from 60 ml platinum crucibles. By cooling [6] this melt from 1250 to 1000°C at a rate of 0.5°C/h crystals of dimensions up to 5 mm along the edge were obtained.

We have found that the crystal dimensions could be increased by addition of SiO₂ to the melt in a similar way as reported by Bonner [7] for the growth of ZnAl₂O₄. Using a melt composition given in table 1 and the growth procedure described above, crystals measuring up to 10 mm along the edge were obtained (see fig. 1).

The Si content of the crystals, as measured by spectrochemical analysis, is of the order of 0.002 atoms per formula unit, which is the same as in crystals grown without the addition of SiO₂ to the melt. Thus SiO₂ apparently has only beneficial effects on the growth of ZnGa₂O₄.

In the search for crystallization systems which are

<table>
<thead>
<tr>
<th>Reference</th>
<th>PbO</th>
<th>PbF₂</th>
<th>B₂O₃</th>
<th>SiO₂</th>
<th>ZnO</th>
<th>Ga₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chase and Osmer [5]</td>
<td>20.0</td>
<td>68.0</td>
<td>2.0</td>
<td>—</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Bonner [7]</td>
<td>29.34</td>
<td>32.65</td>
<td>5.22</td>
<td>15.13</td>
<td>7.57</td>
<td>10.09</td>
</tr>
</tbody>
</table>
less volatile than PbO—PbF₂—B₂O₃ and which might allow top seeded growth of ZnGa₂O₄ we have tried the system Na₂O—ZnO—Ga₂O₃. The melt compositions (given in table 2) are similar to those used for the growth of spinel ferrites MFe₂O₄ from the system Na₂O—MO—Fe₂O₃ [8,9]. By cooling these melts from 1400 to 900°C at a rate of 5°C/h, however, only tiny ZnGa₂O₄ crystals (<0.5 mm) were obtained.

Better results have been obtained by using Pb₂P₂O₇ as a solvent, this is non-volatile, relatively low melting (824°C [10]) and it provides good nucleation conditions [11]. Wickham [12] reported the preparation of Pb₂P₂O₇ from Pb(NO₃)₂ and H₃PO₄ and used it as a flux for the crystal growth of MgFe₂O₄. In order to avoid the crystallization of second phases, the MgO/Fe₂O₃ molar ratio had to be >4.

In view of these results we have prepared melts of Pb₂P₂O₇, ZnO and Ga₂O₃ with different ZnO/Ga₂O₃ ratios (cf. table 3) in 13 ml platinum crucibles. The melts were cooled from 1300 to 900°C at a rate of 5°C/h. ZnGa₂O₄ was found to be the primary phase

![Fig. 1. Photograph of ZnGa₂O₄ crystals grown from the PbO—PbF₂—B₂O₃ flux with SiO₂ additive.](image)

Table 2
Melt compositions in mole% for ZnGa₂O₄ crystal growth from the Na₂O/ZnO/Ga₂O₃ system

<table>
<thead>
<tr>
<th>Melt</th>
<th>Na₂O</th>
<th>ZnO</th>
<th>Ga₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>22.2</td>
<td>27.8</td>
<td>50.0</td>
</tr>
<tr>
<td>B</td>
<td>20.0</td>
<td>30.0</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Table 3
Melt compositions in mole% for ZnGa₂O₄ crystal growth from a Pb₂P₂O₇ flux

<table>
<thead>
<tr>
<th>Melt</th>
<th>Pb₂P₂O₇</th>
<th>ZnO</th>
<th>Ga₂O₃</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>Ga₂O₃ + ZnGa₂O₄</td>
</tr>
<tr>
<td>II</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>ZnGa₂O₄</td>
</tr>
<tr>
<td>III</td>
<td>40</td>
<td>48</td>
<td>12</td>
<td>ZnGa₂O₄</td>
</tr>
<tr>
<td>IV</td>
<td>40</td>
<td>53.5</td>
<td>6.7</td>
<td>ZnGa₂O₄</td>
</tr>
</tbody>
</table>
crystallizing from melts with a ZnO/Ga$_2$O$_3$ molar ratio $\geqslant$2. Although the habit of the ZnGa$_2$O$_4$ crystals was chiefly octahedral also a few ZnGa$_2$O$_4$ needles and plates (confirmed by X-ray diffraction) were observed. The largest crystals, about 3 mm along the edge, were obtained from melt III with a ZnO/Ga$_2$O$_3$ molar ratio equal to 4.

The crystal dimensions could be increased to 7 mm along the edge by using 60 ml platinum crucibles and applying a temperature gradient of about 5°C/cm. This was achieved by locating the crucible directly on the relatively cold furnace floor or by applying a jet of cold air to the bottom.

Because the crystals are intended to be used as substrates for LPE of spinel ferrites, knowledge of the temperature dependence of the lattice constant is important. This temperature dependence was determined in steps of 200°C between 20 and 1200°C with the aid of high temperature diffractometry. The data could be fitted within 0.002 Å to the expression:

$$a(\text{Å}) = 8.332 + 6.18 \times 10^{-5} T + 1.60 \times 10^{-8} T^2,$$

where $T$ is the temperature in °C.

The ZnGa$_2$O$_4$ crystals have been used successfully as substrates for LPE growth of gallium substituted MgFe$_2$O$_4$. Epitaxial thin films were grown on the (111) growth facets of the substrate crystals.

In order to obtain substrates with higher lattice constants, we have grown indium substituted ZnGa$_2$O$_4$ crystals. However, hardly any indium was incorporated in the crystals: by substitution of 20% of the Ga$_2$O$_3$ in the melt by In$_2$O$_3$ the lattice constant of the crystals increased with only 0.002 Å.

High quality crystals of ZnGa$_2$O$_4$ can be grown from a PbO–PbF$_2$–B$_2$O$_3$ flux with SiO$_2$ as an additive. The size of the resulting crystals is large enough to allow their use as substrates in preliminary LPE growth of spinel ferrites. It is found that Pb$_2$P$_2$O$_7$ is an attractive non-volatile solvent for the growth of ZnGa$_2$O$_4$ crystals. This system might be a good candidate for topseeded growth.

The authors would like to thank Mr. F.C. Krüger for the high temperature diffractometry work.

References