Flux growth of the rare earth germanates

BARBARA M. WANKLYN
Clarendon Laboratory, University of Oxford, UK

The growth of the compounds $R_2Ge_2O_7$ from lead fluoride flux, and of $R_2GeO_5$ and $R_2GeO_5$ from lead germanate fluxes, is described ($R = Tb$ to $Lu$). The magnetic transition temperatures are given.

1. Introduction
The present interest in this system arose from the probability that the rare earth germanate compounds, being concentrated in rare earth ions, would have interesting magnetic properties. Studies of the reaction of precipitated and sintered samples [1, 2] indicate that, besides the solid solution of $GeO_2$ in $R_2O_3$, the system contains three phases: $R_2GeO_8$, $R_2GeO_5$ and $R_2GeO_5$ ($R = Tb$ to $Lu$), and the present work describes crystal growth experiments in this system.

The compounds $R_2Ge_2O_7$, with $R = Tb$ to $Lu$, are tetragonal, space group $D_4^4$ [3], while $Gd_2Ge_2O_7$ is of lower symmetry [4]. The $R_2GeO_5$ compounds, isostructural with $R_2SiO_5$, are monoclinic, $C_{2h}$ or $C_{1h}$ [5]. $R_2Ge_2O_7$ [6] and $R_2GeO_5$ [5] have been grown as single crystals from $Bi_2O_3$ as flux. The space group of $R_2GeO_5$ indicates that the crystals should be optically active and, below their transition temperatures, potentially magnetoelectric. In the case of $R_2GeO_5$, its space group does not exclude the magnetoelectric effect. Single crystals of $R_4GeO_8$ have not previously been prepared and the structure was not known.

Since $Bi^{3+}$ tends to replace $R^{3+}$ to an extent varying from 3 to 20%, and since 4% $Bi$ was found in the $Er_2GeO_5$ crystals [5], an alternative flux system was sought which would contaminate the crystals to a lesser degree. For the proposed experiments, contamination of the crystals with up to 1% of a non-magnetic impurity could be tolerated.

2. Materials and equipment
99.9% $R_2O_3$, “Analar” grade PbO and PbO$_2$, BDH Laboratory reagent grade GeO$_2$, and BDH “extra pure” PbF$_2$ were used.

Crucibles of pure platinum, with closely fitting lids, were used to contain the melts. The crucibles were embedded in hollows in M.1.3000 refractory brick, with alumina powder packed around the crucible bases. When volatile fluxes were used (PbF$_2$, PbO + PbF$_2$), the crucibles were supported in refractory brick within a sillimanite muffle, with the open end blocked with brick at the furnace entrance. By this means the furnace and elements were protected from the highly-reactive vapour. In both cases the position of each crucible was such that the bottom was cooler than the top by a few degrees. The furnaces have been described previously [7].

3. Crystal growth experiments
3.1. PbF$_2$ as flux
Preliminary experiments with the following fluxes gave negative results: PbO, Li$_2$Mo$_2$O$_7$, PbO.2B$_2$O$_3$, Pb$_2$V$_2$O$_7$ and Na$_2$B$_4$O$_7$. Where crystals were obtained, they were found to be compounds with the flux.

$R_2Ge_2O_7$ was produced from its solution in PbF$_2$ when the temperature was held above 1200°C, allowing the flux to evaporate, but at lower temperatures ROF crystallized.

3.1.1. Identification
To assist in phase identification, samples of composition corresponding to $Er_2Ge_2O_7$, $Er_2GeO_5$ and $Er_2GeO_5$ were sintered in small platinum crucibles with closely fitting lids at 1200 to 1300°C, for 12 to 24 h. In the first two cases, the resulting X-ray powder patterns agreed closely with published data for the compounds, and for isostructural $Y_2GeO_5$ [2] and $Y_2Ge_2O_7$ [2, 8]. With sintered material of
composition $R_2GeO_5$, the strong lines agreed with published data for $Y_4GeO_9$ [2, 9], but there was not complete correspondence with the weaker lines.

### 3.1.2. Results

The $R_6Ge_2O_7$ crystals were identified by their X-ray powder patterns which closely resembled that of the sintered $Er_2Ge_2O_7$ and agreed with published data [2, 8]. The crystal platelets were transparent and optically isotropic under the polarizing microscope, indicating that the $c$-axis was perpendicular to the platelets. There was a tendency for cleavage to occur in the $\{010\}$ planes. The crystals showed optical activity, and the typical colours of the rare earth ions. Only a few crystals nucleated and grew, but layer growth tended to occur with flux occluded between the layers. In growth by flux evaporation, good quality is achieved only in exceptional cases.

The phase $R_2Ge_2O_7$ remained the primary phase when the ratio $R_2O_3:GeO_2$ was near 1:2. $R_4GeO_8$ did not occur at all, but a second phase for which the strong lines of the X-ray powder pattern were in agreement with that of the compound “$R_4GeO_8$” [2, 9] sometimes appeared as small, transparent, faceted crystals which showed extinction under the polarizing micro-

<table>
<thead>
<tr>
<th>Composition of mixture</th>
<th>Holding time and rate of cooling</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7g $Er_2O_3$, 1.5g $GeO_2$, 1g $PbO_2$, Held at 1270°C for 1 week</td>
<td></td>
<td>$Er_2GeO_7$, thin rectangular plates, 8 mm edge</td>
</tr>
<tr>
<td>43g PbF$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4g $Er_2O_3$, 2.5g $GeO_2$, Held at 1290°C overnight. Cooled at 6°C h$^{-1}$ to 800°C</td>
<td></td>
<td>$Er_2GeO_7$ rods, 1 cm x 3 mm wide. The long axis is the 2-fold monoclinic axis. Fig. 3a (Crucible was attacked)</td>
</tr>
<tr>
<td>0.5g $PbO_2$, 18g PbO</td>
<td></td>
<td>$Ho_2GeO_4$ and $Ho_2Ge_2O_7$ prisms. Figs. 3b, 4a and c.</td>
</tr>
<tr>
<td>2.5g $Ho_2O_3$, 6.7g $GeO_2$, 4g $PbO_2$, Held at 1270°C for 10 h. Cooled at 25.2g PbO, 5°C h$^{-1}$ to 800°C</td>
<td></td>
<td>$Er_2GeO_7$ only. Fig. 4b</td>
</tr>
<tr>
<td>2.0g $Er_2O_3$, 5.7g $GeO_2$, 3g $PbO_2$, Held at 1270°C for 10 h. Cooled at 17.4g PbO, 5°C h$^{-1}$ to 800°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 Crystals of $Yb_2GeO_7$ at the base of a 1.5 cm diameter crucible, after evaporation of PbF$_2$. 

650