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Flux growth of the rare earth germanates

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The growth of the compounds $R_2Ge_2O_7$ from lead fluoride flux, and of $R_2Ge_2O_7$ 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_4GeO_8, R_2GeO_5 and $R_2Ge_2O_7$ (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 $R_2Ge_2O_7$ 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, $Li_2Mo_2O_7$, $PbO.2B_2O_3$, $Pb_2V_2O_7$ and $Na_2B_4O_7$. 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_4GeO_8 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_4GeO_8, the strong lines agreed with published data for Y_4GeO_8 [2, 9], but there was not complete correspondence with the weaker lines.

3.1.2. Results

The $R_2Ge_2O_7$ 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_2GeO_5 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 I Conditions for flux growth of rare earth germanates

Composition of mixture	Holding time and rate of cooling	Result
2.7g Er_2O_3, 1.5g GeO_2, 1g PbO_2, 43g PbF_2	Held at 1270°C for 1 week	$Er_2Ge_2O_7$, thin rectangular plates, 8 mm edge
1.4g Er_2O_3, 2.5g GeO_2, 0.5g PbO_2, 18g PbO	Held at 1290°C overnight. Cooled at 6° h^{-1} to 800°C	Er_2GeO_5 rods, 1 cm × 3 mm wide. The long axis is the 2-fold monoclinic axis. Fig. 3a (Crucible was attacked)
2.5g Ho_2O_3, 6.7g GeO_2, 4g PbO_2, 25.2g PbO	Held at 1270°C for 10 h. Cooled at 5° hr^{-1} to 800°C	Ho_2GeO_5 and $Ho_2Ge_2O_7$ prisms. Figs. 3b, 4a and c.
2.0g Er_2O_3, 5.7g GeO_2, 3g PbO_2, 17.4g PbO	Held at 1270°C for 10 h. Cooled at 5° h^{-1} to 800°C	Er_2GeO_7 only. Fig. 4b

Figure 1 Crystals of $Yb_2Ge_2O_7$ at the base of a 1.5 cm diameter crucible, after evaporation of PbF_2.

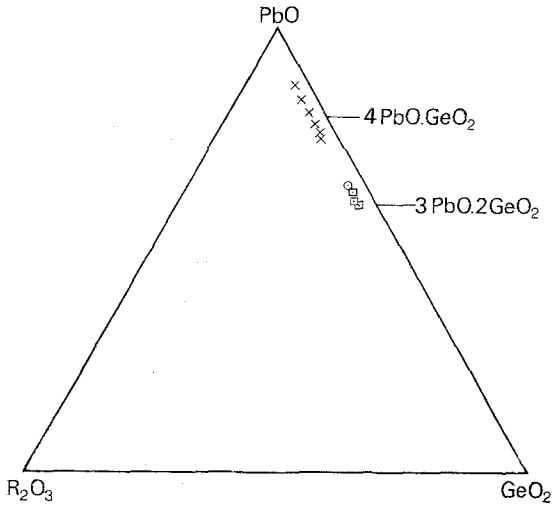


Figure 2 Composition diagram for the system R_2O_3–GeO_2–PbO. X: R_2GeO_5 crystallized. ⊡: $R_2Ge_2O_7$ crystallized. ○: Both phases crystallized.

scope. It appeared that $R_2Ge_2O_7$ crystallized until the solution became too deficient in the rather volatile GeO_2 for further crystallization of $R_2Ge_2O_7$ to continue, and R_4GeO_8 then appeared. This phase is being investigated, and results will be published at a later date.

Fig. 1 shows crystals of $Yb_2Ge_2O_7$ which grew at the base of a 10 ml. crucible, and Table I gives typical flux growth compositions and conditions.

3.2. Experiments in the system R_2O_3-GeO_2-PbO

The system R_2O_3–GeO_2–PbO should contain regions where the rare earth germanates are stable, and since part of the PbO–GeO_2 phase diagram [11] has low liquidus temperatures (minimum 710° C), the growth of crystals of the relatively high-melting germanates in this system was considered to be feasible. The presence of Ge^{4+} in the (effective) flux would be an advantage, as an ion in common with the crystal phase is preferable to contamination by foreign ions. Since Pb^{2+} normally replaces R^{3+} to a limited degree only, typically from 0.03% (in $GdVO_4$ [12]) to 0.3% (in $GdAlO_3$ and $DyAlO_3$]13]), lead contamination would be small.

Crystal growth experiments in the system were carried out in 10 cc crucibles using varied proportions of PbO, GeO_2 and R_2O_3. PbO_2 was included to provide initial oxidizing conditions, and the furnace was heated at approximately 120° C h^{-1} to the maximum temperature. The soak temperature chosen at first was 1290° C, but as the crucibles were severely attacked this was reduced to 1270° C. After 10 h at this temperature, the furnace was slowly cooled to 750° C, and then more rapidly to room temperature.

Fig. 2 shows the phases obtained at various

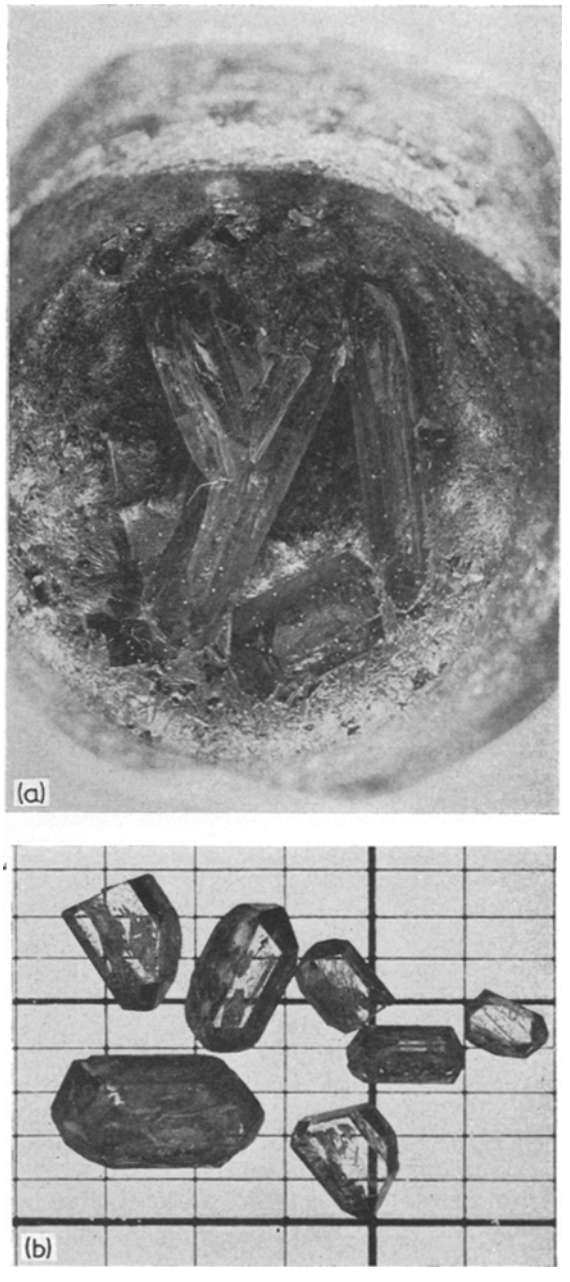
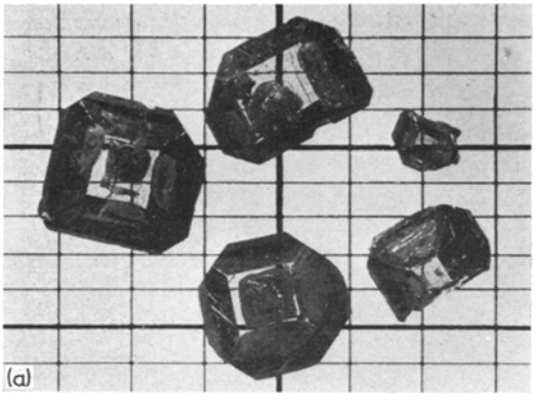
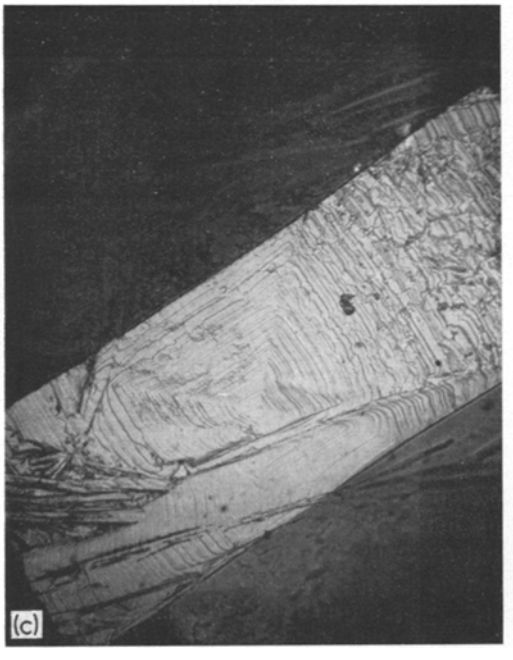


Figure 3 (a) Crystals of Er_2GeO_5 in 1.5 cm diameter crucible. (b) Ho_2GeO_5 crystals on mm grid.





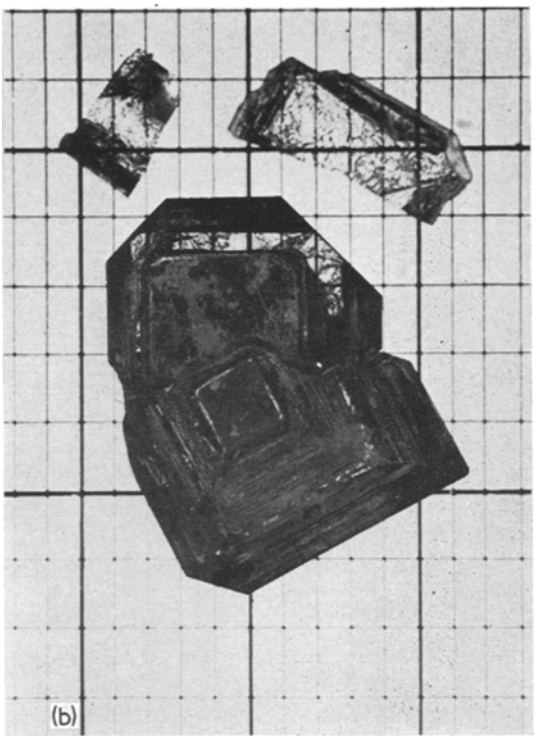


Figure 4 (a) $Ho_2Ge_2O_7$ crystals on mm grid. (b) $Er_2Ge_2O_7$ crystals on mm grid. (c) Vicinal faces on {100} face of $Ho_2Ge_2O_7$, indicating stable growth under low supersaturation (× 82).

compositions, and Table I gives the compositions and conditions which produced the largest crystals.

3.2.1. Results

$PbO–GeO_2$ was found to be extremely satisfactory as a flux. The phase obtained depended on the $PbO:GeO_2$ ratio, as shown in Fig. 2. Rods of Er_2GeO_5 8 mm on edge, shown in Fig. 3a, were produced from a batch only 5 cc in volume, with a cooling rate as rapid as 5°C h^{-1}. The typical weight loss was 8% with a loosely fitting lid and near zero with a close-fitting lid. Fig. 3b shows Ho_2GeO_5 prisms on a mm grid after cleaning in hot dilute nitric acid. $R_2Ge_2O_7$ crystals grew as platelets at the melt surface, with the *c*-axis perpendicular to the plates. As shown in Fig. 4a and b, these were typically transparent and faceted at their under surfaces.

In Fig. 4c, the {100} face underneath a $Ho_2Ge_2O_7$ crystal, which grew floating on the melt surface, is shown; vicinal faces such as these are characteristic of stable crystal growth under conditions of low supersaturation.

With a high $PbO:GeO_2$ ratio, all the crystals grew at the surface, presumably because the flux was of higher density than the crystals. With decreasing $PbO:GeO_2$ ratio, and decreasing flux density, multi-faceted crystals grew also at the crucible base.

4. Magnetic transitions

These were observed in four of the compounds $R_2Ge_2O_7$ and in two of the compounds R_2GeO_5 [10]. The transition temperatures are given in Table II.

5. Conclusion

Good quality crystals of the phases R_2GeO_5 and

TABLE II Magnetic transition temperatures. (T, K) [10]

$R_2Ge_2O_7$	T(K)	R_2GeO_5	T(K)
$Tb_2Ge_2O_7$	2.05 ± 0.05		
$Dy_2Ge_2O_7$	2.15 ± 0.05	Dy_2GeO_5	2.5 ± 0.1
$Ho_2Ge_2O_7$	1.45 ± 0.05	Ho_2GeO_5	—
$Er_2Ge_2O_7$	1.15 ± 0.05	Er_2GeO_5	1.25 ± 0.1
$Tm_2Ge_2O_7$	—		

$R_2Ge_2O_7$ have been grown from PbO–GeO_2 as flux, and with larger batches and slower cooling rates, larger, better quality crystals may be expected. PbO–GeO_2, which has not been reported previously as a flux system, may prove suitable for the growth of additional germanates and possibly for other compounds. Work is being continued in these directions.

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