Flux growth of ZnGa_2O_4 single crystals

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FLUX GROWTH OF ZnGa_2O_4 SINGLE CRYSTALS

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Single crystals of ZnGa_2O_4 have been grown from a $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$ flux. By addition of SiO_2 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 ZnGa_2O_4 from less volatile melts, such as the $\text{Na}_2\text{O-Zn}_2\text{O}_3\text{-Ga}_2\text{O}_3$ system and a $\text{Pb}_2\text{P}_2\text{O}_7$ flux. From the $\text{Na}_2\text{O-ZnO-Ga}_2\text{O}_3$ system only very small ZnGa_2O_4 crystals could be grown. From the $\text{Pb}_2\text{P}_2\text{O}_7$ flux, inclusion free crystals, the largest about 7 mm along an edge, have been obtained using a $\text{ZnO/Ga}_2\text{O}_3$ 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 ZnGa_2O_4 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 ZnGa_2O_4 have been grown by Chase and Osmer [5] from a $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$ flux containing ZnO and Ga_2O_3 in a 1 : 1 molar ratio. We have used this melt composition (cf. table 1) for the growth of ZnGa_2O_4 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 SiO_2 to the melt in a similar way as reported by Bonner [7] for the growth of ZnAl_2O_4 . 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 SiO_2 to the melt. Thus SiO_2 apparently has only beneficial effects on the growth of ZnGa_2O_4 .

In the search for crystallization systems which are

Table 1

Melt compositions in mole % for ZnGa_2O_4 crystals growth from a $\text{PbO/PbF}_2/\text{B}_2\text{O}_3$ flux

Reference	PbO	PbF ₂	B ₂ O ₃	SiO ₂	ZnO	Ga ₂ O ₃
Chase and Osmer [5]	20.0	68.0	2.0	—	5.0	5.0
Bonner [7]	29.34	32.65	5.22	15.13	7.57	10.09

Fig. 1. Photograph of ZnGa_2O_4 crystals grown from the $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$ flux with SiO_2 additive.

less volatile than $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$ and which might allow top seeded growth of ZnGa_2O_4 we have tried the system $\text{Na}_2\text{O-ZnO-Ga}_2\text{O}_3$. The melt compositions (given in table 2) are similar to those used for the growth of spinel ferrites MFe_2O_4 from the system $\text{Na}_2\text{O-MO-Fe}_2\text{O}_3$ [8,9]. By cooling these melts from 1400 to 900°C at a rate of 5°C/h, however, only tiny ZnGa_2O_4 crystals (<0.5 mm) were obtained.

Better results have been obtained by using $\text{Pb}_2\text{P}_2\text{O}_7$ as a solvent, this is non-volatile, relatively low melting (824°C [10]) and it provides good nucle-

ation conditions [11]. Wickham [12] reported the preparation of $\text{Pb}_2\text{P}_2\text{O}_7$ from $\text{Pb}(\text{NO}_2)_2$ and H_3PO_4 and used it as a flux for the crystal growth of MgFe_2O_4 . In order to avoid the crystallization of second phases, the $\text{MgO/Fe}_2\text{O}_3$ molar ratio had to be >4.

In view of these results we have prepared melts of $\text{Pb}_2\text{P}_2\text{O}_7$, ZnO and Ga_2O_3 with different $\text{ZnO/Ga}_2\text{O}_3$ 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. ZnGa_2O_4 was found to be the primary phase

Table 2

Melt compositions in mole% for ZnGa_2O_4 crystal growth from the $\text{Na}_2\text{O/ZnO/Ga}_2\text{O}_3$ system

Melt	Na_2O	ZnO	Ga_2O_3
A	22.2	27.8	50.0
B	20.0	30.0	50.0

Table 3

Melt compositions in mole% for ZnGa_2O_4 crystal growth from a $\text{Pb}_2\text{P}_2\text{O}_7$ flux

Melt	$\text{Pb}_2\text{P}_2\text{O}_7$	ZnO	Ga_2O_3	Result
I	40	30	30	$\text{Ga}_2\text{O}_3 + \text{ZnGa}_2\text{O}_4$
II	40	40	20	ZnGa_2O_4
III	40	48	12	ZnGa_2O_4
IV	40	53.5	6.7	ZnGa_2O_4

crystallizing from melts with a $\text{ZnO}/\text{Ga}_2\text{O}_3$ molar ratio ≥ 2 . Although the habit of the ZnGa_2O_4 crystals was chiefly octahedral also a few ZnGa_2O_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 $\text{ZnO}/\text{Ga}_2\text{O}_3$ 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 $5^\circ\text{C}/\text{cm}$. 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 $0.002 \text{ \AA}$ to the expression:

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

where T is the temperature in $^\circ\text{C}$.

The ZnGa_2O_4 crystals have been used successfully as substrates for LPE growth of gallium substituted MgFe_2O_4 . Epitaxial thin films were grown on the $\langle 111 \rangle$ growth facets of the substrate crystals.

In order to obtain substrates with higher lattice constants, we have grown indium substituted ZnGa_2O_4 crystals. However, hardly any indium was incorporated in the crystals: by substitution of 20%

of the Ga_2O_3 in the melt by In_2O_3 the lattice constant of the crystals increased with only $0.002 \text{ \AA}$.

High quality crystals of ZnGa_2O_4 can be grown from a $\text{PbO}-\text{PbF}_2-\text{B}_2\text{O}_3$ 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 $\text{Pb}_2\text{P}_2\text{O}_7$ is an attractive non-volatile solvent for the growth of ZnGa_2O_4 crystals. This system might be a good candidate for topseeded growth.

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