

## Growth of yttrium iron garnet single crystals in $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ flux system in air

TARUN BANDYOPADHYAY and PRASENJIT SAHA  
Central Glass and Ceramic Research Institute, Jadavpur, Calcutta 700 032

MS received 23 December 1976; revised 6 April 1977

**Abstract.** Detailed studies of growth of yttrium iron garnet (YIG) in the flux system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$  were made to delineate the phase stability regions of YIG and the neighbouring crystalline phases, and a tentative working diagram of  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ -YIG in air was drawn from the results of small batch crystal growth runs and solubility studies. The occurrence of a rather narrow field of YIG crystallization in this system was explained on the basis of relative solubilities of different oxides constituting YIG. Several long-time growth runs with some typical compositions were carried out in this system to evaluate its suitability for bulk growth of YIG crystals. The system, although possessing some inherent advantages, was found to suffer from limitations because of which the maximum size of the self-nucleated crystals grown hardly exceeded 2.00 mm.

**Keywords.** Yttrium iron garnet; flux; phases; crystal growth; solubility; self-nucleation.

### 1. Introduction

Single crystals of yttrium iron garnet (YIG) have been successfully grown from  $\text{PbO}-\text{PbF}_2$  (Nielsen 1960),  $\text{PbO}-\text{PbF}_2-\text{B}_2\text{O}_3$  (Titova 1960; Grodkiewicz *et al* 1967),  $\text{BaO}-\text{B}_2\text{O}_3$  (Linares 1962, 1964; Kestigian 1967) and several other flux systems. However, the lead-based flux systems suffer from some inherent disadvantages of high toxicity and high volatilization loss. In this respect the alkali borate flux systems, as suggested by Linares (1962), appear to be quite promising. But except for  $\text{BaO}-\text{B}_2\text{O}_3$  none of them has been studied extensively. Recently,  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$  solvents have been used by a number of investigators for the growth of several other oxide crystals (Ganguli *et al* 1969; Chase *et al* 1973; Burnett *et al* 1968). The present work gives details of attempts to grow YIG crystals from this flux system.

### 2. Experimental technique and results

Reagent grade chemicals:  $\text{Y}_2\text{O}_3$  (99.9% Indian Rare Earths),  $\text{Fe}_2\text{O}_3$  (AR, Fischer),  $\text{Na}_2\text{CO}_3$  (AR, BDH) and  $\text{H}_3\text{BO}_3$  (AR, BDH) were used to prepare starting mixtures for the growth runs. The molar ratios of  $\text{Y}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in all the mixtures were kept at 3 : 5 to maintain strict stoichiometry of YIG. Crystal growth runs were carried out in a vertical tube furnace using a temperature programme controller. After complete melting, the mixtures were soaked for 3-4 hr at the same temperature

and later a cooling schedule at a programmed rate varying between 2.5° C/hr and 20°C/hr was maintained to a lower temperature limit of 900°C; the crucibles were then quenched in water. In some cases cooling was extended to 800°C in order to observe occurrence and nature of associated crystalline phase or phases, if any. Crystalline phases were identified using either a polarizing microscope or by taking x-ray powder photographs. Later, the residual mass was dissolved away in hot nitric acid and the insoluble crystalline phases, mainly YIG, were collected.

Table 1. Results of some typical crystal growth runs.

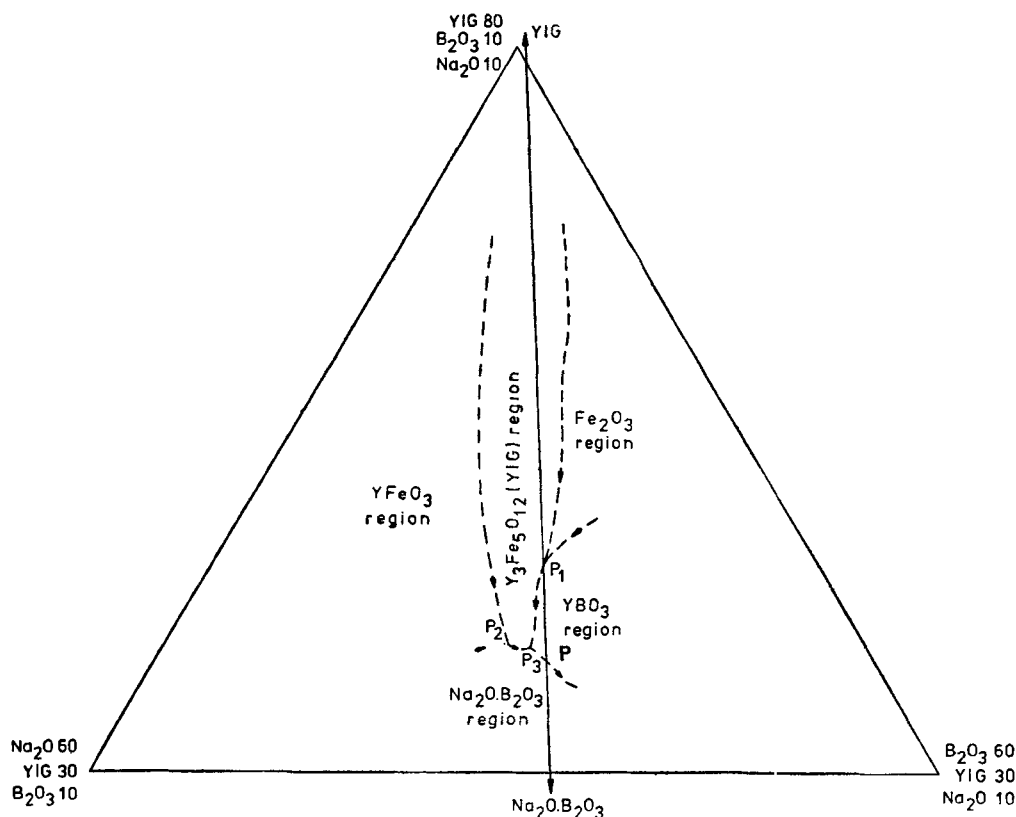
Run No.	Starting mixture (wt %)			Cooling Schedule (°C/hr)	Crystalline products	YIG crystal size (mm)
	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	YIG			
1	19	26	55	10	YIG + Fe <sub>2</sub> O <sub>3</sub>	0.05
2	30	30	40	4	YIG	0.02–0.08
3	15	20	65	20	YIG + Fe <sub>2</sub> O <sub>3</sub>	0.2–0.4
4	22	18	60	10	YIG + YFeO <sub>3</sub>	0.05–0.15
5	27	23	50	10	YIG + YFeO <sub>3</sub>	0.12–0.25
6	28	25	47	11	YIG + YFeO <sub>3</sub>	0.07–0.15
7	23.5	26.5	50	10	YIG + YBO <sub>3</sub>	—
8	15	18	67	15	YIG	0.2–0.7
9	19	21	60	10	YIG	0.3–0.9
10	21	24	55	5	YIG	0.15–0.35
11a	23	22	55	20	YIG	0.2–0.4
11b	23	22	55	2.5	YIG	0.4–0.8
12	25	28	47	5	YIG	1.0–1.5
13	28	28	44	3	YIG	0.5–1.0
14	27	27	46	5	YIG	1.0–2.0

Table 2. Results of some typical phase equilibrium runs

Run No.	Mixture wt %			Temp (°C)	Product
	Na <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	YIG		
1	15	20	65	1100	L + YIG + Fe <sub>2</sub> O <sub>3</sub>
2	17	23	60	1150	L + YIG + Fe <sub>2</sub> O <sub>3</sub>
3	19	26	55	1000	L + Fe <sub>2</sub> O <sub>3</sub> + YIG(tr)
4	22	28	50	1050	L + Fe <sub>2</sub> O <sub>3</sub>
5	23.5	26.5	50	900	L + YIG + YBO <sub>3</sub>
6	25	28	47	920	L + YBO <sub>3</sub> + YIG
7	25	30	45	905	L + YBO <sub>3</sub>
8	30	30	40	900	L + YIG
9	30	26	44	950	L + YFeO <sub>3</sub>
10	28	25	47	1050	L + YFeO <sub>3</sub> + YIG
11	27	23	50	890	L + YIG + YFeO <sub>3</sub>
12	25	20	55	1000	L + YFeO <sub>3</sub>
13	21	24	55	1000	L + YIG
14	22	18	60	1070	L + YIG + YFeO <sub>3</sub> (tr)
15	20	15	65	1030	L + YFeO <sub>3</sub>
16	19	21	60	1050	L + YIG

About 100 crystal growth (table 1) and phase equilibrium runs (table 2) were performed in the system, the phase equilibrium runs delineating the approximate primary phase fields of YIG and associated phases, and the crystal growth runs giving some idea of the crystallization paths taken by the compositions studied. Demarcation of the nature and extent of the primary phase field of YIG towards the high YIG region was not attempted since (1) phase stability relations in this region would be extremely complicated because of incongruent melting nature of YIG and possibility of magnetite ( $\text{Fe}_3\text{O}_4$ ) crystallizing out (Van Hook 1961), and (2) high melting temperatures ( $>1350^\circ\text{C}$ ) of the mixtures and consequent loss of solvent by evaporation increasing from normal 5 to 30%, making this region quite unsuitable for growth of YIG crystals. For most of the compositions studied YIG was the first phase to appear and persisted below  $900^\circ\text{C}$ . Other associated phases started to crystallize around  $950^\circ\text{C}$ . However, proportions of the secondary crystalline phases varied from melt to melt.

Figure 1 shows the approximate field of crystallization of YIG in air. It appears as a lenticular area bounded by  $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$  wt% ratio of 13 : 17 to 29 : 31.5 on the



**Figure 1.** Working diagram (in wt %) showing the approximate fields of crystallization of YIG,  $\text{YFeO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{YBO}_3$  in the system  $\text{YIG-Na}_2\text{O-B}_2\text{O}_3$ . Arrow on boundary curves indicates direction of falling temperature of primary phase field boundaries or projections of primary phase field boundaries. Dotted curve indicates conjectured projection of primary phase field boundary between yttrium orthoferrite and sodium borate derived from theoretical consideration.

$B_2O_3$ -YIG side, and of 15 : 14 to 30.5 : 30 on the  $Na_2O$ -YIG side, with a narrowed down protrusion at the YIG-deficient end. Excluding this constricted region YIG field is found to encompass both sides of the  $Na_2O.B_2O_3$ -YIG join from 39 wt% of YIG towards YIG apex.

Solubility studies of YIG single crystals in a particular flux composition, viz., the compound  $Na_2O.B_2O_3$ , of this system were carried out in the same furnace set-up with a Lawrence-Smith crucible. Weighed amount of YIG single crystals (inclusion-free 1.0–1.5 YIG cm crystals grown from  $PbO$ - $PbF_2$ - $B_2O_3$  flux system (Bandyopadhyay *et al* 1976) mixed with a measured quantity of  $Na_2O.B_2O_3$  was heated to a desired temperature for a fixed duration of time, the crucible quenched, and the solidified melt dissolved away in hot nitric acid. The undissolved YIG grains were left at the bottom of the crucible. From the difference in weight of the YIG crystals before and after the run the amount of YIG in solution, i.e., percentage solubility at a particular temperature, was determined (table 3). Runs of varying duration at several temperatures were carried out to draw the saturation solubility curve at different temperatures. The phase boundary  $P_1P_3$  between YIG and  $YBO_3$  was determined from those runs where  $YBO_3$  was observed in the residue along with the partly dissolved YIG crystals. Some of these data along with the results of crystal growth runs were later utilized to project portions of some of the isobaric (in air, i.e. 0.21 oxygen partial pressure) phase boundaries on the pseudobinary join  $Na_2O.B_2O_3$ -YIG (figure 2).

Table 3. Results of solubility runs of YIG in  $Na_2O.B_2O_3$  flux.

Run No.	Temp. (°C)	Duration (hrs)	Loss of mix. (wt. %)	Solubility (wt. %)
1(a)	935±5	4	1.1	59.03
1(b)	935±5	4	1.0	59.11
2(a)	955±5	4	1.5	63.24
2(b)	955±5	6	1.6	65.68
3(a)	1005±5	4	1.75	67.01
3(b)	1005±5	4	1.9	69.10
4(a)	1025±5	4	2.10	70.81
4(b)	1025±5	4	2.18	71.80
5(a)	1103±5	4	3.20	82.80
5(b)	1103±5	4	3.31	83.12
6(a)	1205±5	2	4.1	100.51
6(b)	1205±5	4	4.5	103.86
7(a)	1282±5	2	5.0	134.10
7(b)	1282±5	4	5.8	138.21

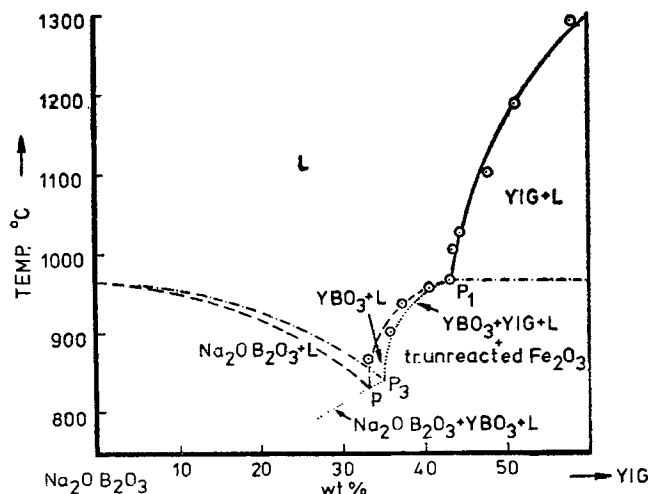


Figure 2. Saturation solubility curve of YIG and projections of associated phase boundary curves of the quaternary system  $\text{YFeO}_3\text{-Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$  in air, along the pseudobinary join  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-YIG}$ . Solid lines and dashed lines indicate determined and undetermined saturation solubility curves along  $\text{YIG-Na}_2\text{O-B}_2\text{O}_3$  join respectively. Dotted lines are projections of phase boundaries.

### 3. Phase equilibrium considerations

Variable oxidation state of iron implies that crystallization of YIG in  $\text{Na}_2\text{O-B}_2\text{O}_3$  flux system in air atmosphere should be considered in the perspective of the quinary system  $\text{FeO-Fe}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ .

However, compositions of all starting mixtures investigated during the present work were confined to the plane  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  (YIG)- $\text{Na}_2\text{O-B}_2\text{O}_3$ . Furthermore, the temperature range of investigation was restricted to  $1300^\circ\text{C-900}^\circ\text{C}$ . Van Hook (1961a, 1961b) has shown that below  $1300^\circ\text{C}$  YIG not only attains molar stoichiometry of  $\text{Y}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in the ratio 3 : 5, but also the proportion of the ferrous component in YIG reduces to negligible amount. None of the other crystalline phases synthesized during the present investigation contained iron in the ferrous state. Quenched melts of several starting mixtures were analysed chemically and were found to contain at most 0.42% FeO by weight (table 4), indicating overwhelming preponderance of  $\text{Fe}^{3+}$  in the liquid phase.

Table 4. Results of chemical analyses of FeO and the total iron (in wt %) of five glass compositions in the system  $\text{YIG-Na}_2\text{O-B}_2\text{O}_3$ .

Sample No.	Starting mix. wt %				Approx. melting temp. ( $^\circ\text{C}$ )	Loss of mixture during melting (wt %)	Chemical analysis in melts	
	$\text{Na}_2\text{O}$	$\text{B}_2\text{O}_3$	$\text{Y}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$			Wt % total iron	Wt % $\text{Fe}_2\text{O}_3$
1	23.6	26.4	23.0	27.0	1170	1.4	24.97	0.26
2	30.0	30.0	18.4	21.6	1050	1.2	21.0	Tr
3	32.0	31.0	17.0	21.0	1000	1.0	18.87	Tr
4	26.0	32.0	19.3	22.7	1070	1.4	20.33	Tr
5	22.0	28.0	23.0	27.1	1200	0.4	26.67	0.42

Complications arise with the gas phase. High volatility of alkali flux systems suggests that a substantial part of the alkali component is released to the gas phase, making the total composition alkali-deficient. However, as mentioned before, total volatilization loss of compositions investigated hardly exceeded 5% even in open crucible runs, pointing to the possibility of considering the present work in the perspective of the quaternary system  $\text{Fe}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ .

Invariant situation (i.e. a point) on the liquidus would be given by the coexistence of six phases, i.e., four crystalline phases, a liquid, and a gas. Under isobaric restriction, as in the present case (in air atmospheres, i.e.  $P_{\text{O}_2} = 0.21$  atm.), a five-phase assemblage, i.e. three crystalline phases, a liquid, and a gas, would give rise to invariance on the liquidus.

Thus  $P_1$  (ca.  $965^\circ\text{C}$ ),  $P_2$  (ca.  $850^\circ\text{C}$ ) and  $P_3$  (ca.  $840^\circ\text{C}$ ) of figures 1 and 2 would be projections of peritectics of the quaternary system on the plane  $\text{YIG-Na}_2\text{O-B}_2\text{O}_3$ .  $P_1$  also corresponds with the intersection of the saturation solubility curve of YIG with that of  $\text{YBO}_3$ , and  $p$  (ca.  $830^\circ\text{C}$ ) corresponds with the intersection of the saturation solubility curve of  $\text{YBO}_3$  with that of  $\text{Na}_2\text{O.B}_2\text{O}_3$ . At  $P_3$  YIG already crystallized will react with the liquid and composition of the liquid cannot move away from  $P_3$ , until all the YIG crystals are dissolved. However, since all the starting compositions were very rich in YIG, rather the liquid would become exhausted at  $P_3$ , leaving behind three-phase assemblage of  $\text{Na}_2\text{O.B}_2\text{O}_3$ ,  $\text{YBO}_3$  and YIG, and some trace unreacted  $\text{Fe}_2\text{O}_3$ . This also explains the corroded appearance of the YIG crystals if the crystal-liquid mixture is cooled below  $P_3$  (ca.  $840^\circ\text{C}$ ).

#### 4. Discussion of results

The occurrence of this narrow field of YIG crystallization in this system can easily be explained, as has already been done by other investigators working in alkali borate systems, if the relative solubilities of the different oxides constituting YIG, i.e.,  $\text{Y}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , in  $\text{Na}_2\text{O}$ - and  $\text{B}_2\text{O}_3$ -rich melts are considered.  $\text{B}_2\text{O}_3$  being a poorer solvent of  $\text{Fe}_2\text{O}_3$  precipitates during cooling compounds richer in  $\text{Fe}_2\text{O}_3$ , i.e. haematite;  $\text{Y}_2\text{O}_3$  dissolved in  $\text{B}_2\text{O}_3$  of the melt can appear as  $\text{YBO}_3$  only at temperatures below  $965^\circ\text{C}$ . On the other hand, mixtures containing higher proportions of  $\text{Na}_2\text{O}$  retain a fair amount of  $\text{Fe}_2\text{O}_3$  in the melt, and since during subsequent cooling requisite amount of  $\text{Fe}_2\text{O}_3$  as needed for the crystallization of YIG ( $\text{Y}_2\text{O}_3 : \text{Fe}_2\text{O}_3$  in the molar proportion 3 : 5) cannot precipitate out, a phase containing higher proportion of  $\text{Y}_2\text{O}_3$  i.e.  $\text{YFeO}_3$ , separates out as flaky crystals. A further confirmatory proof of this phenomenon can be obtained by adding excess amount of  $\text{Fe}_2\text{O}_3$  to mixtures in the high  $\text{Na}_2\text{O}$  side, but within the approximately demarcated projection of the primary phase field of  $\text{YFeO}_3$  in the  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-YIG}$  plane (figure 1). From such mixtures YIG can be obtained as the initial crystalline phase instead of  $\text{YFeO}_3$ . Thus by adding excess  $\text{Fe}_2\text{O}_3$  to YIG- $\text{YFeO}_3$  border line compositions, the field of crystallization of YIG can be considerably enlarged. However, for better growth of YIG crystals it is always desirable to have certain optimum compositions so that maximum advantage of both the equilibrium and kinetic steps of the self-nucleation and growth processes can be gained.

Figure 3 shows the solubility of YIG in  $\text{Na}_2\text{O.B}_2\text{O}_3$  solvent as a function of temperature, and associated evaporation loss of the mixture. As compared to solubility of

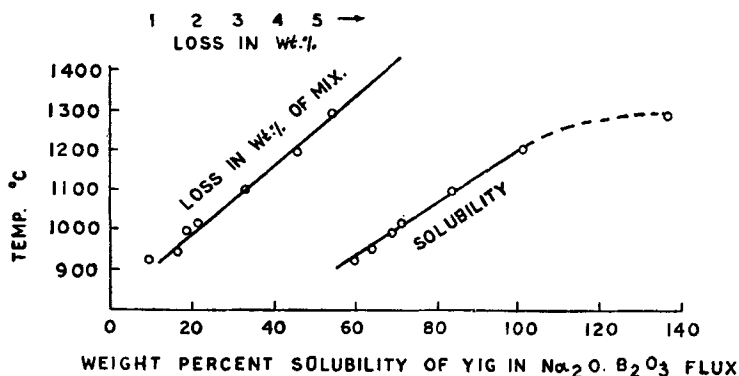


Figure 3. Variation in saturation solubility (in wt%) of YIG in  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$  flux and the corresponding loss of melt at different temperatures.

YIG in conventional  $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$  flux system, the solubility of YIG here is found to be very high at considerably lower temperatures. The maximum solubility of YIG in the lead-based flux system is 50 wt% at 1370°C (Timofeeva *et al* 1970), pertaining to a flux composition of 55 PbO 33.6  $\text{PbF}_2$  11.4  $\text{B}_2\text{O}_3$  in wt%, whereas in this system 100% solubility is attained at temperatures as low as 1200°C. Moreover, the evaporation loss, which is only 4.4% in soda borate system, exceeds more than 15% in  $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$  system.

Long-time growth runs (4-5 days) were made with some compositions selected within the primary field of crystallization of YIG as determined approximately. YIG crystals grown in all these runs were equidimensional in habit with sizes ranging from 0.1 mm to 1.0 mm; uniformity in size in individual growth runs was however observed. The crystals formed clusters as in the case of other alkali borate systems (Linares 1962). In rare cases individual crystals were found to nucleate on the crucible wall near the melt surface, with development of crystallographic faces on one side only.

Quality of the crystals could not be judged from their appearance because of their small size. However, they seem to be bounded by shining  $\{110\}$  and  $\{211\}$  forms with dominance of  $\{211\}$  in crystals grown from high borate compositions. On the other hand, the associated phases, viz.,  $\text{Fe}_2\text{O}_3$  and  $\text{YFeO}_3$ , are flaky in habit and were concentrated on the upper surface of the melt; individual flakes ranged in size from 2.0 to 3.0 mm. Thus, in comparison to YIG crystals grown from conventional lead fluoride fluxes, YIG crystals from  $\text{Na}_2\text{O-B}_2\text{O}_3$  melt were markedly different in appearance and seem to have grown by a self-nucleation process.

## 5. Conclusion

The soda borate flux system was investigated for growth of YIG single crystals because of its inherent advantages of low volatility at working temperature, negligible toxicity and low degree of attack of the container. But from kinematic considerations it could be surmised that this solvent would not be very promising for bulk growth of YIG single crystals and it was found to be so. The suspected low diffusion rates as compared to lead-based fluxes, and coexistence of YIG with liquid through a wide range of temperature (figure 2) aided by high solubility of YIG components in the

liquid, would generate a large number of nuclei and limit their ultimate sizes to very small dimensions, since subsequent reduction of the number of nuclei and further two-dimensional growth of the reduced number of nuclei do not occur here.

Largest crystals (2.00 mm in dia, run no. 14 of table 1) were found from a composition very close to YIG- $\text{Fe}_2\text{O}_3$  boundary curve. For a substantial portion of its crystallization path YIG and  $\text{Fe}_2\text{O}_3$  would crystallize simultaneously until the reaction point ( $P_1$  of figure 1) is reached. From phase equilibrium considerations it could be surmised that the  $\text{Fe}_2\text{O}_3$  crystals should dissolve here, eliminating the haematite nuclei, but the already existing YIG nuclei would continue to grow at their expense. However the number of such nuclei of YIG would be considerably lesser if YIG had been the only crystallizing phase. Thus the relatively larger sizes of YIG crystals precipitating out from this composition can also be explained on the basis of equilibrium three-dimensional nucleation and growth.

### Acknowledgements

The authors are thankful to Dr K D Sharma for his kind permission to publish this paper and to staff members of x-ray laboratory and Chemical Section of the Institute for their kind cooperation.

### References

- Bandyopadhyay T, De A and Saha P 1976 *Trans. Ceram. Soc.* **35** 1  
Burnett D, Clinton D and Miller R P 1968 *J. Mat. Sci.* **3** 47  
Chase A B and Morse Jr F L 1973 *J. Cryst. Growth* **19** 18  
Ganguli D and Saha P 1969 *Indian J. Tech.* **7** 320  
Grodziewicz W H, Dearborn E F and Van Uitert L G 1967 *J. Phys. Chem. Solids Suppl.* p. 441  
Kestigian M 1967 *J. Am. Ceram. Soc.* **50** 165  
Linares R C 1962 *J. Am. Ceram. Soc.* **45** 307  
Linares R C 1964 *J. Appl. Phys.* **35** 433  
Nielsen J W 1960 *J. Appl. Phys. Suppl.* **31** 51s  
Timofeeva V A and Luk'yanova N I 1970 *Sov. Phys. (Crystallogr.)* **14** 757  
Titova A G 1960 *Sov. Phys. (Solid State)* **1** 1714  
Van Hook H J 1961a Rep. U.S. Dept. of Commerce, Office of Technical Services Washington 25 D.C.  
Van Hook H J 1961b *J. Am. Ceram. Soc.* **44** 208