Growth of Oxide Crystals by the Flux Method

by MICHAEL SCHIEBER

SINGLE crystals of β-Ga_2O_3, rare-earth gallium garnets, $SmFeO_3$, $Sm_3Fe_5O_{12}$, $Y_3Fe_5O_{12}$, magnetoplumbite, NaCl and $LiFe_5O_8$, and rare-earth scheelites were grown using the flux method. The present note describes the growth of $Sm_3Ga_5O_{12}$ *with PbO–PbF_2 as the flux. It was recently reported that it was* impossible to grow pure single crystals of this compound by the Nielsen procedure.[2,3] Recommended mixtures for all these crystals are given in Table I.

β-Ga_2O_3 crystals containing various amounts of rare-earth impurities (1.2 to 6.4 wt% Sm_2O_3 or Nd_2O_3) were grown from various mixtures in the systems Ga_2O_3–R_2O_3–PbO/PbF_2 and Ga_2O_3–R_2O_3–MoO_3 (R = rare-earth ion). In both systems large platelets of β-Ga_2O_3 single crystals[1] were formed by a chemical decomposition process. Single crystals of a low-temperature stable phase decomposed in the presence of the flux and yielded single crystals of a different phase. In the system Ga_2O_3–R_2O_3–PbO/PbF_2 the reaction is

$$2Sm_3Ga_5O_{12} \xrightarrow[PbO/PbF_2]{\sim 1300^\circ C} 3Sm_2O_3 + 5\beta\text{-}Ga_2O_3$$

The Sm_2O_3 is dissolved by the flux. In the system Ga_2O_3–R_2O_3–MoO_3 the decomposition occurs at ~1050°C, i.e., β-Ga_2O_3 is formed only at temperatures above 1050°C.

The study of several compositions in the system Ga_2O_3–R_2O_3–PbO/PbF_2 has shown that the stability field of the garnet phase is much more restricted in the case of samarium gallium garnet than in the other rare-earth gallium garnets, thus explaining the difficulty[1] of growing $Sm_3Ga_5O_{12}$.

Decomposition reactions were also found in the system Sm_2O_3–Fe_2O_3–PbO/PbF_2 in which the reaction was

$$12Sm_3Fe_5O_{12} + 5PbO \xrightarrow{\sim 1300^\circ C} 18Sm_2O_3 + 5PbFe_{12}O_{19}$$

Below ~1300°C large samarium iron garnet crystals were grown and above this temperature large crystals of $PbFe_{12}O_{19}$ were obtained. It was also found that the variation of the PbO:PbF_2 ratio can control the amount of $PbFe_{12}O_{19}$ and $Sm_3Fe_5O_{12}$ which may be found together at certain compositions and temperatures. Therefore, the molar ratio PbO:PbF_2 = 1:1 favors formation of the garnet phase. It should be mentioned also that the garnet stability field of the system Y_2O_3–Fe_2O_3–PbO/PbF_2 is much larger than that of the respective Sm_2O_3 field. The composition limits for growing yttrium iron garnet, therefore, are much broader *than those for samarium iron garnet; compositions including* yttrium may yield garnets whereas similar compositions including samarium may yield magnetoplumbite or perovskite crystals.

$LiFe_5O_8$ decomposed to α-Fe_2O_3 at temperatures above 1250°C in the presence of B_2O_3. The decomposition reaction can be written as

$$2LiFe_5O_8 + B_2O_3 \xrightarrow{\sim 1250^\circ} Li_2B_2O_4 + 5Fe_2O_3$$

When lower temperatures in the order of 1050°C were used the stability field for the spinel-type lithium ferrite is broader than the one reported earlier at 1100°C.[4] Neither $LiFeO_2$ nor α-Fe_2O_3 is decomposed by the B_2O_3-containing flux.

Large crystals of $Na_{0.5}Ga_{0.5}MoO_4$ were grown in the system Na_2O–Gd_2O_3–MoO_3. The magnetic susceptibilities and unit cell

Table I. Data on Single Crystals Grown by Flux Method

Compound	Molar composition (%)				Temp. range (°C)	C_0* (g/100 g sol'n)	C†/C_0	Weight (mg)
	Ga_2O_3	Sm_2O_3	MoO_3					
β-Ga_2O_3	11.3	1.7	87.0		1050–70	14.1	0.53	30
	Ga_2O_3	R_2O_3	PbO	PbF_2				
β-Ga_2O_3	35	5	40	20	1390–900	29.0	0.85	100
$Nd_2Ga_5O_{12}$	15	5	26.7	53.3	1240–900	12.2	0.83	300
$Sm_3Ga_5O_{12}$	35	10	17.7	37.3	1240–900	41.9	0.66	85
$Eu_3Ga_5O_{12}$	15	5	26.7	53.3	1240–900	12.2	0.97	1800
$Gd_3Ga_5O_{12}$	15	5	26.7	53.3	1240–900	12.3	0.95	1200
	Fe_2O_3	R_2O_3	PbO	PbF_2				
$SmFeO_3$	11	11	26	52	1280–900	23.4	0.95	100
$Sm_3Fe_5O_{12}$	40	10	16.6	33.4	1240–900	34.4	0.78‡	250
$PbFe_{12}O_{12}$					1390–900	22.2	0.94	800
$Y_3Fe_5O_{12}$	23	8	23	46	1280–900	21.4	0.97	1800
	Fe_2O_3	B_2O_3	Li_2O	LiF				
$LiFeO_2$	8	34	58		1050–700	15.5	0.42	2
$LiFe_5O_8$	33	20	20	27	1050–700	13.6	0.76	5
Fe_2O_3	25	50	25		1150–800	48.6	0.52	5
	Na_2O	Gd_2O_3	MoO_3					
$Na_{0.5}Gd_{0.5}MoO_4$	37.1	5.7	57.2		1050–700	46.0	0.85	1200

* Theoretical concentration.
† Experimental concentration.
‡ $PbFe_{12}O_{19}$ + $Sm_3Fe_5O_{19}$.

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[1] B. Bleaney, "Properties of Rare Earth and Transition Group Ions," Oxford University Clarendon Lab. Rept. No. (AFCRL–63–192) April 4, 1963; Contract No. AF 61(052)–125. 205 pp.

[2] J. W. Nielsen and E. F. Dearborn, "Growth of Single Crystals of Magnetic Garnets," *Phys. and Chem. Solids*, **5**, 202–207 (1958).

[3] J. W. Nielsen, "Improved Method for the Growth of Yttrium-Iron and Yttrium-Gallium Garnets," *J. Appl. Phys.*, **31** [5, Suppl.] 51–52S (1960); *Ceram. Abstr.*, **1960**, October, p. 237*i*.

[4] J. C. Anderson and M. Schieber, "Crystal Growth in the System Lithium Oxide–Boron Trioxide–Ferric Oxide," *J. Phys. Chem.*, 67 [9] 1838–40 (1963).

dimensions of these and other rare-earth sodium molybdenum scheelites are reported elsewhere.[5]

A few general remarks should be made concerning the optimum conditions for growing large crystals of oxides by the flux method:

(*a*) Use a large amount of material with the crucible filled with molten mass as near to the top as possible.

(*b*) Minimize loss of flux by volatilization through the use of internal lids to cover the platinum crucibles.

(*c*) Use high-purity raw materials as impurities segregate mainly in larger crystals.

(*d*) Compare the total yield of crystals with the theoretical yield (ratio C/C_0 in Table I). This ratio will indicate if the growth started well above liquidus and stopped below the solidus curve. A higher temperature, however, may sometimes decompose the desired crystal, growing a different and undesired one.

(*e*) Use a low rate of cooling to assure proper heat transfer during solidification.

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[5] M. Schieber and L. Holmes, "Crystal Growth and Magnetic Susceptibilities of Some Rare-Earth Sodium Molybdenum Scheelites," *J. Appl. Phys.*, **35** [3, Part 2] 1004–1005 (1964); *Ceram. Abstr.*, **1964**, July, p. 202*c*.

Metallographic Preparation of Sintered CeO_2

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CURRENT investigation of the sintering of CeO_2 has shown the need for a method of polishing and etching CeO_2 for microscopic study. As there is no reference to the metallography of CeO in the literature, metallographic techniques as developed in this laboratory were followed. These procedures gave excellent results.

Ceria requires some special handling. To preserve the complex microstructure, severe etching methods, such as boiling concentrated acids, were ruled out. Syntron polishing was superior to manual polishing, because of the long polishing period needed to eliminate scratches. The HCl wash is needed to remove a thin, hazy film which forms during the HF etching.

This procedure works on CeO_2 sintered from 1200° to 1800°C. The microstructure to be described is present also in lower fired material but is less pronounced. The ceria used in these experiments is 99+ % pure.

The specimens were mounted in Maraset thermosetting epoxy (The Marblette Corporation, resin No. 655 and hardener No. 555). They were cast in molds $1^1/_4$ in. in diameter by $1^1/_4$ in. high of Silastic Dow Corning R.T.V. 501 Silicone Rubber. The Maraset was cured for 12 hours at 95°C and for 2 hours at 125°C; it was used as potting material because of its abrasion resistance.

Rough grinding was done on 180, 240, 320, 400, and 600 grit abrasive papers from Buehler Ltd. at 1150 rpm with water as the lubricant. The fine grinding was done with 600 grit soft abrasive paper at 550 rpm with water as the lubricant. All grinding was done on Buehler grinding wheels.

Polishing was done with a Linde B 0.05μ alumina-distilled water slurry on Buehler microcloth. Polishing took 4 to 5 hours on a Syntron vibratory polisher. The specimens were washed with liquid soap using surgical cotton and were rinsed with cold water between each grinding paper and before and after vibratory polishing.

The best etching method found was immersion in a 1:1 solution of 48% HF and distilled water for 15 minutes at ambient temperature. This was followed by swabbing for 1 to 2 seconds with a 1:1 solution of concentrated HCl and distilled water to remove a thin residue formed during etching with HF. The specimens were then washed in cold water and dried. The results of this procedure are shown in Fig. 1.

No detailed explanation of this microstructure is available yet. The specimen is very porous, and the large number of inclusions appears to be a second phase. This phase has not been identifiable by X-ray analysis and a microprobe analysis will be made. As the density of this specimen is greater than 95% of theoretical, the porosity is also difficult to explain. The grains appear to be equiaxed and the grain boundaries are well defined.

This type of microstructure is typical for the high-fired ceria specimens examined. It is present but less pronounced in material fired at lower temperatures.

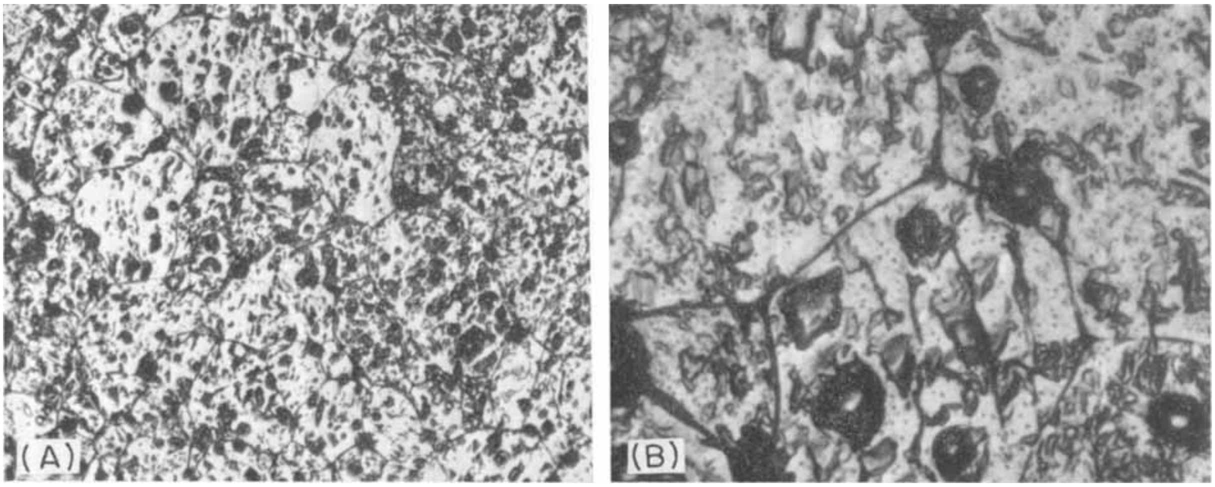

Fig. 1. Specimens of CeO_2 fired at 1800°C for 12 hours and etched with HF. (*A*) ×100, and (*B*) ×500.

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