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SYNTHESIS OF THORIANITE CRYSTALS FROM BISMUTH OXIDE-LEAD FLUORIDE MELTS

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Oxides that can be readily grown as single crystals, and into which rare-earth ions can be incorporated, are of research interest and may be of value for certain electronic applications. Uranium and the lanthanides substitute for thorium in natural occurring thorianite (Palache *et al.*, 1944). The growth of thorianite by long continued fusion of ThO_2 in Borax has been previously described (Mellor, 1960). However, the synthesis of thorianite by this method results in either minute crystals or trellis-like aggregates of crystals. The purpose of this report is to describe a method for the growth of large thorianite crystals.

It has been found that ThO_2 crystals can be readily synthesized from the PbO-PbF_2, Bi_2O_3-PbF_2, and PbF_2 flux systems. The melts from which the largest ThO_2 crystals were grown contained 7 mole per cent ThO_2, 15 mole per cent Bi_2O_3, and 78 mole per cent PbF_2. Melts containing 10 mole per cent ThO_2 and 90 per cent PpF_2 also produced large crystals. The materials employed were 99.99 per cent pure ThO_2, reagent grade Bi_2O_3, and a purified grade of PbF_2. The powders were mechanically mixed (generally in 100 gram lots) and fused in tightly covered 50 ml platinum crucibles.

The crucibles were placed in two Super Kanthal heated horizontal muffle furnaces. The melts were held at 1250° C. for 4.5 to 8 hr and cooled

at a uniform rate (2 to 4° C/hr) to 1000° C. At this temperature the crucibles were removed from the furnace and allowed to cool to room temperature. The vertical temperature gradients in these furnaces are small (less than 3° C/in.) and probably have little effect on crystal growth. Between 35 and 50 per cent of the melt is lost by evaporation during a normal run, despite care in capping the crucibles. The major portion of this weight loss is probably PbF_2, which has an appreciable vapor pressure at these temperatures. The crystals were recovered by

TABLE I. THORIANITE GROWTH DATA

Run No.	Mole %			Low Temp, ° C.	High Temp, ° C.	Soak Time, hr	Cooling Rate, ° C./hr	Wt % Loss	Yield %	Comments
	ThO_2	Bi_2O_3	PbF_2							
1	3	30	67	1000	1250	8.5	3.5	—	71.5	Colorless crystals up to 3 mm grew on {111} dendrites, {100} habit
2	5	30	65	1000	1250	19	3.5	38.9	94.0	Very clear subhedral crystals, 1–1.5 mm, {100} habit
3	5	15	80	950	1260	8	4.0	43.9	64.2	Large crystals, inclusions in larger ones, 3.5–5 mm
4	5	47	48	1000	1250	12	2.4	—	65.0	Clear, colorless crystals up to 3 mm.
5	7	15	78	950	1260	8	4.0	38.7	67.0	Large, clear crystals 3.5–6 mm. Largest have inclusions. BEST RUN
6	10	15	75	1015	1250	14.5	2.4	57.5	98.0	Good quality crystals 0.1–1.5 mm in size
7	15	15	70	1000	1260	7	2.4	53.9	68.0	Good quality. Cubic {100}, average size 1–1.5 mm
8	10	—	90	1015	1240	4.5	4.0	41.3	25.8	Very good quality. Cubic {100}, 2–5 mm

digesting the contents of the crucibles in hot 50 per cent acetic acid and were identified by microscopic examination and confirmed by *x*-ray powder patterns. The average yield was approximately 70 per cent, based on the original content of ThO_2 in the melt. The results from a number of different runs are listed in Table 1. Runs 3, 5 and 8 gave the best results as far as crystal size is concerned. It is felt that this is due to decreased nucleation because of reduced losses of PbF_2 during the comparatively shorter soaking times and more rapid cooling rates.

The crystals obtained from a typical melt ranged from 2 to 6 mm (Fig. 1), with the largest crystals occurring on the bottom of the crucible. The crystals also occurred on the top surface of the melt and attached to the walls of the crucible. The crystals were generally subhedral, with the

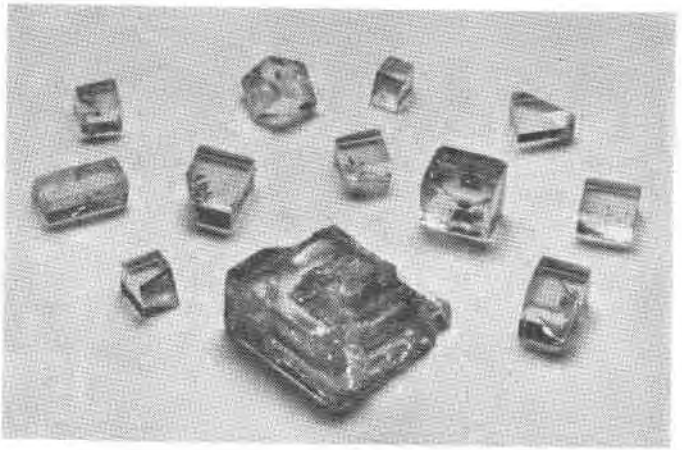

FIG. 1. Thorianite crystals grown from a typical melt (4×).

{100} being the dominant habit. Microscopic examination revealed the outline of dendrites within some of the crystals. The arms of the dendrites extended along [111] directions. The material outlining the dendrites is finely divided and appears to be flux that was trapped during growth. During later growth the ends of the dendritic arms come in contact with each other, trapping melt in the regions between them. Further growth of the crystals is fairly uniform, and the exterior regions are free of occlusions and macroscopic defects. There are a few crystals from each batch that have not occluded melt during growth. These crystals are colorless and appear to be of good optical quality.

It has been found that the crystals grown by this technique are easily doped with the rare-earth sesquioxides and UO_2. Preliminary investigations indicate that some of the rare-earth ions fluoresce strongly in single crystals of thorianite.

The authors wish to express appreciation to G. M. Wolten who identified the crystals by *x*-ray techniques.

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