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CRYSTAL GROWTH OF BISMUTH TUNGSTATE

by

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ABSTRACT

Bi_2WO_6 is a polar material in the bismuth titanate family, $Bi_2M_{n-1}R_nO_{3n+3}$. Additions of NaF to a Na_2WO_4 - WO_3 flux yielded large single crystals up to 0.8 mm thick, which were free of inclusions. Total impurities were less than 500 ppm, and the crystals were single domain.

INTRODUCTION

Bismuth tungstate is a member of the bismuth titanate family of layered compounds which have a mica like morphology with $(Bi_2O_2)^{2+}$ layers interleaved by $(WO_4)^{2-}$ layers stacked in the c direction. The structure at room temperature is orthorhombic mm2. Bi_2WO_6 melts congruently at 1080°C, but passes through a disruptive phase transformation in the temperature range 840-960°C. Crack free single crystals cannot be grown from the melt, and thus lower temperature methods of crystal growth are required.[1,2,3] This paper reports on our results with hydrothermal and flux growth techniques.

The interest in this compound is due to its high accentricity (0.44 Å) and calculated value of spontaneous polarization (0.42 c/m^2) which makes it a candidate material for piezoelectric, pyroelectric, and possibly ferroelectric applications.[4,5,6,7]

HYDROTHERMAL GROWTH

The source material was a polycrystalline boule of Bi_2WO_6 formed by prereacting Bi_2O_3 - WO_3 powders in a platinum crucible and melting at 1200°C. Various modifications were made to the relative amounts of nutrient and mineralizer, percentage-fill of autoclave and growth temperatures. The nutrient was always placed in the bottom of the pressure vessel and a perforated baffle separated dissolution and growth zones. At all times the assembly was placed vertically in an electrically heated furnace which had a programmable temperature gradient, and the base of the pressure vessel was always at a higher temperature. Out of the many conditions investigated, results for successful hydrothermal growth are summarized in Table I.

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DISCLAIMER

Pressure Vessel: 71 cc, Inconel
Growth Conditions

Bi_2WO_6	15 g	Temperature	
Mineralizer	4 N KF	Top	400°C
H_2O_2, 30%	10 cc	Bottom	450°C
% Fill	70	Pressure	3500 psi
Baffle	Ni/Cr alloy	Duration	6 days

Table I. Typical conditions for hydrothermal growth of Bi_2WO_6.

The experiments yielded a large number of crystals which were of average size 1 x 1 x 1 mm. A large concentration of fluoride ions were found necessary to modify the habit of the crystals so as to inhibit planar growth.

FLUX GROWTH

Many solvents have been used to grow Bi_2WO_6, e.g., B_2O_3, LiCl, KF, PbO, V_2O_5, alkali molybdates and tungstates, bismuth borates, etc. For example, the latter yielded large surface area crystals which are extremely thin (∿50 μm). The general problem is one of suppressing lateral growth and aiding transverse growth. To date, the best results were those of Muramatsu, et. al.,[3] who grew 3 x 3 mm by 0.2 mm thick crystals from a Na_2WO_4 flux. From our experience on hydrothermal growth, where fluoride additions yielded near isometric crystals, we decided to modify Na_2WO_4 with fluorides; and subsequently grew thicker crystals. Typical growth conditions are summarized in Table II.

$Na_2WO_4;2H_2O$	0.1 mole	33 g	Initial temperature	900°C
NaF	0.21 mole	8.82 g	Thermal gradient	None
WO_3	0.24 mole	55.62 g	Soaking time	12-24 hr
Bi_2O_3	0.66 mole	30.76 g	Cooling rate	4°/C/hr
			Cut-off temperature	780°C

Table II. Starting composition and growth conditions for flux grown Bi_2WO_6.

One day was allowed for dissolution of the solute before cooling to 780°C at 4°C/hr. The following observations were made.

(1) The starting temperature of 900°C was notably higher than the reported value for the disruptive transformation of Bi_2WO_6 at 840°C on cooling. The low temperature phase appeared stable in the flux up to 960°C.

(2) Nucleation of crystals appeared anomalous in that they occurred within the mass of the flux and not at the surface of the liquid or along the wall of the crucible, which are naturally cooler. This phenomenon persisted in the presence of a strong thermal gradient along the crucible. It was repeatedly observed that most of the crystals grew in near vertical planes within the liquid.

(3) All crystals, even the largest ones, were single domain, as judged by cross polarized light microscopy.

(4) The rate of cooling was critical. Nucleation rate approached its maximum at lower supersaturations than the growth rate. All experiments carried out at cooling rates < 3.5°C/hr provided evidence for increased nucleation by a factor of 100. On the other hand, a rate of 4.5°C/hr yielded crystals containing many inclusions and evidence of dendritic growth. 3.8 to 4°C/hr appeared to be the optimum cooling rate for obtaining large and thick, inclusion-free single crystals.

(5) The most successful experiments were those which had a minimum thermal gradient along the crucible, with the top cooler than the bottom. This allowed for the crystals to develop throughout the liquid as large vertical lamellae.

(6) Typical dimension were 10 x 6 x 0.8 mm for clear crystals after dissolution of the flux by cleaning in water.

ANALYSIS

The crystals were analyzed by mass spectrometry for impurities. (Table III)

Na		200	Si	30
Fe		70	Ca	30
AP	≲	50	Ti	10
CP		40		

Table III. Trace impurities in flux-grown Bi_2WO_6. (concentration in atomic ppm)

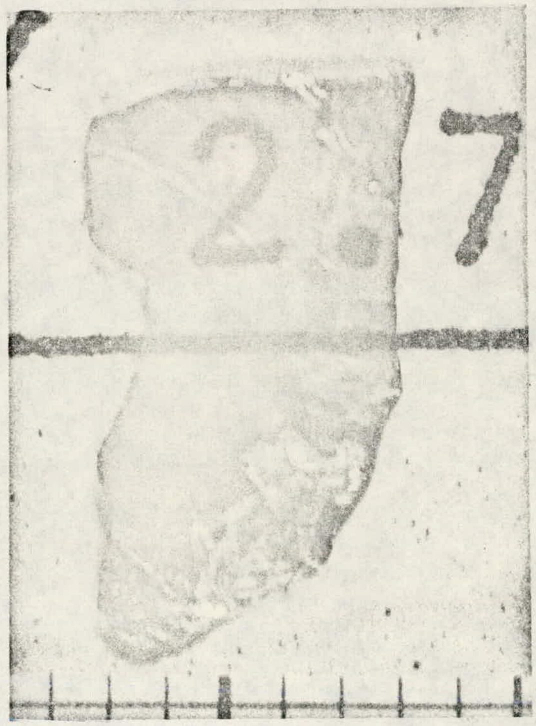

Fig. 1. Bi_2WO_6 single crystal (scale in mm).

No trace elements exceeding 100 atomic ppm were present, except Na which probably came from the flux.

CONCLUSIONS

It is now possible to grow Bi_2WO_6 crystals from Na_2WO_4 - NaF fluxes which are now thick enough for a complete materials characterization. We hope that this material will find electrical applications in the near future.

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