

TABLE II Room-temperature elastic constants of Si_3N_4 and SiC [6]

| | Young's modulus $E(\text{MN m}^{-2})$ | Poisson's ratio |
|--------------------------------|--|-----------------|
| HS-130 Si_3N_4 | 31×10^4 | 0.218 |
| NC-203 SiC | 45.5×10^4 | 0.226 |

average values of γ obtained by double-cantilever and double torsion techniques [7, 8] (solid lines) are also included in Fig. 2. The agreement between the γ values for Si_3N_4 appears to be quite good (Fig. 2a); the agreement between γ values for SiC also appears to be reasonable (Fig. 2b).

Since the γ values in Fig. 2 were calculated from microcrack dimensions and indenter loads, it is important to be able to clearly observe the microcracks on the fracture surfaces of the specimens. Since this may be difficult in some cases, further simplification of the calculations was made by assuming the microcracks to be exactly semi-circular with $2c$ equal to the long diagonal length L of the indentation (see Fig. 1). Under this assumption the actual determination of the microcrack dimensions is not a requirement and the γ values can be calculated simply (solid circles in Fig. 2) from the dimensions of the hardness impression. Comparison of these values to those represented by the solid line shows that the agreement is not particularly good; however, these simple modifications permit the prediction of γ values to within 30% of those obtained by more sophisticated techniques.

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In conclusion, this study has shown that the approximate values of fracture-surface energies of hot-pressed Si_3N_4 and SiC can be predicted from microhardness-indentation loads and dimensions.

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The surface tension of Bi_2O_3 -based fluxes used for the growth of magnetic garnet films

Thin films of rare earth iron garnet are commonly grown from solution in a $\text{PbO}-\text{B}_2\text{O}_3$ flux onto non-magnetic garnet substrates by the liquid-phase epitaxy (LPE) dipping process [1]. Such films are important for magnetic bubble domain, magneto-optic and microwave applications. For magneto-optic applications [2] it is desirable for the film to have a large Faraday rotation (θ) and a low optical absorption coefficient (α), the

ratio θ/α defining the magneto-optic figure of merit at a given wavelength.

It is well known that the partial substitution of Bi in the garnet lattice enhances θ and that to obtain appreciable Bi substitution in garnet films, low growth temperatures are required [3]. However, at such temperatures divalent Pb from the flux is readily incorporated into the garnet, substantially increasing α . Although the $\text{BaO}-\text{BaF}_2-\text{B}_2\text{O}_3$ flux system may be used for garnet LPE, the combination of its high viscosity [4] and high surface tension [5] prevent a clean separation of the film from the flux on termina-

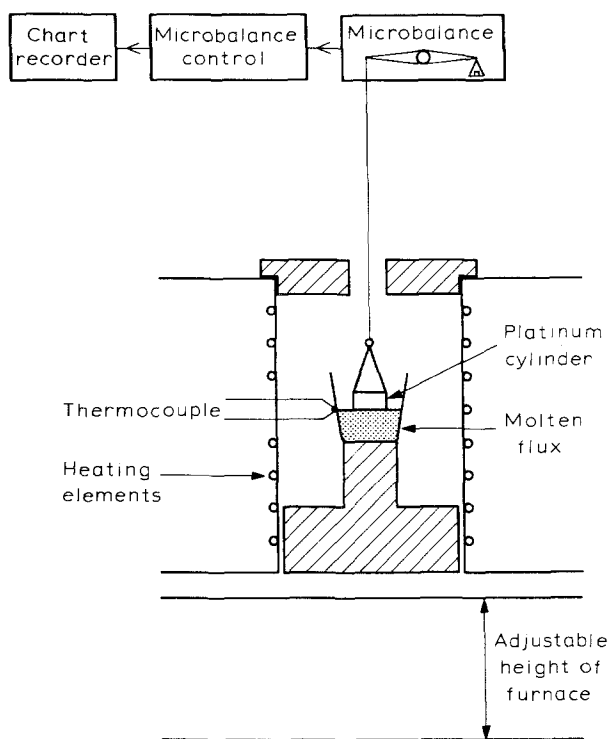


Figure 1 Apparatus for measuring surface tension.

ting growth, thus causing irregularities in the film surface. Consequently, it would be advantageous to develop a Pb-free flux having a low viscosity and surface tension and from which Bi-substituted garnet films can be grown at temperatures below 800°C.

Robertson and Brice [6] have used flux systems consisting of mixtures of Bi_2O_3 with small amounts of RO_2 ($R = \text{Ce}, \text{Sn}, \text{Ti}, \text{Si}, \text{or Ge}$) for the growth of garnet layers but encountered difficulties in removing the melt from the grown film. Bruton [7] has measured the viscosities of Bi_2O_3 and mixtures of Bi_2O_3 with SiO_2 and TiO_2 at various temperatures. As part of a study to optimize flux systems for the LPE growth of Bi-substituted garnet films, surface tension measurements on a series of modified Bi_2O_3 -based fluxes are reported here.

The apparatus used to measure surface tension is shown in Fig. 1. Essentially it is a modification of the dipping cylinder method reported by Babcock [8] and Shartsis *et al.* [9]. The furnace is seated on a rigid platform which can be raised and lowered smoothly at speeds of up to 1 mm min^{-1} . A pure platinum cylinder of external diameter 0.75 cm and wall thickness 0.02 cm is

suspended from a Beckman LM600 Microbalance so that the lower edge of the cylinder is horizontal and just above the surface of the flux.

The flux is homogenized overnight at 1000°C cooled to the measurement temperature and then the furnace raised so that the flux contacts the platinum cylinder. The motor is immediately reversed so that the cylinder is effectively being pulled out of the flux. The measured force exerted on the cylinder increases to a maximum and then decreases prior to the cylinder separating from the flux. Surface tension, σ , is then calculated from [10];

$$\sigma = \frac{Wg}{4\pi R} \left[1 - \left(2.8284 + 0.6095 \sqrt{\frac{h}{R}} \right) \frac{\delta}{\sqrt{(hR)}} + \left(3 + 2.585 \sqrt{\frac{h}{R}} \right) \frac{\delta^2}{hR} \right]$$

where W = maximum pull on cylinder, R = mean radius of cylinder, g = gravitational constant, $h = W/(\pi R^2 e)$, e = density of the flux, 2δ = thickness of cylinder wall. For the systems studied, the third term is negligible and the second term is $\sim 2\%$ of the first. Therefore, an accurate value for the flux density is unnecessary, 8 g cm^{-3}

TABLE I

| Flux | Additive (wt %) | σ at 850°C (dyn cm ⁻¹) | Lowest operating temperature (°C) |
|--|------------------------------------|---|-----------------------------------|
| Bi ₂ O ₃ | | 213 | 830 |
| Bi ₂ O ₃ /CeO | | 208 | 850 |
| | 1% K ₂ O | 175 | |
| | 2% K ₂ O | 164 | <725 |
| | 4% K ₂ O | 151 | 670 |
| | 6% K ₂ O | 141 | 665 |
| Bi ₂ O ₃ /CeO ₂ | 4% Na ₂ O | 166 | 730 |
| | 4% Cs ₂ O | 155 | 730 |
| | 2% BaO | 192 | 830 |
| Bi ₂ O ₃ /SnO ₂ | 4% K ₂ O | 166 | 670 |
| Bi ₂ O ₃ /TiO ₂ | 4% K ₂ O | 155 | 700 |
| Bi ₂ O ₃ /SiO ₂ | 4% K ₂ O | 162 | 700 |
| Bi ₂ O ₃ /GeO ₂ | 4% K ₂ O | 156 | 710 |
| Bi ₂ O ₃ | 4% Li ₂ O | 171 | 630 |
| | 4% Na ₂ O | 157 | 615 |
| | 4% K ₂ O | 152 | 670 |
| | 4% Rb ₂ O | 168 | 740 |
| | 4% Cs ₂ O | 169 | 740 |
| Bi ₂ O ₃ | 2.5% B ₂ O ₃ | 201 | 670 |
| | 52% MoO ₂ | 132 | 650 |
| | 4% V ₂ O ₅ | 187 (950°C) | 940 |
| Bi ₂ O ₃ | 66% PbO | 140 | 720 |
| Bi ₂ O ₃ | 46% PbO | 155 | 565 |
| | 2% B ₂ O ₃ | | |
| PbO | 2% B ₂ O ₃ | 131 | <800 |

Note: For fluxes of the type Bi₂O₃/MO₂, the molar ratio of Bi₂O₃:MO₂ is 49:1.

being assumed for all systems.

Measurements were made at least three times at each temperature. Reproducibility was to better than 3%. By comparison of measured values with published values for a number of liquids at room temperature, accuracy was estimated as ±5%. Measurements were made over a wide temperature range, the lower limit being set by the flux freezing point or the point at which a second phase separated.

The data obtained for pure Bi₂O₃ and modifications are collated in Table I. For comparison, values have also been measured for some PbO-based fluxes which are commonly used for garnet LPE. Surface tension values are shown only for 850°C since the temperature coefficient of surface tension is small for all the systems studied. Typic-

ally, surface tension was found to increase by ~1% for each 100°C decrease in temperature. Of interest here is that for compositions containing PbO the surface tension actually decreases slightly with decreasing temperature, a trend previously observed by Shartsis *et al.* [9] for PbO-B₂O₃ and PbO-SiO₂.

Clearly the addition of alkali metal oxides has two beneficial effects. First, there is a marked lowering of the surface tension for both the Bi₂O₃ and Bi₂O₃-MO₂ fluxes. On a weight % basis K₂O gives the maximum lowering of surface tension. Indeed, garnet films have now been successfully grown from both the Bi₂O₃-K₂O and Bi₂O₃-CeO₂-K₂O fluxes. Preliminary results indicate that the K₂O addition does reduce flux adhesion to the film surface [11]. Second, there is a substantial reduction in the film growth temperatures that can be employed. Since the garnet film composition depends on the growth temperature, extending the range of growth temperatures enables a wider variety of film compositions to be grown. In particular, the Na₂O additive allows film growth temperatures ~200°C lower than the freezing point of the Bi₂O₃ and Bi₂O₃-CeO₂ fluxes.

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Spherulitic cracking in high density polyethylene

A recent report [1] has shown that cracks occur in spherulites of nylon 6 deformed in tension. These were observed to appear as circumferential defects in sectors of $\pm 30^\circ$ to the tensile direction on the surface of yielded bulk specimens, and were

suggested to allow the formation of larger cavities leading to eventual fracture. We wish to report a similar phenomenon on the surface of HDPE deformed in plane-strain compression.

The surface of the polyethylene was prepared by etching in a beam of argon ions [2], and positive metal replicas similar to those described by Wu *et al.* [3] were made of the surface at

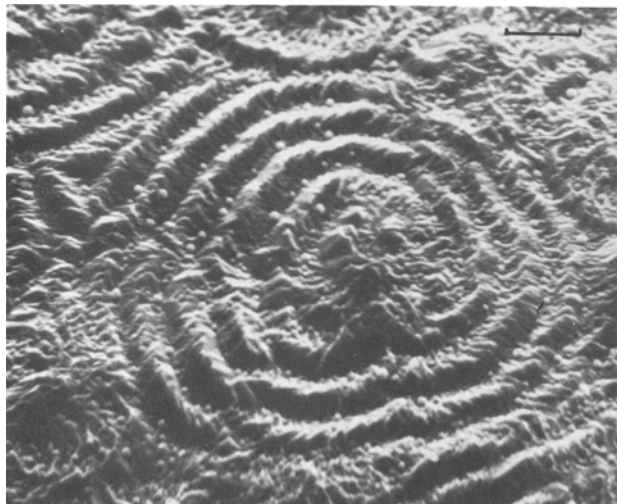


Figure 1 Scanning electron micrograph of an undeformed spherulite of HDPE. The small spheres are artefacts. Scale = 10 μm .



Figure 2 The same spherulite compressed to a strain of 30% showing deformation cracks (refer Fig. 3). Scale = 10 μm .