Identification and Control of Gravity Related Defect Formation during Melt Growth of Bismuth-Silicate ($Bi_{12}SiO_{20}$)

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In the light of strong indications that a majority of critical defects formed in BSO during growth from the melt is related directly or indirectly to gravitational interference, it is suggested to use the reduced gravity environment of outer space for experimentation directed at the identification and control of these defects. The results of these experiments are expected to lead to advances in our understanding of crystal growth related defect formation in general and will establish a basis for effective defect engineering, the approach to efficient achievement of defect related, application specific properties in opto-electronic materials

Introduction

It has been established that growth of BSO from the melt requires Platinum as a confinement material. Thus, current induced growth interface demarcation, which is considered essential for studies of growth kinetics and defect formation, is complicated in conventional Bridgman geometries, because of the high electrical conductivity of the confinement material. The effectiveness of other than conventional Bridgman geometries (structured confinement walls, solidification through an orifice) is strongly dependent on the wetting behavior of the confined BSO. It is considered essential therefore, to investigate for the system under consideration the wetting behavior in contact with platinum through measurements of contact angles as well its dependence on composition of the melt and the gas phase. The approach taken to the study of the wetting behavior of high temperature melts is simple, provides for reproducible data which are consistent with published results and is applicable to implementation in a reduced gravity environment.

PRELIMINARY STUDY OF THE WETTING BEHAVIOR OF PLATINUM IN CONTACT WITH BSO MELT

Axi-symmetric Drop Shape Analysis:

Surface tension and the gravity effect determine the shape of a sessile drop. Surface tension tends to make the drop spherical while gravity tends to flatten it. Since the gravity effect is known, the surface tension can be determined by analyzing the drop shape. The three-phase contact angle (θ) can be obtained as a side-output from the drop-shape analysis, with accuracy, which is superior to that of direct angle measurements.

The shape of the sessile drop is governed by the Laplace equation. It relates the interfacial tension and curvature at the liquid-vapor (or liquid-liquid) interface to the pressure difference across it:

$$\gamma(\frac{1}{\boldsymbol{R}_1}+\frac{1}{\boldsymbol{R}_2})=\Delta \boldsymbol{P} \tag{1}$$

where γ is the interfacial tension, R_1 and R_2 are the two principal radii of curvature and ΔP is the pressure difference across the interface. If gravity is the only effective external force, ΔP is linear along a vertical axis z:

$$\Delta \boldsymbol{P} = \Delta \boldsymbol{P}_0 + (\Delta\rho)\boldsymbol{g}\boldsymbol{z} \tag{2}$$

where ΔP_0 is the pressure difference at a reference plane, $\Delta\rho$ is the density difference across the interface, and g is the gravitational acceleration.

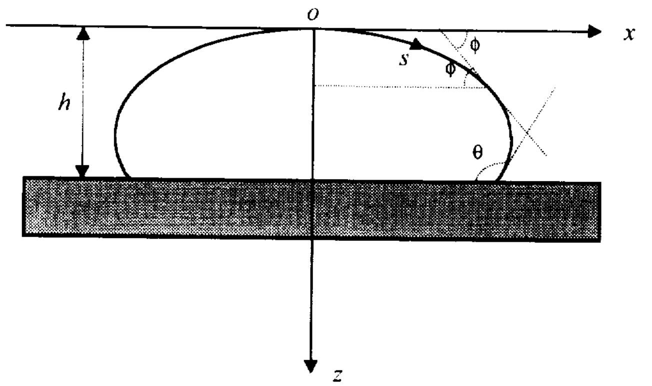

Fig. 1 Coordinate system for axi-symmetric sessile drop shape analysis.

By choosing a coordinate system as in Fig.1, we have the set of differential equations:

$$\frac{d\phi}{ds} = \frac{2}{R_0} + cz - \frac{\sin\phi}{x} \tag{1}$$

$$\frac{dx}{ds} = \cos\phi \tag{2}$$

$$\frac{dz}{ds} = \sin\phi \tag{3}$$

$$\frac{dV}{ds} = \frac{(\pi x^2 \leftarrow dz)}{ds} = \pi x^2 \sin\phi \tag{4}$$

where s is the arc length,

C is a capillary constant defined as_

$$c = \frac{(\Delta\rho)g}{\gamma} \tag{5}$$

The boundary conditions at the origin of the coordinate system are:

$$x(0) = z(0) = \phi(0) = V(0) = 0 \tag{6}$$

$$\left.\frac{d\phi}{ds}\right|_{s=0} = \frac{1}{R_0} \tag{7}$$

where R_0 is the radius of the drop at its apex.

The boundary conditions at the three-phase contact line is given by:

$$\phi\big|_{z=h} = \theta \tag{8}$$

$$V\big|_{z=h} = V_0 \tag{9}$$

where h is the height of the drop, and V_0 is the total drop volume.

Parameters involved are: c (or g/γ), R_0, θ, h and V_0.

By solving the set of differential equations (1)-(4), the shape of a drop can be uniquely generated with the parameters, c, R_0 and h. θ and V_0 can be calculated from equations (8) and (9). Only 2 of R_0, θ, h and V_0 are independent parameters and any two of them are sufficient to establish the boundary conditions of the problem.

In theory, knowing the exact location of two arbitrary points on the surface of the drop as well as the origin, ***O***, the values of ***c*** and ***R₀*** can be obtained by fitting the Laplace curve to these two points.

In reality, the surface line (a projection of the surface on the 2 dimensional *X-Z* coordinate system) can be localized only with an accuracy, determined by the optical system used. Since in computational analysis each point on the line has an inevitable uncertainty at the order of 1 pixel, a significant number of points were selected from the surface line to increase the accuracy of the extracted ***c*** and $\boldsymbol{R_0}$ values. It should also be mentioned that the origin, O, (X_0, Z_0), is difficult to locate; considering this quantity, like ***c*** and $\boldsymbol{R_0}$, as optimization parameter for the curve-fitting process can avoid the problem.

Images of sessile drops were acquired using a NEC, CCD (640×480) camera fit to a stereomicroscope. For photography of BSO melts the emitted, unfiltered radiation was used; sessile drop studies of organic liquids were carried out using an external light source (Fig 2). The contour of the drop shape was obtained by applying a 'Sobel' edge operator (that finds the pixels have the maximum gradient of intensity) to the drop image monitored on the screen (Fig 3).

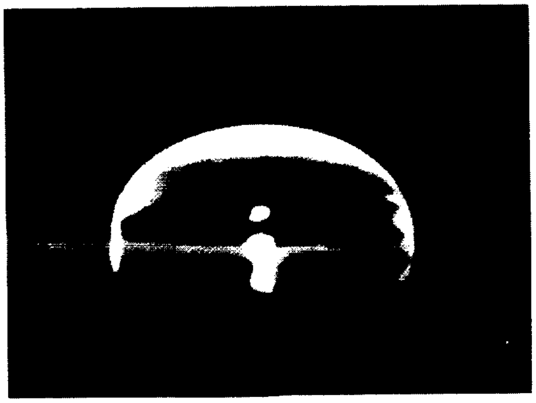

Fig. 2 Drop of glycerol on Teflon in reflection mode.

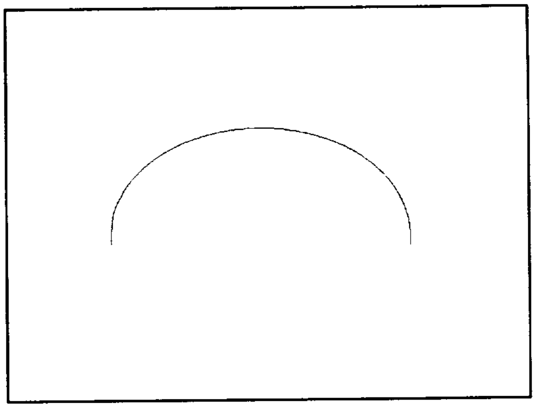

Fig. 3 Contour of the liquid-vapor interface as obtained by a 'Sobel' edge operator, applied to fig.2.

The sample points selected from the interface contour (Fig 3) were chosen to be uniformly spaced, so that every section of the curve is equally weighted during the curve-fitting process.

Experimental set-up

The determination of drop shapes and contact angles was carried out in an optical cell (with controlled ambient) with controlled heat input via a sodium heat pipe. Imaging was accomplished with an operational microscope and a CCD camera connected to a Macintosh. Image processing and analysis was done using the NIH image 1.6 software.

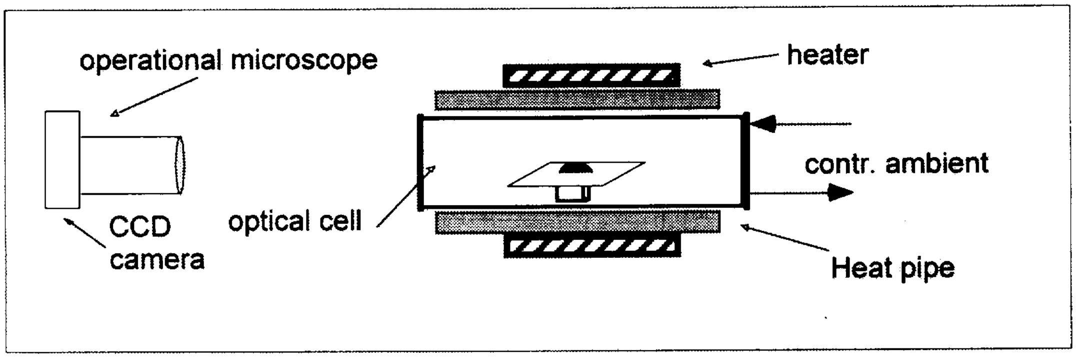

Fig.4 Schematic of optical cell used for the determination of drop shapes and contact angles.

Analysis of selected organic liquids with known surface tension

To test the viability of the adopted experimental and theoretical approach, we determined the surface tension of some organic liquids at room temperature in an argon atmosphere. The results are presented in Figs. 5, 6 and Table 1

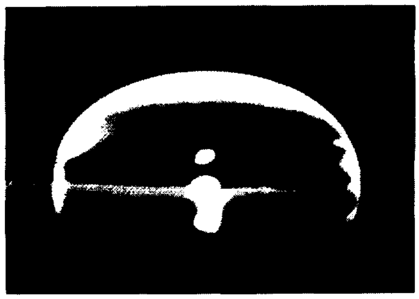

Fig. 5 Drop of glycerol on Teflon in reflection mode.

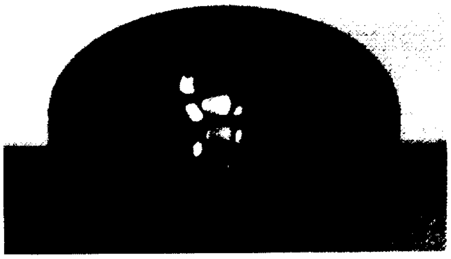

Fig.6 Drop of glycerol on Teflon in transmission mode.

Table 1 Surface tension of organic liquids according to drop shape measurements

Sessile Drop	Liquid-vapor surface tension, γ (MJ/m^2) 10 data-fitting processes for each drop		γ (mJ/m^2) from reference
	Mean	Standard deviation	
Diethylene glycol	44.2	1.7	44.77*
Glycerol (Fig. 4)	65.3	0.8	63.14**
Glycerol (Fig. 5)	62.1	0.7	

* CRC Handbook of Physics and Chemistry.

** Lange's Handbook of Chemistry

Wetting analysis on BSO:

Fig. 7, BSO (I a) at $P_{O2} = 10^{-4}$ atm

Fig. 8, BSO (I b) at $P_{O2} = 10^{-4}$ atm

Fig. 9, BSO (II a) at $P_{O2} = 10^{-4}$

Fig. 10, BSO (II b) at $P_{O2} = 10^{-3}$ atm

Table 2 Liquid-Vapor interfacial energies and contact angles obtained by drop shape analysis:

	P_{O2} (atm)	γ (MJ/m^2)		Contact Angle			
				Left		Right	
		Mean	Std.	Mean	Std.	Mean	Std.
I a	10^{-4}	206.0	13.6	43.47°	0.48°	44.66°	0.58°
II a	10^{-4}	184.2	7.8	-*	-	51.95°	0.93°
II b	10^{-3}	207.9	10.4	-	-	39.84°	0.55°
III a	10^{-4}	194.8	5.5	48.26°	0.35°	-	-
III b	10^{-3}	204.5	10.7	40.33°	0.76°	-	-

* The contact angle was not determined because contact line was not focused well on that side of the image. (but it was well focused on the other side)

Table 3 Contact angles by direct measurement:

Sessile Drop	Contact Angle (γ)			
	Left		Right	
	Mean	Std.	Mean	Std.
I a	44.05°	0.78°	44.7°	1.3°
I b	46.86°	0.79°	39.36°	0.85°

Preliminary Results of Wetting Study

Drop shape measurement indicate that the surface tension of (undoped) BSO melts is unaffected by the oxygen partial pressure in the ambient, yielding values ranging from 195 to 206 MJ/m^2.

The contact angle (θ) is however found to vary measurably with the oxygen partial pressure, increasing from zero degrees (complete spreading) at p_{ox} of 0.2 atm to about 48° at p_{ox} of 10^{-4}atm. Contact angle hysteresis is found to be small. This finding indicates that the dependence of the wetting behavior on the oxygen partial pressure is due to changes in the spreading pressure ($\gamma_{SV}-\gamma_{SL}$). The preliminary data suggest that "free" solidification is achievable in modified Bridgman geometry, provided the wetting behavior in space is not substantially different from that on the ground.

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