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Effect of oxygen on the molten BGO/Ir wetting and sticking

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Abstract In order to better understand the BGO-crucible interaction, the wetting of the molten BGO on Ir substrates has been studied by the sessile drop method at 1050 °C. It was found that the oxygen partial pressure in the surrounding atmosphere is an important parameter. For $P_{O_2} > 0.1$ mbar, full wetting is observed without any visible contact angle. X-ray diffraction analyses have shown that $Bi_2Ir_2O_7$ is formed at the interface. For $P_{O_2} < 0.1$ mbar, a drop is observed with a contact angle of 70° and no chemical reaction is detected. Attempts to grow BGO samples under low oxygen partial pressure resulted in ingot without sticking with the crucible.

Introduction

Bismuth germinate $Bi_4Ge_3O_{12}$ commonly abbreviated as BGO, is used for its scintillator capabilities. When exposed to high energy particles, gamma-rays or X-rays, BGO emits a green fluorescent light with a peak wavelength at 480 nm which can be easily measured by classical, cheap, light detectors. Due to its high stopping power, high scintillation efficiency, good energy resolution and non-hygroscopy, BGO is a good scintillation material and has found a wide range of applications in high energy physics, nuclear physics, space physics, nuclear medicine, geological prospecting, and other industries.

Single crystals are usually grown by the Czochralski technique but this technique involves diameter control problems and high thermal gradients that are detrimental to the crystal quality. An alternative growth method could be the Bridgman technique, where the crystal is grown in an Ir crucible. However experiments have shown that the crystal sticks to the crucible, with associated stresses and damages.

More generally, the wetting behavior of molten oxides on crucible materials is an important knowledge for the crystal grower of these materials. However a recent review [1] did not give any paper directly related to systems interesting to the crystal grower. The available literature in this field only concerns the wetting of oxide slags on metals.

This short note presents results obtained in studying the wetting behavior of molten BGO on Ir, with the aim to find an appropriate crucible material for the growth of BGO single crystals.

Experiments

The wetting experiments were performed by the sessile drop technique in closed ampoules. The experimental set-up and procedure were designed, developed, and validated by Harter [2] and are also described in [3]. They were essentially used for the study of the wetting of molten III–V and II–VI semiconductors on various substrates but no significant modification has been necessary for the present study.

Experiments were performed inside closed transparent silica ampoules (Herasil grade from Heraeus) previously evacuated under high vacuum during 24 h at 200 °C. Then the substrate and BGO sample (approx. 1 g, provided from cutting lost of single crystals by CRISMATEC) were introduced and the ampoule closed by a silica stopper.

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A remaining small silica tube was then connected to the vacuum pumps and gas bottles for cleaning again and filling the ampoule with the appropriate atmosphere. Then this tube was molten and pinched in order to hermetically close the ampoule.

The ampoule was introduced in a resistance furnace where previous thermal measurements have shown that the substrate temperature remains constant at ±0.5 °C. All measurements were performed at 1050 °C, slightly above the melting temperature of BGO (1044 °C). Molten drops were photographed through the optical stopper with a SINAR camera, see Fig. 1. In the cases where drops were obtained, the pictures were analyzed by comparison of theoretical shapes calculated by a classical Runge–Kutta method, in order to get the surface tension and the wetting angle. The density of molten BGO at 1050 °C was taken as 6530 kg m^{-3} [4].

Substrates were mirror polished iridium square plates, except some experiments where sandblasted iridium plates were used. Platinum substrates were also used but they always showed full wetting.

The atmosphere was controlled as follows:

- The nitrogen bottles were provided by the producer (Air liquid) with an analysis certificate of 5 ppm of O_2. This gas was used in order to fill the ampoules for the experiments with the lowest oxygen content.
- For the other experiments, the ampoules were first filled with pure O_2 at the appropriate pressure and then nitrogen was added in order to reach the targeted total pressure.

Results and discussion

The results are presented in the Table 1. Platinum always showed full wetting and sticking, in agreement with the reported interaction of Pt with BGO [5]. The experiments

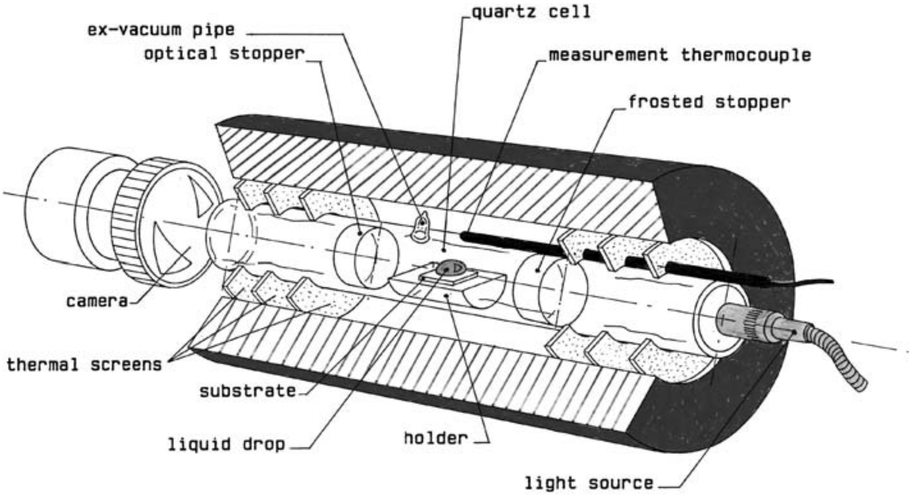

Fig. 1 Schematic view of the experimental device

Table 1 Experimental results of wetting of molten BGO on various substrates and under various atmospheres

Atmosphere	P_{tot} (1050 °C mbar)	P_{O_2} (1050 °C mbar)	Substrate	Result
Air	1000	200	Pt	Full wetting
Air	1000	200	Polished Ir	Full wetting
99.8% N_2+ 0.2% O_2	54	0.1	Polished Ir	Drop
98% N_2+ 2% O_2	1000	20	Polished Ir	Full wetting
99.8% N_2+ 0.2% O_2	1000	2	Polished Ir	Full wetting
99.9% N_2+ 0.1% O_2	1000	1	Polished Ir	Full Wetting
99.95% N_2+ 0.05% O_2	1000	0.5	Polished Ir	Full wetting
99.99% N_2+ 0.01% O_2	1000	0.1	Polished Ir	Full wetting
N_2+ 5 ppm O_2	1000	5×10^{-3}	Polished Ir	Drop, $\theta = 70°$
Ar+ 5 ppm O_2	1000	5×10^{-3}	Polished Ir	Drop, $\theta = 85°$
N_2+ 5 ppm O_2	2000	10^{-2}	Polished Ir	Drop, $\theta = 70°$
N_2+ 5 ppm O_2	1000	5×10^{-3}	Rough Ir	Drop, $\theta = 70°$

Table 2 Surface tension, σ, wetting angle, θ, work of adhesion, W_a, and work of cohesion, W_c, of BGO on polished Ir

Atm.	σ mJ/m^2	θ°	$W_a = \sigma(1+\cos\theta)$ mJ/m^2	$W_c = 2\sigma$ mJ/m^2	W_a/W_c %
N_2	208 ± 6	70 ± 5	279 ± 25	416 ± 25	67
Ar	243 ± 7	85 ± 5	264 ± 34	486 ± 34	54

Gases had a purity of 5 ppm

then focused on Ir, not surprisingly as this material is regularly used for crucible in the Czochralski pulling of BGO. It appeared that the partial pressure of oxygen was a key parameter for the wetting. Two cases should be distinguished.

For a partial pressure of O_2 higher than approximately 0.1 mbar, full wetting of the substrate by the molten BGO is observed (no detectable drop or wetting line). X-ray diffraction analysis of the substrate surface was performed and showed unambiguously a layer of $Bi_2Ir_2O_7$. Traces of IrO_2, Bi, and Ge were also detected. It is proposed that the following reactions take place between the sample and the IrO_2:

$$2Bi + 3/2IrO_2 \leftrightarrow Bi_2O_3 + 3Ir$$

$$2Bi + 2IrO_2 + 3/2O_2 \leftrightarrow Bi_2Ir_2O_7$$

The oxides may also react:

$$Bi_2O_3 + 2IrO_2 \leftrightarrow Bi_2Ir_2O_7$$

For a partial pressure of O_2 lower than approximately 0.1 mbar, there is no detectable reaction between the substrate and the BGO and a drop is obtained under Ar as well as N_2 atmospheres. The measurements in these cases are given in the Table 2.

These values are in agreement with the conclusions of [1]: in non-reactive molten oxide/solid metal systems (as in molten metal/solid oxide systems), adhesion results from weak, van der Waals, interactions leading to values of work of adhesion W_a of a few hundreds of mJ m^{-2}. However molten BGO wets the metallic substrates, because its surface tension is lower than W_a, leading to $\theta < 90°$.

The decrease of contact angle in the molten oxide/metal systems, when the partial pressure of oxygen increases, has already been reported by Ownby in the case of silico-alumina melt on W [6], but without discussion of a possible mechanism. Using data of [7–10], Chatillon (Chatillon C SIMaP laboratory, personal communication of data analysed in (1993)) computed the standard free energy of formation of $Ir0_2$ as function of temperature. It follows that, at the temperature of the experiment, the equilibrium pressure of O_2 is of the order of 10^{-13} mbar, and then IrO_2 was present in all experiments. The wetting transition at 0.1 mbar cannot be simply explained in terms of oxidation transition. Following the mechanism proposed by Pech et al. [11] in the case of a molten glass on stainless steel, it appears that, at low oxygen partial pressure, the IrO_2 layer is not stable versus the molten BGO in which it dissolves at a rate faster than its production by reaction of the substrate with the atmosphere.

At high P_{O_2}, the quantity of IrO_2 increases and the liquid is saturated close to the interface. This results in $Bi_2Ir_20_7$ formation at the substrate surface in contact with the liquid, which is responsible for the observed wetting transition.

Concerning the difference between Ar and N_2 atmosphere, it should be taken cautiously because only one measure has been performed under Ar. BGO is usually pulled under air and does not react with N_2. N_2 adsorbs on Ir [12] at room temperature, but with a low binding energy [13], so that it is desorbed at high temperature.

On the practical point of view, the best results were obtained in the case of the sand-blasted Ir substrates because the drops detached spontaneously from the substrate during cooling. This is attributed to thermo-mechanical stresses due to differential dilatation [14]. Therefore Bridgman solidification experiments of BGO in sand-blasted Ir cylindrical crucibles and under pure nitrogen were performed. It was observed that slightly conical crucibles enhanced the detachment and allowed a gentle removing of the sample from the crucible. However the low partial pressure of oxygen resulted in a high concentration of oxygen vacancies in the BGO, likely to decrease the scintillation efficiency of the material.

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