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Preparation of a crack-free and grain oriented Bi_2O_3 film with fcc structure

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Geometry, grain orientation and electrical conduction of a rapidly quenched Bi_2O_3 film were investigated. The high temperature form of Bi_2O_3 was retained within the compositional range from 4 to 16 mol % MoO_3 of which 4 mol % is discussed. Among the four sets of quenching apparatus tested, single-roller was the best suited for the preparation of a crack-free film. Other methods such as twin-roller, roller-plate and centrifugal spinning caused cracks in a quenched specimen. They were unidirectionally solidified and the direction of the grain elongation coincided with ⟨1 1 1⟩. Electrical conductivities along the film length and width were close to $10^{-2}\,\Omega\,cm^{-1}$ around 400° C. Conduction along the thickness was about three orders of magnitude smaller than other directions. The quenched film became unstable above 450° C.

1. Introduction

The high temperature form of Bi_2O_3 is the face centred cubic (fcc) structure of fluorite type [1]. This phase is stable above 730° C and exhibits a high oxygen ion conductivity of about $1\,\Omega\,cm^{-1}$ up to the melting point 824° C.

Below 730° C, the monoclinic structure becomes stable and the conductivity falls remarkably down to the order of $10^{-3}\,\Omega\,cm^{-1}$ around 700° C [2]. This phase transformation accompanies a large volume change and, therefore, pure Bi_2O_3 is not suitable for practical use as a solid electrolyte.

Extensive studies have been undertaken to stabilize the fcc structure to lower the temperature region by adding a variety of oxides. Takahashi *et al.* have shown that the solid solutions of Bi_2O_3 with Y_2O_3 [3], Gd_2O_3 [4], V_2O_5 [5], Nb_2O_5 [5], Ta_2O_5 [5] and WO_3 [6] retained fcc structure. The stabilization of the fcc structure is also reported in the Bi_2O_3–Ln_2O_3 (Ln = lanthanide) systems [7, 8].

A close examination of the reported data reveals that the smallest amount of second oxide is preferable for the optimum conductivity.

These materials have been synthesized as sintered bodies in which crystalline grains are randomly oriented. This type of grain arrangement is not always suitable for a fast ionic conductor. When an oxygen ion passes through the body, it encounters grains of various orientations. Some grains have orientations convenient for ionic migration, and others are obstructive.

If all grains are oriented, a certain direction of the specimen will give the optimum results. Recently the grain orientation of $La_{0.33}NbO_3$ was achieved by Torii *et al.* [9]. It consists of spreading a melt on a cold substrate and quenching it very rapidly. This technique enables us not only to attain the grain orientation but also to retain the high temperature crystal structure.

The purpose of this investigation is to apply the rapid quenching technique for the preparation of a grain oriented Bi_2O_3 film with fcc structure and see if the quenched polycrystalline specimen can be a candidate for a solid electrolyte.

2. Experimental details

The starting materials were Bi_2O_3 and MoO_3 of 99.9% purity from Furuuchi. Powders were thoroughly mixed and sintered in a platinum crucible for 5 h at 800° C in air. Small pieces of the sintered bodies were, then, melted in a platinum tube (10 cm long with 5 mm inner diameter), the bottom of which is drilled through a hole of

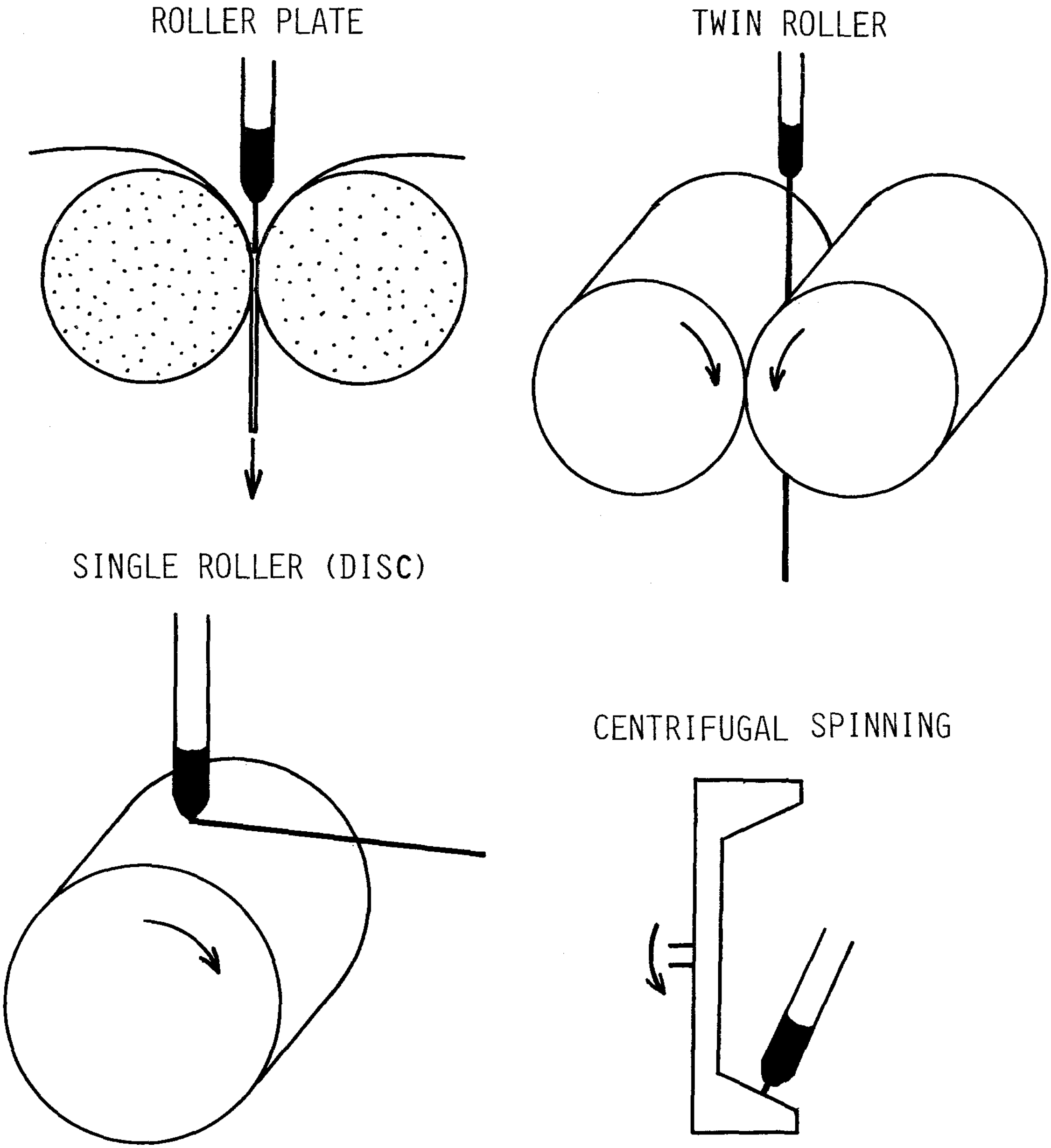

Figure 1 Schematic drawings of the four sets of quenching apparatus tested.

0.3 mm (diameter). Temperatures of the melts were controlled 60° C above the melting point or liquidus temperatures. Melts were ejected on a metallic substrate with compressed air of 0.5 atm.

Four sets of quenching apparatus, twin-roller [10, 11], roller-plate [12], centrifugal spinning [13] and single-roller [14] were tested. They are shown schematically in Fig. 1 and their working conditions are summarized in Table I.

The crystal structures and the grain orientations

TABLE I Comparison of working conditions of the four sets of quenching apparatus

Quenching method	Substrate speed (m sec^{-1})	Force/pressure/acceleration
Twin-roller	10	Force : 10 ~ 50 kg
Roller-plate	0 ~ 2.5	Pressure : ~ 1 kg cm^{-2}
Centrifugal spinning	14 ~ 56	Acceleration: 200 ~ 3200 g
Single-roller	16 ~ 63	Acceleration: – 250 ~ – 4000 g

of the quenched specimens were examined by a Rigaku Denki SG-9 diffractometer. Cu$K\alpha$ was used with a nickel filter.

The grain arrangements of the etched samples were observed with an optical microscope, type optiphoto-pol XTP Nikon. Silver electrodes were pasted on the faces of the quenched film and electrical conductivity was measured in air using YHP 265B a.c. bridge at 1 kHz within the temperature range from 300 to 700° C.

3. Results and discussion

3.1. Apparatus

Pure Bi_2O_3 was quenched with the four sets of apparatus but the f c c structure was not retained. Polycrystalline specimens were filled with cracks caused by the volume shrinkage. To retain the high temperature form with a small amount of additive as possible, MoO_3 was chosen as a second oxide from a phase diagram consideration [15].

Quenching was carried out from 2 to 16 mol% MoO_3 in 2 mol% steps and the monophasic f c c structure was obtained within the compositional range from 4 to 16 mol% MoO_3. As we are interested in the composition with the smallest amount of second oxide, $96Bi_2O_3 \cdot 4MoO_3$ is discussed hereafter. The diffraction pattern of the 4 mol% MoO_3 is shown in Fig. 2.

Among the four sets of apparatus tested, the twin-roller and the roller-plate formed flakes and some cracks were observed by the optical microscope. This forms a marked contrast to the case of glass formation. When a glass, such as $BaTiO_3$ doped with BaO [16], is formed the quenched specimen is large and without cracks.

We suppose that the difference is based on the degree of undercooling. Undercooling of the $96Bi_2O_3 \cdot 4MoO_3$ is small and the melt crystallizes before the mechanical pressure weakens. Crystalline specimens become fragile and are crushed by the substrate (roller or plate).

On the other hand, a glass forming material passes a comparatively long undercooled state during which it is flexible and the applied mechanical force cannot break it into pieces.

The centrifugal spinning method produced film-like samples but they also had cracks due to the centrifugal force exerted on the curved films (see Section 3.2). Only the single-roller technique gave samples with no cracks.

Since the existence of cracks does not allow us to study the intrinsic anisotropy of the film, we concluded that the single-roller method is the best suited for the conductivity measurement.

3.2. Geometry of the quenched film

Relation between the geometry of the quenched film and the single-roller speed was examined.

Temperature of the melt, pressure of the compressed air and the orifice diameter were kept at 970° C, 0.5 atm and 0.3 mm, respectively. A stainless steel roller of 20 cm in diameter was run at 1500, 2000, 3000, 4000 and 6000 rpm. The average thickness of the film changed from 18 to 8 μm and the width from 0.6 to 0.2 mm as the roller revolved from 1500 to 6000 rpm.

The effect of the compressed air was examined by varying the pressure from 0.5 to 1.5 atm but no remarkable change was observed.

From a practical point of view of handling and electroding the samples, an appropriate thickness and width are required. 2000 rpm and 0.5 atm were chosen and the quenching under these conditions produced films typically 2 cm long, 0.4 to 0.6 mm wide and 15 μm thick. They are yellowish transparent. A film is shown in Fig. 3. Parabolic lines imprinted at the surface reflect the flow of the melt on the roller surface polished with 0.3 μm alumina paste prior to quenching.

A cross-sectional perpendicular to the length shows that the film is bent toward the roller (Fig. 4). When a liquid film is cooled and the lower part starts to crystallize, the volume shrinkage of the crystalline layer causes a bending stress. This is why the quenched film is not flat and the centrifugal spinning method cannot produce a crack-free film.

3.3. Grain orientation

Fig. 5 represents a free surface of a film on which grains ranging from 1 to 8 μm can be seen. A cross-section perpendicular to the length is polished and etched for about 30 sec in a mixture of 20% sulphuric acid and 10% nitric acid.

The grain boundary arrangement was observed to be nonuniform; some grains grow upward increasing their volume whereas some others shrink and disappear midway (Fig. 6). The growth direction is not always normal to the surface but, on the whole, grains are unidirectionally solidified.

The driving force of the directional solidification depends on the temperature gradient along the film thickness [17]. An instantaneous generation of heat on crystallization and heat flow from the

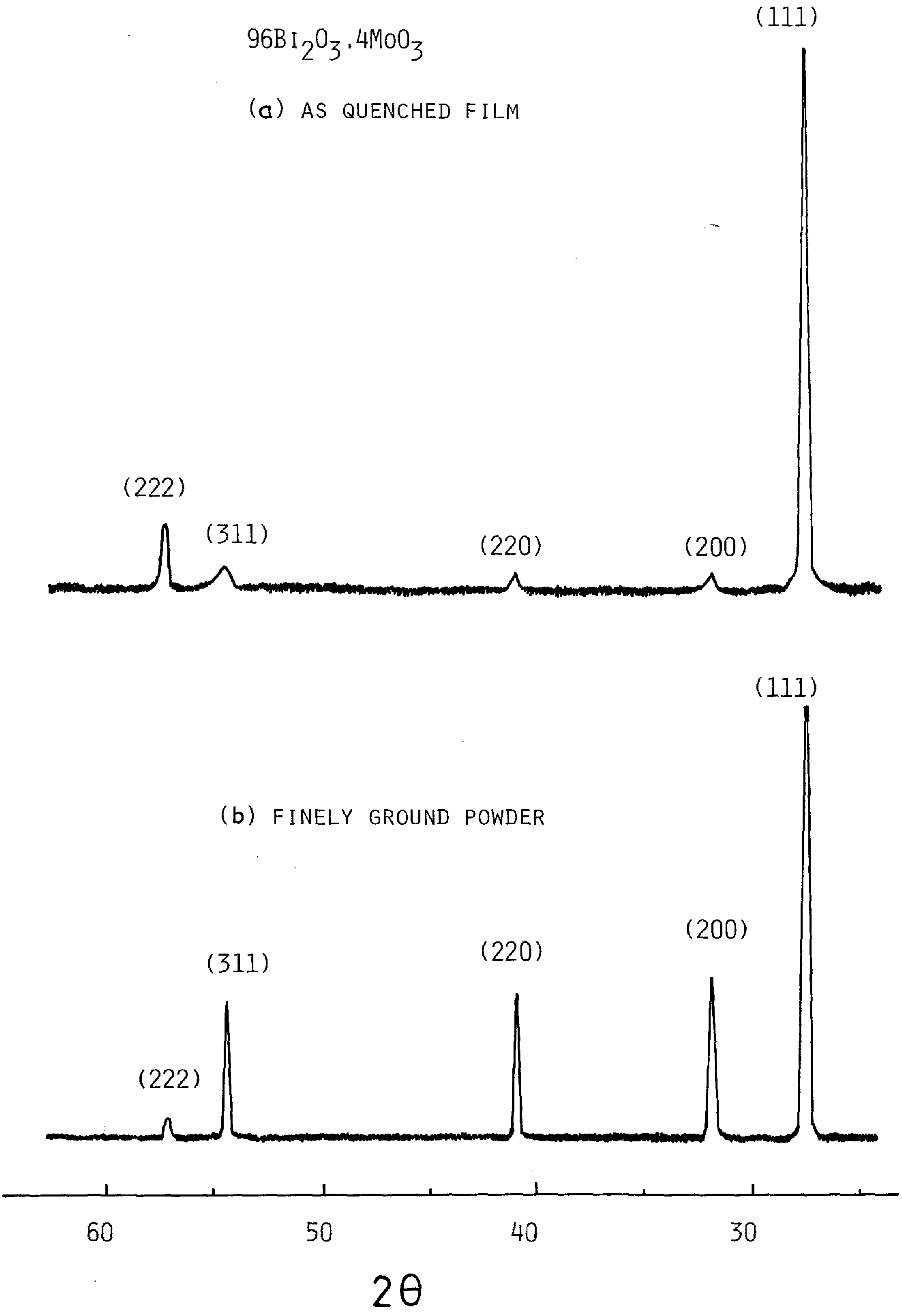

Figure 2 X-ray diffraction pattern of $96Bi_2O_3 \cdot 4MoO_3$ at room temperature. (a) As quenched films; no distinction between the free surface and the roller surface is made. (b) Films are finely ground into powders.

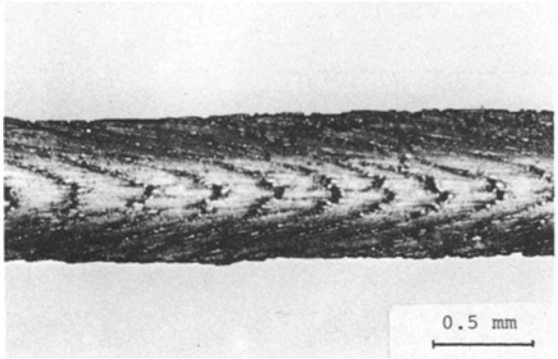

Figure 3 Roller surface of as quenched film.

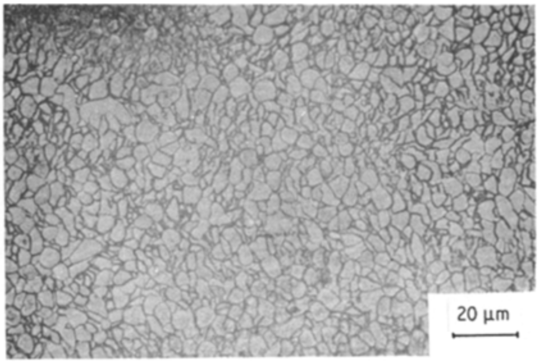

Figure 5 Etched free surface of the quenched film.

film to the roller are the main factors controlling the temperature gradient between the crystallization front and a liquid layer, presumably several hundreds of atomic distances apart. The temperature profile in the film can, in principle, be calculated according to the model of Ruhl [18], however, it is not discussed here. It is only noted that the release of the latent heat of fusion has little influence on the cooling rate be it ideal or Newtonian [18].

Fig. 2 shows the crystallographic characteristics of the quenched film with f c c structure. Preferential ⟨1 1 1⟩ growth is evidenced by the strong reflections from the (1 1 1) and (2 2 2) planes. A quantitative expression of crystallographic orientation was deduced from the diffraction intensities of the as-quenched film (Fig. 2a) against those of a finely ground film (Fig. 2b) after Lotgering [19]. The orientation degree was 0.8 to 0.9; varied from specimen to specimen.

Since the orientation degree is defined so that $f = 1$ when orientation is perfect and $f = 0$ for perfect randomness, it indicates that the quenched films are highly oriented and the direction of grain elongation coincide with ⟨1 1 1⟩.

3.4. Electrical conductivity

Directional differences in conductivity are prominent, as shown in Fig. 7. Conductivities along the film length and width are close to $10^{-2}\,\Omega\,\mathrm{cm}^{-1}$ around 400° C; about three orders of magnitude greater than that along the film thickness.

Quenched films, apparently, were not hygroscopic and distances between the electrodes were 0.3 to 0.5 mm; 20 to 30 times longer than the film thicknesses. So it is supposed that the measured values represent the bulk conductivities [20].

This anisotropy is in striking contrast to a sintered body in which grains are randomly oriented and conduction is isotropic.

The present conductivities, when compared with the literature data [3–8], belong to one of the highest around 400° C. Though measurements of the transference number have not yet been

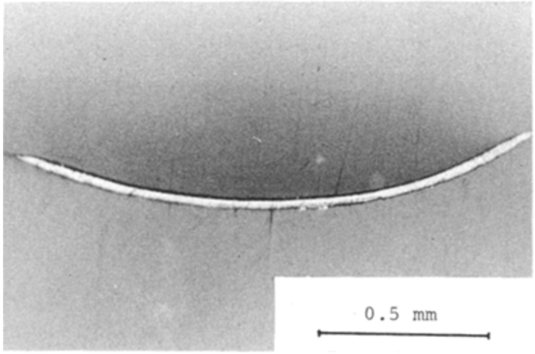

Figure 4 Polished cross-section perpendicular to the length, nozzle of 0.5 mm diameter is used to see the uniformity of the thickness.

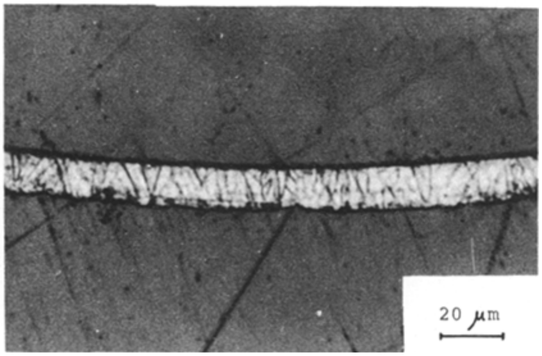

Figure 6 Cross-section perpendicular to the length; polished and etched.

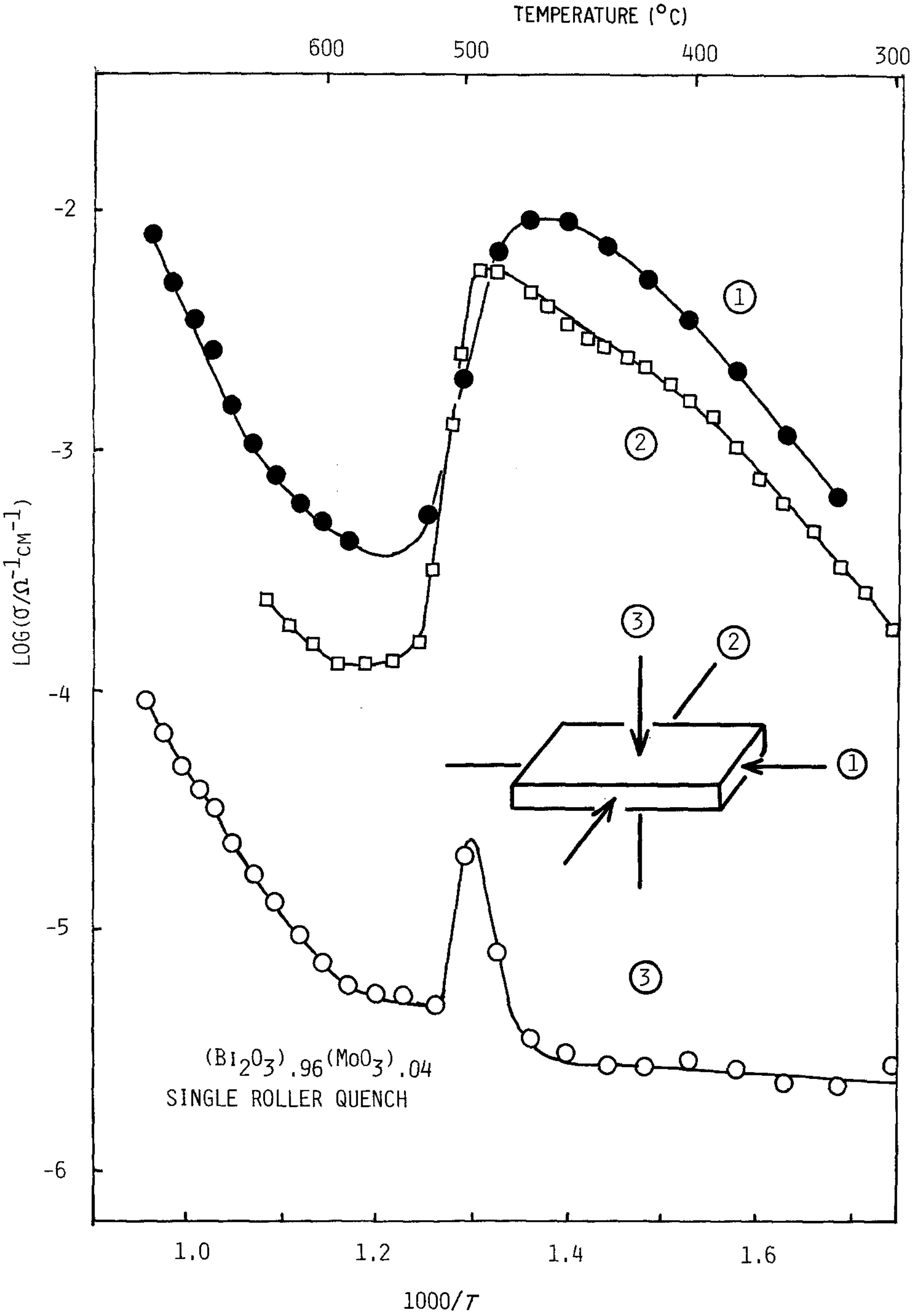

Figure 7 The temperature dependence of directional differences in conductivity of the quenched film, plotted as log (σ) against $10^3/T$, measured at 1 kHz in air.

conducted, grain oriented film of Bi_2O_3 is attractive for its excellent conduction below 400° C and further experiments are now being performed.

4. Conclusions

(a) High temperature form of Bi_2O_3 was retained by rapid quenching from the melt between the compositional range from 4 to 16 mol% MoO_3.

(b) Apparatus such as twin-roller, roller-plate and centrifugal spinning produced cracks in a quenched specimen. Only the single-roller technique could form a crack-free film. The film was typically 2 cm long, 0.4 to 0.6 mm wide and 15 μm thick. A cross-section perpendicular to the length showed that it is bent toward a contact surface.

(c) Grains were nonuniformly elongated along the film thickness and the direction of the grain elongation coincided with ⟨1 1 1⟩. Grain diameters observed at the surface ranged from 1 to 8 μm.

(d) Electrical conductivities along the film length and width were close to $10^{-2}\ \Omega\ \text{cm}^{-1}$ around 400° C; three orders of magnitude greater than that along the film thickness. The quenched film was not stable above 450° C.

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