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In situ observation of crystallization from a superconductor melt of composition $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$

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The surface appearance of a pellet of composition $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$, and crystallization from a melt of this composition, were examined by thermo-microscopy and thermal analysis. The $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ mixture melted incongruently at ~865 to 906 °C. As the temperature dropped below ~835 °C, the melt solidified into plate-like crystals. Analytical results on a videotape indicated that the growth rate of these plate-like single crystals was $\sim 6.6 \times 10^{-3}$ mm s^{-1}. Surface changes caused by heating, and the formation process of the plate-like single crystals with cooling, were clarified by the present investigation.

1. Introduction

The discovery of superconductivity at from ~20 K to about 80 K in the system Bi–Sr–Cu–O by Michel *et al.* [1] and then at about 110 K by the addition of Ca by Maeda *et al.* [2] has caused great scientific interest in this new family of high-T_c superconductors. Chu *et al.* [3] discovered superconductivity above 100 K in the Bi–Sr–Cu–O system. The increase in T_c has been correlated with the number of CuO layers in structures of the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ family, where n varies from 1 to 3 [4, 5]. In this system there are two superconducting phases, $Bi_2Sr_2Ca_1Cu_2O_x$ and $Bi_2Sr_2Ca_2Cu_3O_x$, with different T_cs of 85 and 105 K above the liquid-nitrogen temperature [6]. Pb doping has been proved to stabilize the 105 K phase [7]. Green *et al.* [8] prepared Pb-doped Bi–Sr–Ca–Cu–O superconductor with zero resistance at 107 K.

A homologous family of the type $(Bi, Pb)_2(Ca,Sr)_{n+1}Cu_nO_{2n+4+\alpha}$ has been found to exhibit increasing T_c with increasing n, the number of CuO layers. The phase exhibiting $T_c = 110$ K has been characterized as the $n = 3$ and the $n = 4$ members [9–12].

Recently, Hongbao *et al.* [13] have reported zero resistance at 132 K in $Bi_{1.9-x}Pb_xSb_{0.1}Sr_2Ca_2Cu_3O_\delta$ with $x = 0.3$ and 0.4, and Chandrachood *et al.* [14] have reported zero resistance at 132 K in a lead-free Sb-doped 2:2:2:3 phase composition of the nominal formula $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ by proper control of the preparation conditions.

As described in a later paper [15], the surface appearance of a pellet of the composition $TlCa_2Ba_3Cu_4O_{10-\alpha}$, and crystallization from a melt of this composition, are examined by thermo-microscopy and thermal analysis. The $TlCa_2Ba_3Cu_4O_{10-\alpha}$ mixture melted incongruently at ~975 to 1066 °C. As the temperature dropped below 1060 °C, the melt solidified into plate-like crystals. Analytical results on a videotape indicated that the growth rate of these plate-like single crystals was $\sim 6.0 \times 10^{-2}$ mm s^{-1}.

The purpose of the present work was to directly observe the surface appearance of the composition of nominal formula $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ and crystallization from a melt of this composition, using a thermomicroscopic apparatus and thermal analysis, and to give a detailed report on the findings.

2. Experimental procedure

Samples of nominal composition $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ were prepared. The raw materials were Bi_2O_3, Sb_2O_5, $SrCO_3$, $CaCO_3$ and CuO. Commercial, chemical-grade reagents were used. The powders were mixed and ground completely in methanol and pressed at 400 kg cm^{-2} (40 MPa) to obtain a pellet with 20 mm diameter and ~2 mm thick.

A small piece of this pellet was then put on to a small platinum plate in the heating stage of a Linkam thermo-microscopic apparatus, shown schematically in Fig. 1. The apparatus consisted of a light-emitting diode and optical fibre, an optical sensor, a heating stage made of platinum, and a VTR photographing apparatus. The surface of the small pellet and crystallization from the $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ melt were observed.

This small pellet was heated to 300 °C at a rate of 50 °C min^{-1}, to 1200 °C at 20 °C min^{-1}, and then held at 1200 °C for 3 min. Subsequently, the pellet was cooled to 800 °C at 20 °C min^{-1} in a stream of dry argon. A continuous videotape (×1000) was taken of all processes.

3. Results and discussion

3.1. Results of thermal analysis

A thermogram of a small pellet with the composition

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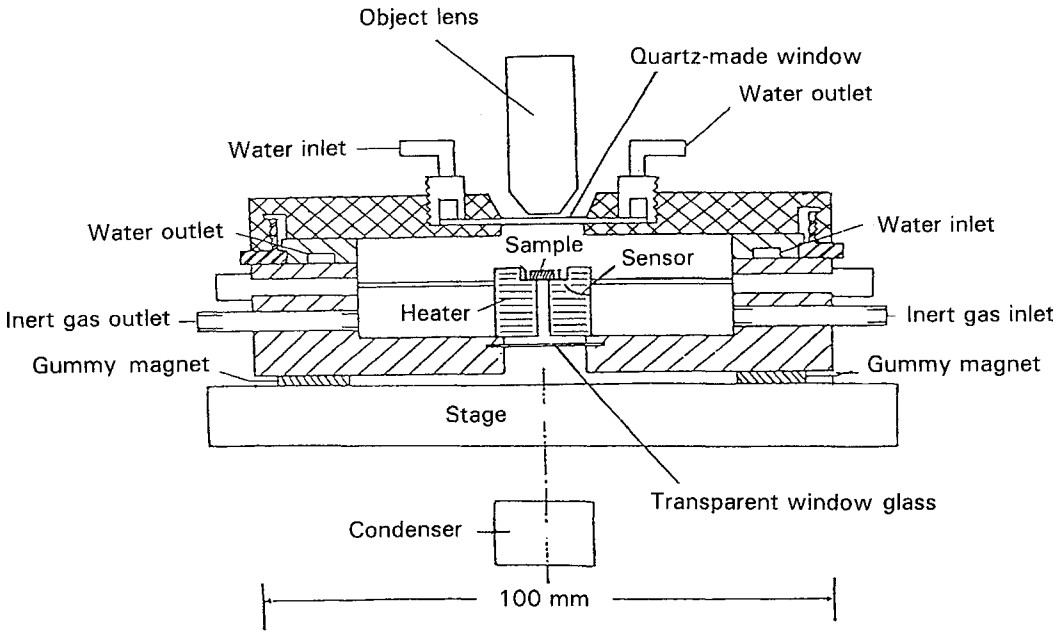

Figure 1 Schematic arrangement of thermo-microscopic apparatus (Linkam Heating Freezing Stage).

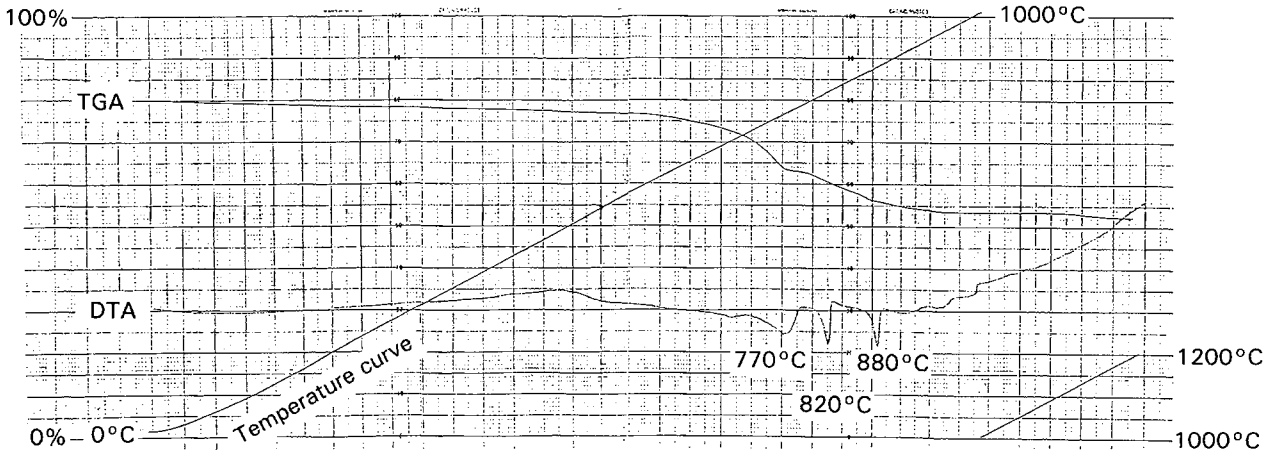

Figure 2 Plots of DTA and TGA for the pyrolysis of $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ presursor.

$Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ up to 1200 °C is shown in Fig. 2. Differential thermal analysis (DTA) revealed three large, endothermic peaks at 770, 820 and 880 °C; other weaker peaks occurred at 550 and 700 °C. The three strong peaks indicate decarboxylation from $SrCO_3$ and $CaCO_3$. The end-point at ~898 to ~1010 °C of the very wide peaks may correspond to the incongruent melting of the $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ mixture.

Thermogravimetric analysis data, which show a gradual weight loss from 100 to ~970 °C and indicate a series of steps in the melting process, reveal three additional losses at ~770, 820 and 880 °C. These losses, which correspond to the three DTA peaks, are associated with the evolution of CO_2.

A total loss of 33 wt % was estimated from the evaporation of CO_2 gas, part of the Bi_2O_3 and Sb_2O_3, absorbed water, etc; this value is quite high.

3.2. *In situ* observation of surface appearance and crystallization from the $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ melt

To study the surface appearance of the $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ pellet and the crystallization of the same composition of melt, part of the pellet of size ~4 mm × 4 mm × 1 mm was loaded into a small crucible. The pellet was then heated by the apparatus shown in Fig. 1 and pictures taken of all processes by a VTR photographing apparatus in a stream of argon gas. The results of this process are shown in Figs 3–6.

Fig. 3a shows the surface appearance of the small pellet before heating; the particles, appearing grey-white and black, were not uniform. After heating to ~450 °C the surface of the pellet was unchanged. Little change occurred in the pellet at 500 °C, as shown in Fig. 3b.

At 551 °C, as shown in Fig. 3c, however, the neigh-

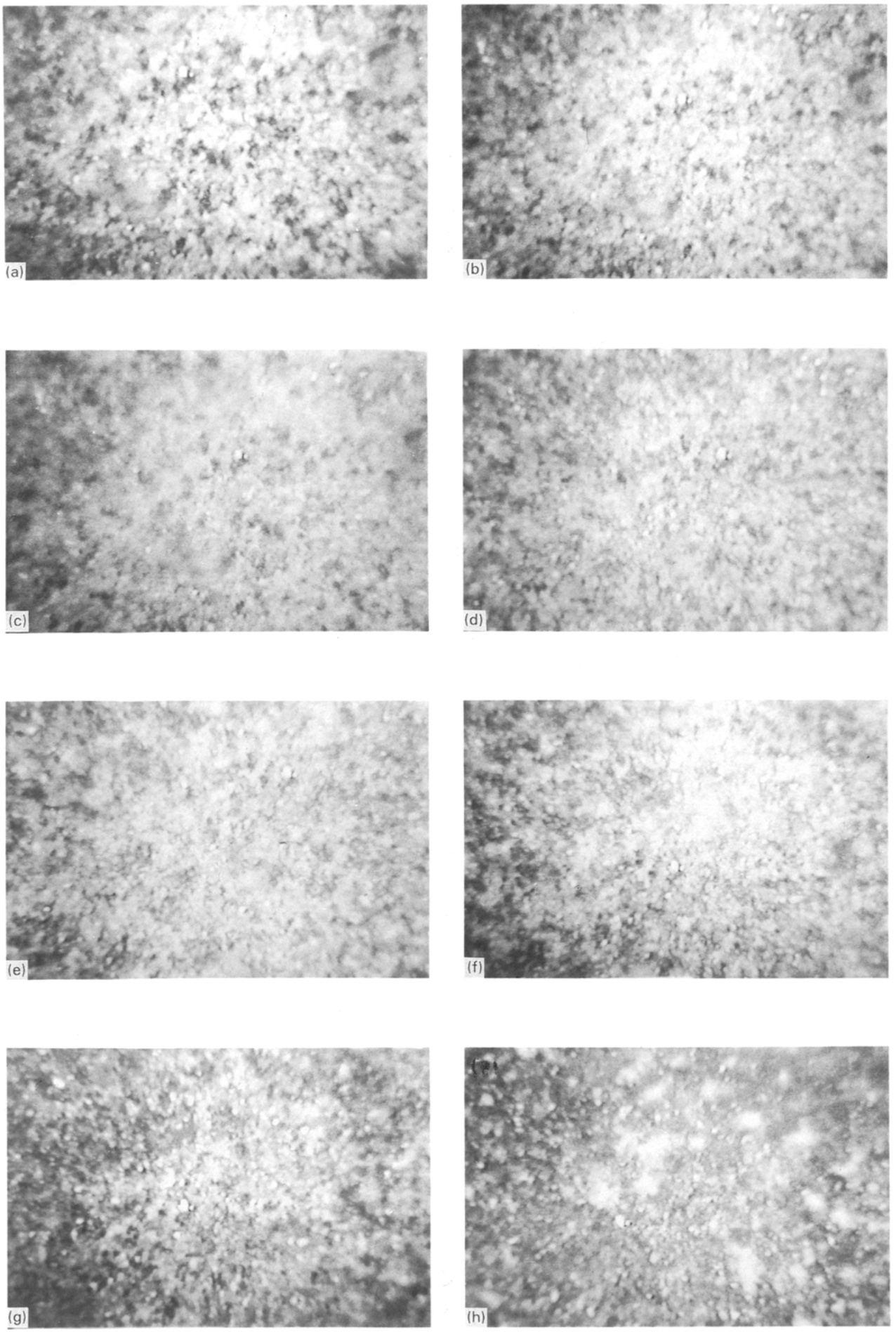

Figure 3 Surface appearances and crystallization from a $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_6$ composition melt, as observed by a thermo-microscopic apparatus: (a) starting material, and heated to (b) 500 °C, (c) 551 °C, (d) 740 °C, (e) 771 °C, (f) 802 °C, (g) 816 °C, (h) 851 °C. The horizontal dimension of each print corresponds to 300 μm.

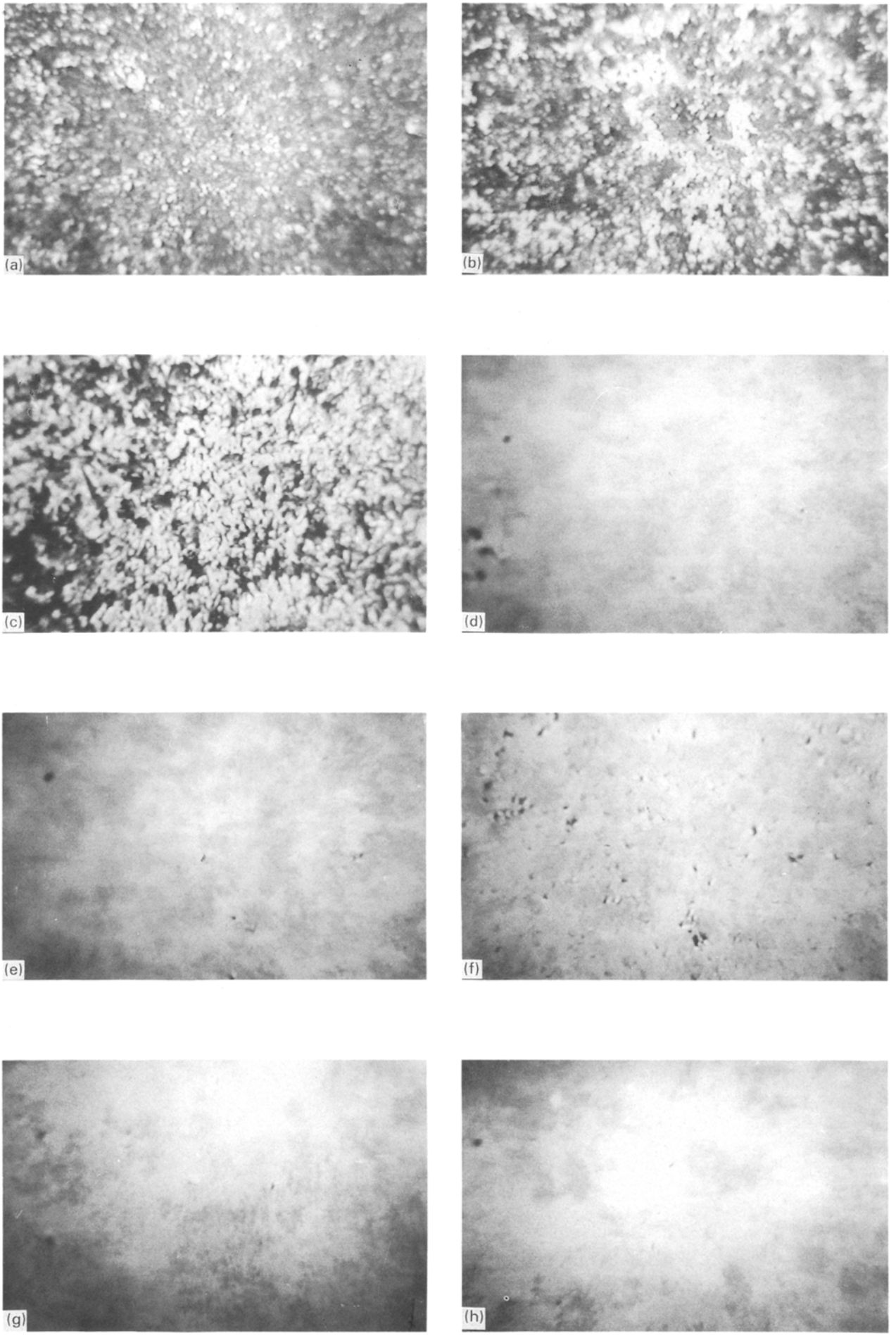

Figure 4 Surface appearances and crystallization from a $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ composition melt, as observed by a thermo-microscopic apparatus: heated to (a) 865 °C, (b) 880 °C, (c) 906 °C, (d) 913 °C, (e) 915 °C, (f) 1002 °C, (g) 1010 °C, (h) 1120 °C. The horizontal dimension of each print corresponds to 300 μm.

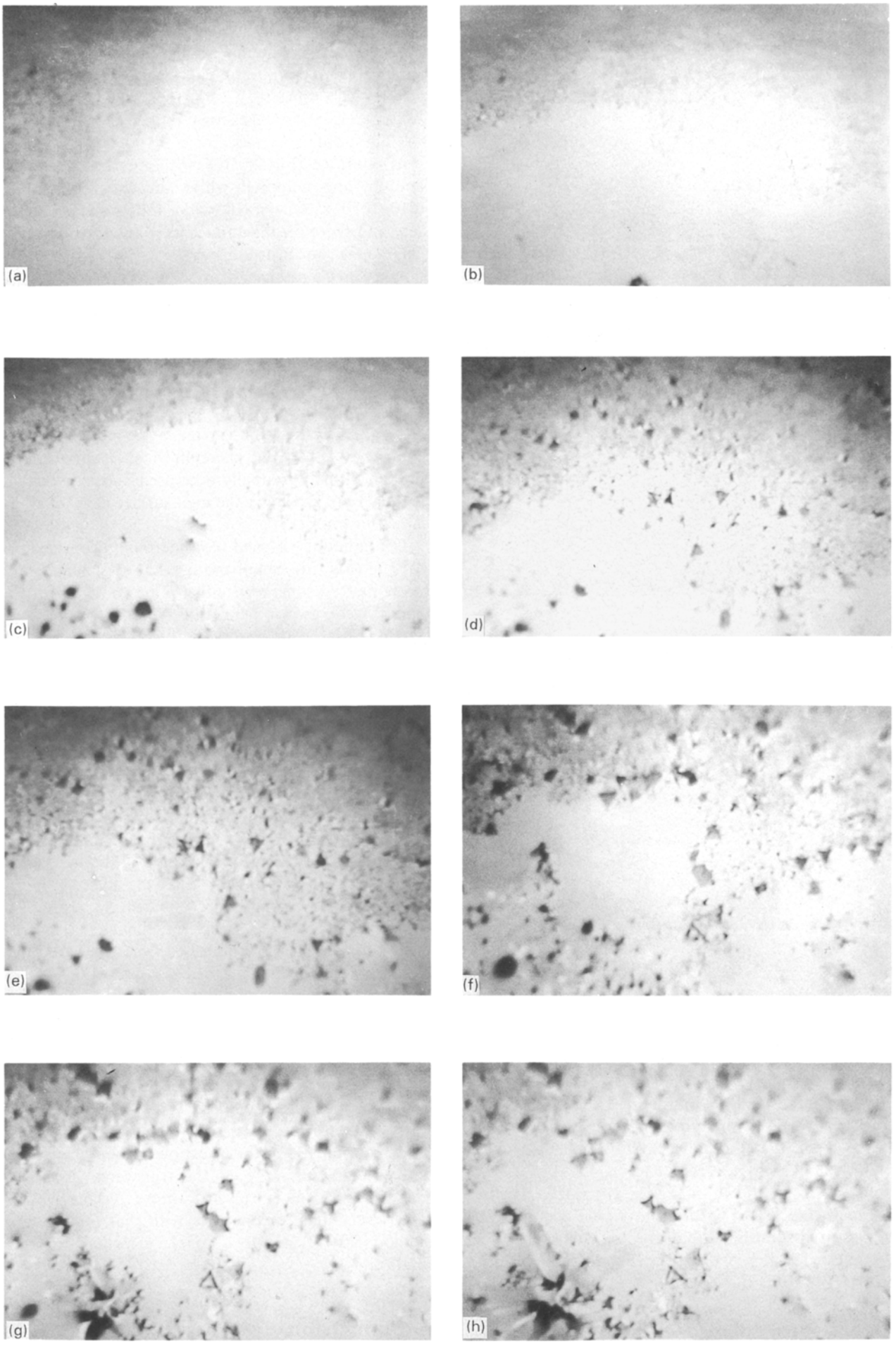

Figure 5 Surface appearances and crystallization from a $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_8$ composition melt, as observed by a thermo-microscopic apparatus: (a) heated to 1200 °C, and then cooled to (b) 1150 °C, (c) 1100 °C, (d) 1070 °C, (e) 1040 °C, (f) 840 °C (g) 835 °C (h) 823 °C. The horizontal dimension of each print corresponds to 300 μm.

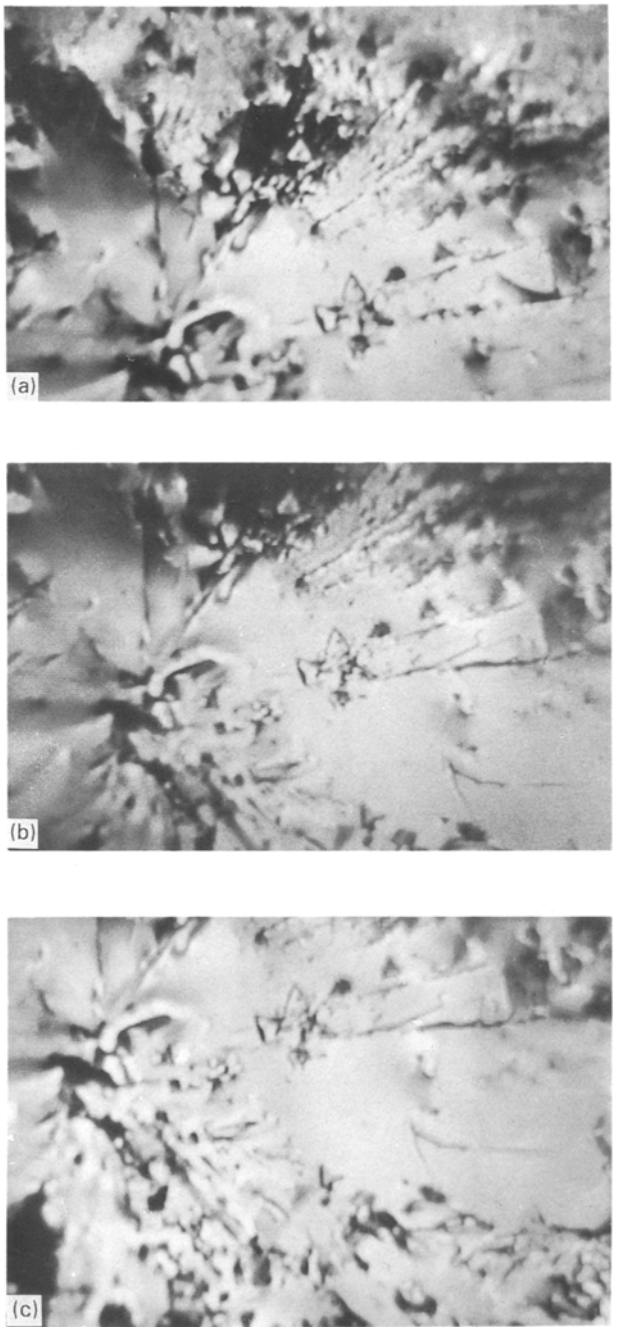

Figure 6 Surface appearances and crystallization from a $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ composition melt, as observed by a thermo-microscopic apparatus: cooling to (a) 812 °C and (b,c) 802 °C. The horizontal dimension of each print corresponds to 300 μm.

bouring particles exhibited some reaction and the surface of the small pellet was made flatter at 740 °C (Fig. 3d). At 771 °C the surface became black here and there, as shown in Fig. 3e, and a small hole like a pinhole appeared at 802 °C (Fig. 3f).

At 816 °C, as shown in Fig. 3g, the surface became gradually black and particle movement occurred due to partial dissolution of the particles. Half of the pellet became black at 825 °C and was completely black at 851 °C (Fig. 3h), but very small white particles remained. At 865 °C, as shown in Fig. 4a, these white particles disappeared and the pellet began to melt. The parts of the melt are coloured white.

At 880 °C (Fig. 4b) the pellet melted by about 60%, and then did so completely at 906 °C (Fig. 4c). However, the analysis seems to indicate an incongruent melting. The surface of the melt at 906 to 913 °C appears white in Fig. 4d, but with interference optics appeared white or pale brown in the original pictures. The surface was pierced with small black holes at 915–995 °C as shown in Fig. 4e, as if vapour had burst out.

At 1002 °C (Fig. 4f) the melt surface was very smooth, and coloured white and pale brown. At 1010–1070 °C very small, white hills were produced here and there on the surface as if an active volcano erupted, as shown in Fig. 4g.

At 1086 °C, gas began to blow off from the small white hills, and continued in this state to 1120 °C (Fig. 4h). A completely mirror-like surface was obtained at 1200 °C (Fig. 5a).

The temperature was decreased hereafter. At 1150 °C (Fig. 5b) very small crystals were produced within the surface of the melt, moved on the melt surface to another thin-crystal layer, and then grew small crystals here and there on the melt surface. The amount of melt gradually decreased and many small crystals were grown on the melt surface at 1100 °C, as shown in Fig. 5c.

The amount of melt considerably decreased at 1070 °C (Fig. 5d). Small triangle-like thin plates and hexagonal crystals with either blue or light brown colour were grown here and there at 1040 °C; as shown in Fig. 5e, three very small needles with a black colour were grown on the melt surface. The triangle-like thin plates and hexagonal crystals gradually increased in size at 950–840 °C (Fig. 5f). At 835 °C (Fig. 5g) the melt was solidified, and large plate-like crystals began to grow at a part of the melt surface.

At 823 °C, as shown in Fig. 5h, these crystals were spreading over the small crystals described above as if flowers had opened. These crystals grew over about 30 s within the field of the television camera at 812 °C (Fig. 6a). At 802 °C (Fig. 6b and c) the television picture was filled by the plate-like crystals.

These observations on crystallization from the $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ melt are all in close agreement with the results established from the DTA and TGA curves. However, in the case of the DTA, TGA and thermo-microscopic apparatus, the heating and cooling rates are very high. Therefore, it is doubtful whether or not a true temperature equilibrium in the specimen was attained.

The growth rates of the $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ single crystals are 5.3×10^{-3} mm s^{-1} from downward to upward in the television pictures, 6.4×10^{-3} mm s^{-1} in the direction to the upper right, and 8.1×10^{-3} mm s^{-1} in the transverse direction. The average value is 6.6×10^{-3} mm s^{-1}. This growth rate is very high, comparable with that for the flux method (5.0×10^{-3} mm s^{-1} for the growth of emerald single crystal).

4. Conclusions

The surface appearance of a $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ composite and crystallization from the melt were examined using a thermo-microscopic apparatus and

thermal analysis. The following conclusions were drawn:

1. Thermo-microscopic observation, as well as the DTA and TGA results, indicate that the melting point of the $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ composition lies in the range $\sim$865 to 906 °C. Apparently, an incongruent melt occurs in this range. Below $\sim$835 °C, the melt solidifies into plate-like single crystals.

2. Powder pellets with the composition $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_\delta$ can help to clarify changes in the surface appearance of this composition during heating and the crystallization process by which plate-like single crystals form during cooling of the melt.

3. The average growth rate of the plate-like $Bi_{1.9}Sb_{0.1}Sr_{2c}Ca_2Cu_3O_\delta$ single crystals is $\sim 6.6 \times 10^{-3}$ mm s^{-1}, according to the results of a video-tape analysis.

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