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Influence of chromium on the formation of the bismuth-system superconductors

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The influence of chromium on the bismuth-system superconductors (Bi–SC) was found as a by-product in a crystal synthesis experiment using a high-temperature-pressure-vessel (HTPV). The main product in the HTPV was found to be a 2201 phase of the Bi–SC, while the product in air from the same raw materials was a 2212 phase. This difference is attributed to an impurity from the HTPV. It was found from other experiments that chromium stabilizes the 2201 phase of the Bi–SC and chromium decreases the 2212 phase.

1. Introduction

Since the discovery of high-T_c superconducting oxides, a number of studies on their crystal growth have been conducted by various methods [1, 2]. Our approach is to use nitrates for the synthesis of oxide crystals. In the present paper, the influence of chromium on the bismuth-system superconductors (Bi–SC), which appeared as a by-product in the crystal growth experiment of Bi–SC by using nitrates in a high-temperature-pressure-vessel (HTPV), is reported.

We have recently been researching into the crystal synthesis using nitrates as a flux in the HTPV. The prime advantage of the use of nitrates is that they melt and decompose at lower temperature than the other salts. The synthesis temperature for crystal growth should be as low as possible if it is desired to reduce lattice defects and residual strain attributed to thermal effects or wish to avoid phase transition during cooling. Another advantage of using nitrates is that the NO_x/O_2 gases generated during the decomposition of nitrates are so oxidative that they would work favourably to prepare an oxide without oxygen defects, because it is known that oxygen defects in some functional oxide materials drastically affect their properties. There are two problems, however, with using nitrates as a flux in crystal growth. One is that the decomposition of nitrates in air is too fast to be controlled. We have employed the HTPV to suppress the decomposition of nitrates and to leave them in the molten state. Preferable decomposition of the nitrates to grow crystals was controlled by degassing of NO_x/O_2 in the HTPV. The other problem is that the molten nitrates in general are so corrosive [3] that crucible materials are restricted. The choice of crucible materials depends on the species of the nitrates and the synthesis temperature, thus they should occasionally be determined.

We previously studied the reactions in the Ba–Y–Cu–O system using $Ba(NO_3)_2$ flux in the HTPV [4]. As a result, single crystals of $Ba_2Cu_3O_{5+y}$ were synthesized which is known to be difficult to prepare by conventional sintering methods because it decomposes at relatively low temperature. Halasz *et al.* [5], who first reported this phase, did not obtain its single phase.

In the present paper, the reaction and crystal growth in the Bi–Sr–Ca–Cu system were studied using nitrates as a flux in the HTPV. The reactions in the HTPV and in air were then compared. It was found as a by-product that chromium influentially prevents the formation of 2212 phase of the Bi–SC; chromium is one of the constitutional elements in the Hastelloy-X, of which the HTPV is made.

2. Experimental procedure

2.1. HTPV and Hastelloy-X

A schematic drawing of HTPV is shown in Fig. 1. The volume of the vessel is ~ 200 cm^3. A crucible, ~ 20 mm inner diameter and ~ 80 mm long, was placed in the HTPV without a lid. The temperature of the HTPV was previously determined by a blank test comparing the temperatures inside and outside, and was controlled from the outside during the synthesis experiment.

Hastelloy-X, of which the HTPV is made, is known to be an excellent heat-resistant and corrosion-resistant material with a composition of Ni 48 wt %, Cr 22 wt %, Fe 18 wt %, Mo 9 wt %, etc. However, Hastelloy-X can be attacked by oxygen at elevated temperatures, and allows the atmosphere in the neighbourhood to become reductive unless nitrates are used as raw materials.

2.2. Preparation of the Bi–SC from nitrates in the HTPV and in air

The raw materials of Bi_2O_3, $Sr(NO_3)_2$, $Ca(NO_3)_2 4H_2O$, and CuO were mixed in an agate

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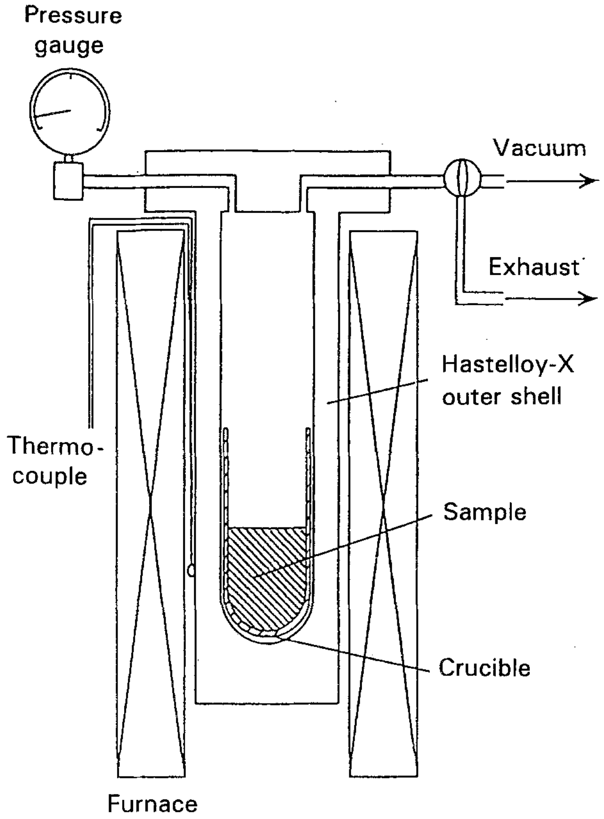

Figure 1 Schematic illustration of the high-temperature-pressure-vessel (HTPV).

mortar with a pestle at the composition of Bi:Sr:Ca:Cu = 4:3:3:4 [6] or 2:2:1:2.4 [7]. KCl or $Ca(NO_3)_2$ was used as a flux. KCl can be easily removed from the product crystals by washing with distilled water. The mixture of raw materials was heated in a high-purity alumina crucible placed in the HTPV; initially the raw materials were heated with ventilation at 300 °C for 2 h in order to dehydrate $Ca(NO_3)_2 4H_2O$, and then the crucible was sealed, heated to 900 °C, held for 10–20 h, and finally, the samples were slowly cooled to room temperature at 1–5 °C h^{-1}.

For a comparison of the reactions in the HTPV and in air, another sample was prepared, without using the HTPV, at atmospheric pressure with the same heat treatment as described above.

Samples were examined by X-ray diffraction (Rigaku: RU-200 CuK_α rad.) and by electron probe microanalysis (JEOL: JXA-8600S/M).

2.3. Factors affecting the formation of the Bi–SC in the HTPV

In order to compare and study further the reactions in the HTPV and in air, other factors, such as NO_x gas produced by the decomposition of nitrates, the total and/or oxygen pressure in the HTPV, and the contamination from the crucible and/or the HTPV, were examined. The following experiments were run in the same manner as mentioned in the previous section.

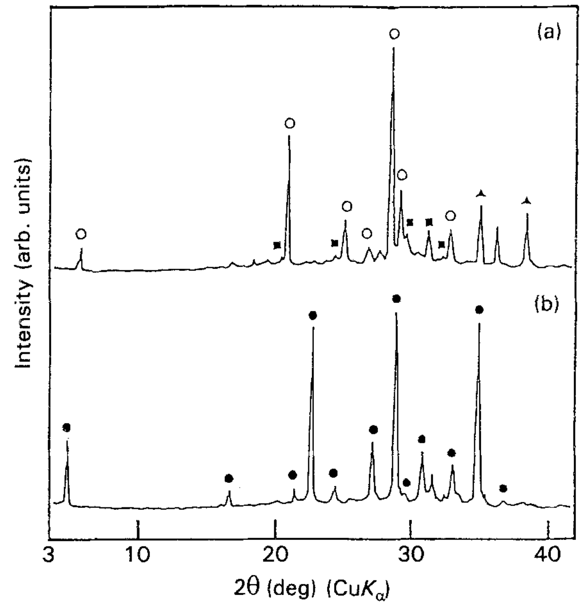

Figure 2 XRD patterns of the samples grown from the 2:2:1:2.4 composition at 900 °C, (a) in the HTPV, P = 1176 kPa, sample A, and (b) in air, sample B. (●) 2212, (○) 2201, (▲) CuO, (■) $Sr_2CaCu_3O_6$.

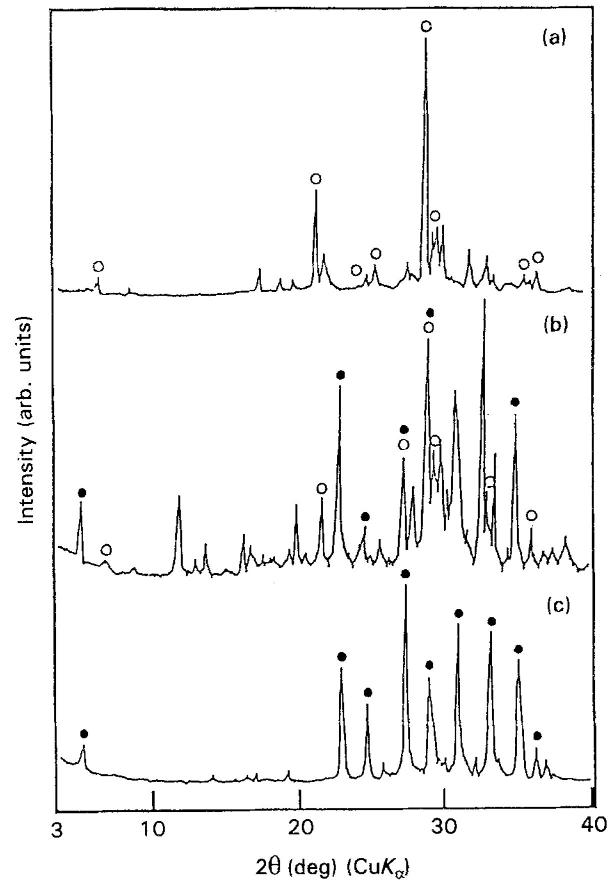

Figure 3 XRD patterns of the samples grown via $Ca(NO_3)_2 4H_2O$ flux. (a) Sample C, 4334:$Ca(NO_3)_2 4H_2O$ = 1:1, in HTPV, P = 490 kPa. (b) Sample D, 4334:$Ca(NO_3)_2 4H_2O$ = 1:3, in HTPV, P = 617 kPa. (c) Sample E, 4334:$Ca(NO_3)_2 4H_2O$ = 1:3, in air. (●) 2212, (○) 2201.

Oxide mixtures, i.e. Bi_2O_3, SrO, CaO and CuO, were used as raw materials. When these oxides are reacted in the HTPV, Hastelloy-X can be oxidized and allows the atmosphere in the HTPV to become reductive. Some studies of the sintering of Bi–SC indicate that low oxygen partial pressure would be favourable to the properties of the Bi–SC [8], while others report the synthesis of Bi–SC at high oxygen pressure [9]. In this experiment using an oxide mixture, oxygen gas at a controlled pressure, P_{O_2}, was introduced into the HTPV to avoid the formation of a reductive atmosphere caused by oxidation of Hastelloy-X and to suit the reaction conditions of the experiment using nitrate.

Alumina, magnesia and Hastelloy-X were used as crucible materials. A preliminary experiment revealed that the melted Bi–SC seriously corroded Hastelloy-X. Therefore, a heat treatment for solid-state reaction, i.e. at 800 °C for 24 h, was employed to examine the influence of the Hastelloy-X crucible.

3. Results and discussion

3.1. Formation of the Bi–SC using nitrates in the HTPV

Figs 2–4 show typical XRD patterns of the samples prepared using nitrates or with the addition of a flux such as KCl or $Ca(NO_3)_2$. In air, ($P = 101$ kPa), a single phase of 2 2 1 2 was obtained, except for when a KCl flux was used. Also in this case (Fig. 4), the crystal phases obtained differed at the upper and lower parts of the HTPV; that is, the upper part of the sample mainly include a 2 2 1 2 phase (Fig. 4f), while the lower part contains a 2 2 0 1 phase (Fig. 4g). The total pressure in the HTPV, which depends on the amount of nitrates filled into a crucible, seems not to

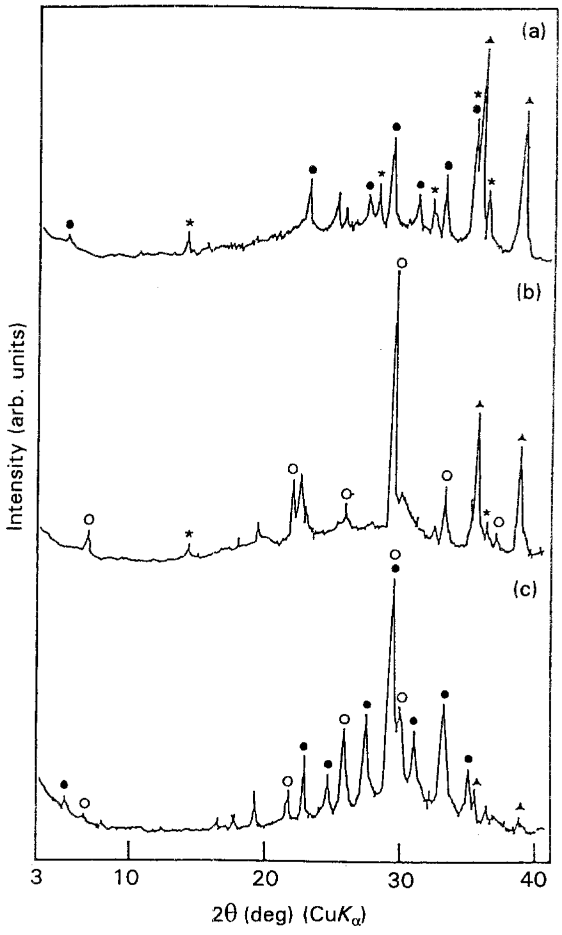

Figure 4 XRD patterns of the samples grown via KCl flux. (a) Sample F, 4334:KCl = 1:10, $P = 490$ kPa, upper part in HTPV. (b) Sample G, 4334:KCl = 1:10, $P = 490$ kPa, lower part in HTPV. (c) Sample H, 4334:KCl = 1:10, in air. (○) 2 2 0 1, (●) 2 2 1 2, (▲) CuO, (★) Ca_2CuO_3.

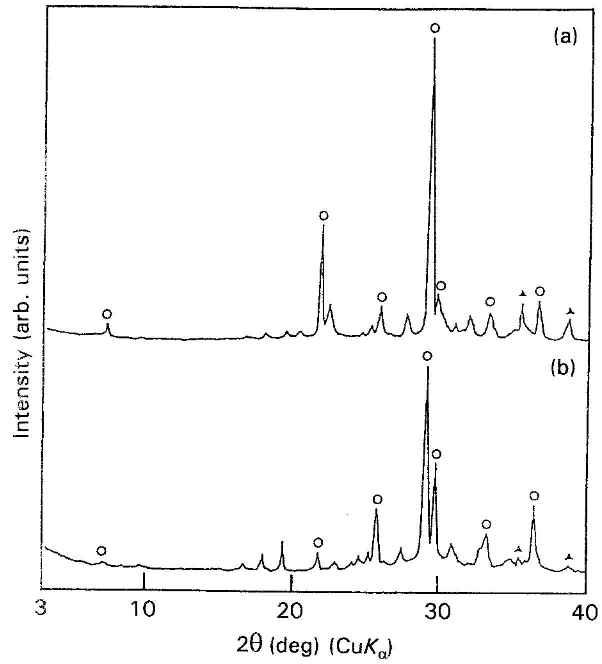

Figure 5 XRD patterns of the samples grown from the 2:2:1:2.4 composition with oxides used (without nitrates). (a) $P_{O_2} = 392$ kPa in an Al_2O_3 crucible. (b) $P_{O_2} = 101$ kPa in an MgO crucible. (○) 2 2 0 1, (▲) CuO.

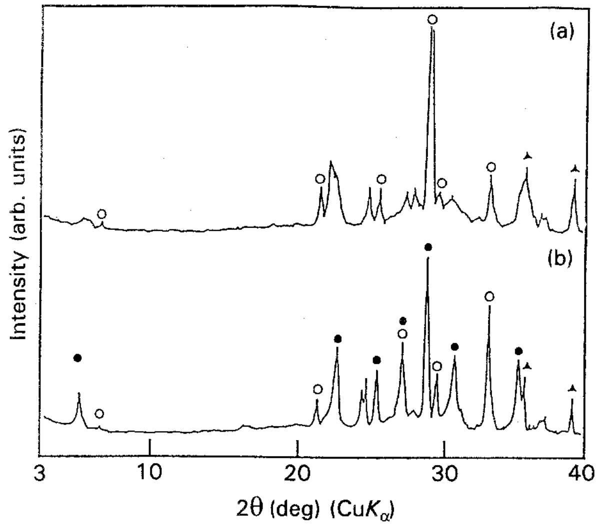

Figure 6 XRD patterns of Samples A and B obtained from a solid-state reaction at 800 °C for 24 h, (a) in a Hastelloy-X crucible, (b) in an Al_2O_3 crucible. (○) 2 2 0 1, (●) 2 2 1 2, (▲) CuO.

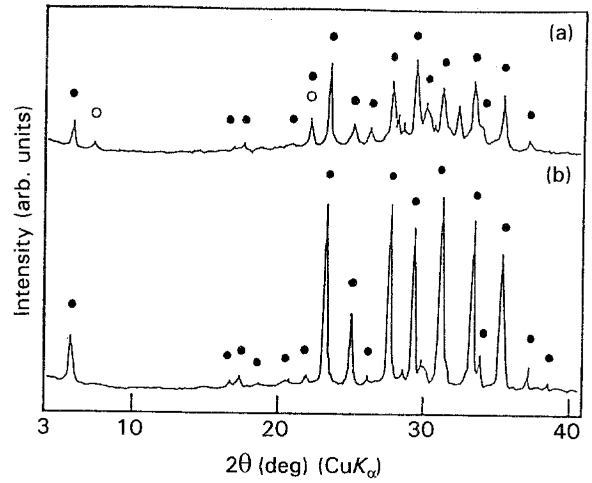

Figure 7 XRD patterns of the 2 2 1 2 sample heated in the HTPV at 800 °C for 24 h: (a) surface part, (b) inner part. (●) 2 2 1 2, (○) 2 2 0 1.

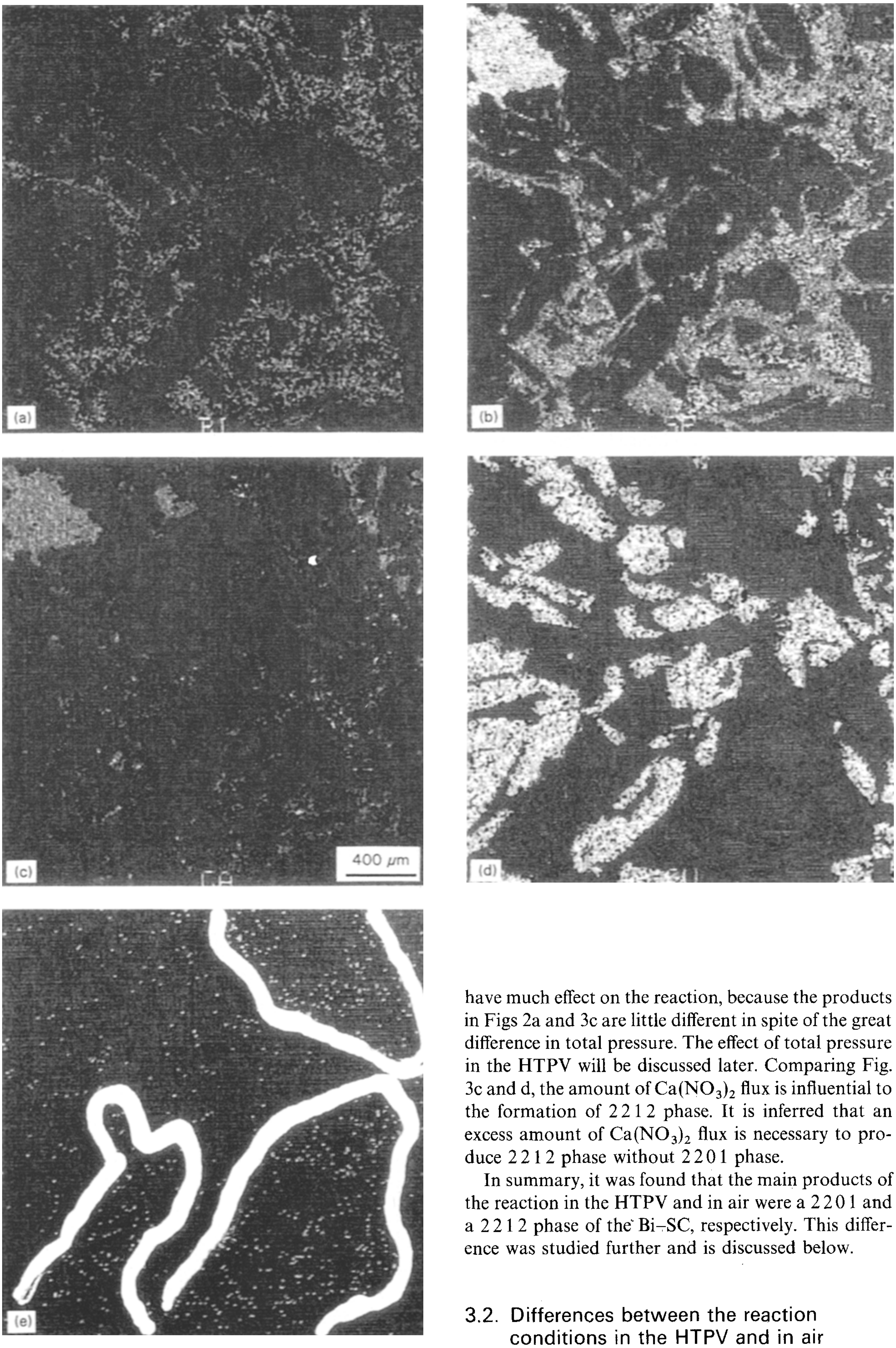

Figure 8 Mapping analysis of each element in Sample A, i.e. grown from the 2 2 1 2.4 composition in the HTPV. (a) Bi, (b) Sr, (c) Ca, (d) Cu, (e) Cr.

have much effect on the reaction, because the products in Figs 2a and 3c are little different in spite of the great difference in total pressure. The effect of total pressure in the HTPV will be discussed later. Comparing Fig. 3c and d, the amount of $Ca(NO_3)_2$ flux is influential to the formation of 2 2 1 2 phase. It is inferred that an excess amount of $Ca(NO_3)_2$ flux is necessary to produce 2 2 1 2 phase without 2 2 0 1 phase.

In summary, it was found that the main products of the reaction in the HTPV and in air were a 2 2 0 1 and a 2 2 1 2 phase of the Bi–SC, respectively. This difference was studied further and is discussed below.

3.2. Differences between the reaction conditions in the HTPV and in air

3.2.1. Influence of NO_x gas and total pressure in the HTPV

Fig. 5 shows the XRD patterns of samples reacted in the HTPV without using nitrates, (a) in an alumina crucible at $P_{O_2} = 392$ kPa and (b) in a magnesia crucible at $P_{O_2} = 101$ kPa. The former oxygen/total pressure roughly approximates to the typical value of the maximum pressure in the HTPV which is caused by the decomposition of nitrates; the latter pressure is equal to atmospheric pressure in air (1 atm). It is seen in Fig. 5 that both samples consist of the 2 2 0 1 phase, as was the case when nitrates were used, and that there is little difference between the samples. Therefore, it can be concluded that neither NO_x gas nor total pressure in the HTPV is influential.

3.2.2. Influence of oxygen atmosphere and the evaporation of Hastelloy-X

A comparison of the solid state reactions at 800 °C in an alumina crucible and in a Hastelloy-X crucible in the HTPV at an oxygen pressure of 101 kPa, is shown in Fig. 6. It is seen that the alumina and the Hastelloy-X crucible mainly yielded the 2 2 1 2 and the 2 2 0 1 phase of the Bi–SC, respectively. The fact that 2 2 1 2 phase was synthesized in the alumina crucible at an oxygen/total pressure of 101 kPa indicates, on considering the results in Fig. 5a, that the influence of the oxygen atmosphere is negligible. On the other hand, it was found that Hastelloy-X inhibits the formation of 2 2 1 2 phase but allows 2 2 0 1 phase. The 2 2 0 1 phase in Hastelloy-X crucibles existed not only at the interface of the sample and the crucible, but also in the inner part of the sample. Considering that the diffusion of Hastelloy-X component is very slow in a solid state, it is inferred that some component in Hastelloy-X evaporates into the Bi–SC sample during the reaction.

To ascertain the influence of Hastelloy-X on the 2 2 1 2 phase itself, a 2 2 1 2 sample previously synthesized in air was put into an alumina crucible and heated at 800 °C for 24 h in the HTPV. The results, shown in Fig. 7, indicate that the X-ray peaks of the 2 2 1 2 sample broadened at the surface part of the sample but not at the inner part; that is, the crystallinity of 2 2 1 2 crystals began to fall at the upper part of the sample facing the "Hastelloy-X atmosphere".

3.3. The component of Hastelloy-X affecting the formation of Bi–SC

EPMA analysis of sample A, which was prepared from the melt nitrates in the HTPV (see Fig. 2a), proved the existence of chromium in addition to bismuth, strontium, calcium and copper. The results are shown in Fig. 8. The blue, white, yellow, and dark areas in Fig. 8 correspond to the 2 2 0 1 phase, CuO, $Sr_2CaCu_3O_y$, and vacant space, respectively. From the distribution of chromium in the sample, it is found that chromium does not invade all over the sample but is selectively incorporated into the 2 2 0 1 phase, as indicated by the white line in Fig. 8. (In this figure, the chromium spectrum is exaggerated because the amount of chromium is much smaller than the amounts of other metallic elements.)

A quantitative analysis using EPMA revealed that 2 2 0 1 phase in the sample contained 0.6 mol % Cr.

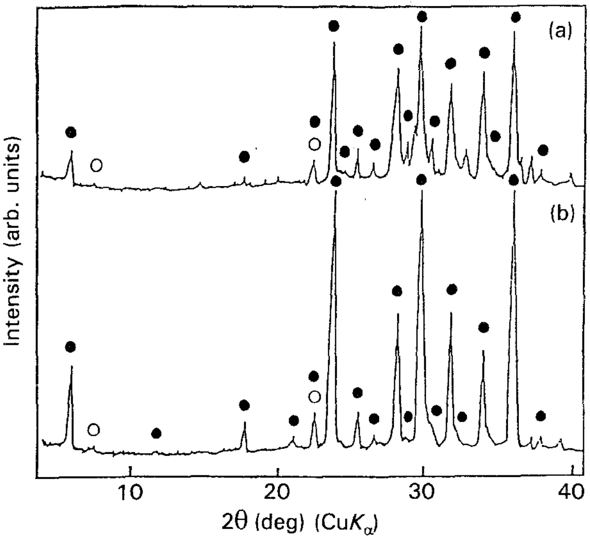

Figure 9 XRD patterns showing the effect of chromium on the 2 2 1 2 phase: (a) synthesized 2 2 1 2 + Cr_2O_3 1 atm% added, 800 °C, 24 h; (b) synthesized 2 2 1 2, before Cr_2O_3 addition. (●) 2 2 1 2, (○) 2 2 0 1.

The ionic radii of the related cations are Bi^{3+} (0.074 nm), Sr^{2+} (0.113 nm), Ca^{2+} (0.099 nm), Cu^{+} (0.096 nm), Cu^{2+} (0.08 nm), Cr^{3+} (0.063 nm), Cr^{6+} (0.052 nm), etc. Even the smallest radius ratio to Cr^{3+}, i.e., $Bi^{3+}/Cr^{3+} = 117\%$, seems to be too large to make a substitutional solid solution, so that the solid solution of chromium ions into the 2 2 0 1 phase is considered to be an interstitial solid solution. Assuming that Cr^{3+} had changed to Cr^{6+} in an oxidative atmosphere, Cr^{6+} can also make an interstitial solid solution because of its small ionic radius.

3.4. Influence of Chromium on the 2 2 1 2 phase

The influence of chromium itself on the 2 2 1 2 phase was investigated by an experiment in which 1 wt % high-purity Cr_2O_3 was added to a prepared 2 2 1 2 powder and subsequently fired in air at 800 °C for 24 h. As shown in Fig. 9, the addition of Cr_2O_3 lowered the crystallinity of the 2 2 1 2 phase. Although Cr_2O_3 is, in general, known to be a stable compound, the present study has proved that it easily reacts with 2 2 1 2 phase of the Bi–SC. In the HTPV experiment, chromium invasion into the Bi–SC would have passed through a vapour state and thus it should have been more reactive than a solid-state reaction.

In the present study, the starting composition of either 2 : 2 : 1 : 2.4 or 4 : 3 : 3 : 4 yielded 2 2 1 2 phase in the Bi–Sr–Ca–Cu–O system, whether in air, in an NO_x atmosphere, or at high pressure. However, chromium addition could have changed the phase relationship in the system. In the new system Bi–Sr–Ca–Cu–Cr–O, the 2 2 0 1 phase should have been a stable phase. As a consequence, CuO and $Sr_2CaCu_3O_y$ were formed so that the mass balance in the system would be preserved. However, the experimental data obtained so far are insufficient to discuss the mechanism of the stabilization by chromium. In the future, the exact distribution of chromium in the 2 2 0 1 phase of the Bi–SC should be determined by some other method.

4. Conclusion

The bismuth-system of superconductors (Bi–SC) were synthesized using nitrates in the high-temperature-pressure-vessel (HTPV) and in air. The main product in the HTPV was found to be a 2 2 0 1 phase while that in air was 2 2 1 2 phase. This difference is due to the impurity of chromium introduced by the evaporation of the vessel material. In the presence of chromium, the 2 2 1 2 phase of the Bi–SC becomes less stable and 2 2 0 1 phase becomes more stable.

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