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The stability of high-T_c phase in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ compounds prepared by hot isostatic pressing

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By using a sequence of hot isostatic pressing (HIP) and intermediate cold pressing, it has been possible to produce high-density Bi-based superconductors containing almost 100% high-T_C 2223 phase, without any post-fabrication heat treatment. The X-ray data showed no decomposition of high-T_C phase in hot isostatically pressed Bi-based superconductors. By using this technique, $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ (where $Z \approx 10$) superconductors could be densified to 6.06 g cm^{-3} at an HIP temperature of 850 °C, and at an HIP temperature of 870 °C the density was close to 6.15 g cm^{-3}. These densities could be compared with about 3 to 4 g cm^{-3} obtained for conventionally sintered compounds. X-ray diffraction data at various stages of fabrication, microstructure and electrical resistivity data are presented.

1. Introduction

Since the individual grains of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ (where $Z \approx 10$) superconductors are in the form of thin plates resulting in a layered structure, it is difficult to densify $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ superconductor to its full theoretical density while maintaining the high-T_c phase.

Hot isostatic pressing is considered to be an effective technique to densify various types of superconductors. HIP densifies through a hot deformation process whereby the powder particles deform under high stress at contact points. Under hydrostatic pressure at elevated temperatures, densification occurs by a rearrangement of plates as well as by diffusion of individual atoms as in any solid-state sintering process. Consequently, relatively rapid densification can occur in shorter times than are necessary for conventional sintering.

HIP has been widely used to densify the $YBa_2Cu_3O_X$ class of superconductors [1–3]. However, HIP-densified $YBa_2Cu_3O_X$ requires extensive post-processing heat treatment to recover the superconducting phase, because $YBa_2Cu_3O_X$ decomposes to other oxide compounds such as Y_2BaCuO_5, CuO, $BaCuO_2$ etc. at the high pressures and high temperatures experienced during HIP densification [4, 5]. In contrast with that, $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ superconductors lose very little oxygen on heating in a vacuum up to the melting temperature [6]. Although the crystal structure of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ superconducting compound is quite stable with respect to oxygen stoichiometry, hot isostatic compaction data for high-T_c (110 K) 2223 phase in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ superconductors has not yet been reported. So far, the reported T_c value of as-hot isostatically pressed Bi-based superconductor is in the range 80–90 K [7–9].

In this paper, the details of a study conducted to investigate the stability of high-T_c (110 K) phase in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ superconducting compounds, densified by the HIP process in an argon atmosphere, are discussed. The X-ray data show that HIP densification performed in an inert atmosphere (Ar) at a temperature of 850 °C did not produce decomposition of the high-T_c 2223 phase of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ superconductors. The present work describes a sequence of densification including hot isostatic pressing which produces high-density superconductors, while maintaining the high-T_c 2223 phase. Furthermore, this process does not require any post-fabrication heat treatment. Also discussed are microstructural aspects and electrical properties of the superconductor obtained by us through such a processing.

2. Experimental procedure

Appropriate amounts of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO were mixed so that the cation ratios of the compound would be Bi:Pb:Sr:Ca:Cu = 1.6:0.4:2:2:3. The mixed compound was calcined at 820 °C for 20 h and ground. To enrich the high-T_c phase in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ an intermediate pressing method was used [10, 11]. For comparison, some of the mixtures were also conventionally sintered for 50–200 h. These different powder preparation procedures are described in Fig. 1.

The prepared powder was first compacted into a cylindrical shape by uniaxial compression. The pressed samples were coated with boron nitride spray and

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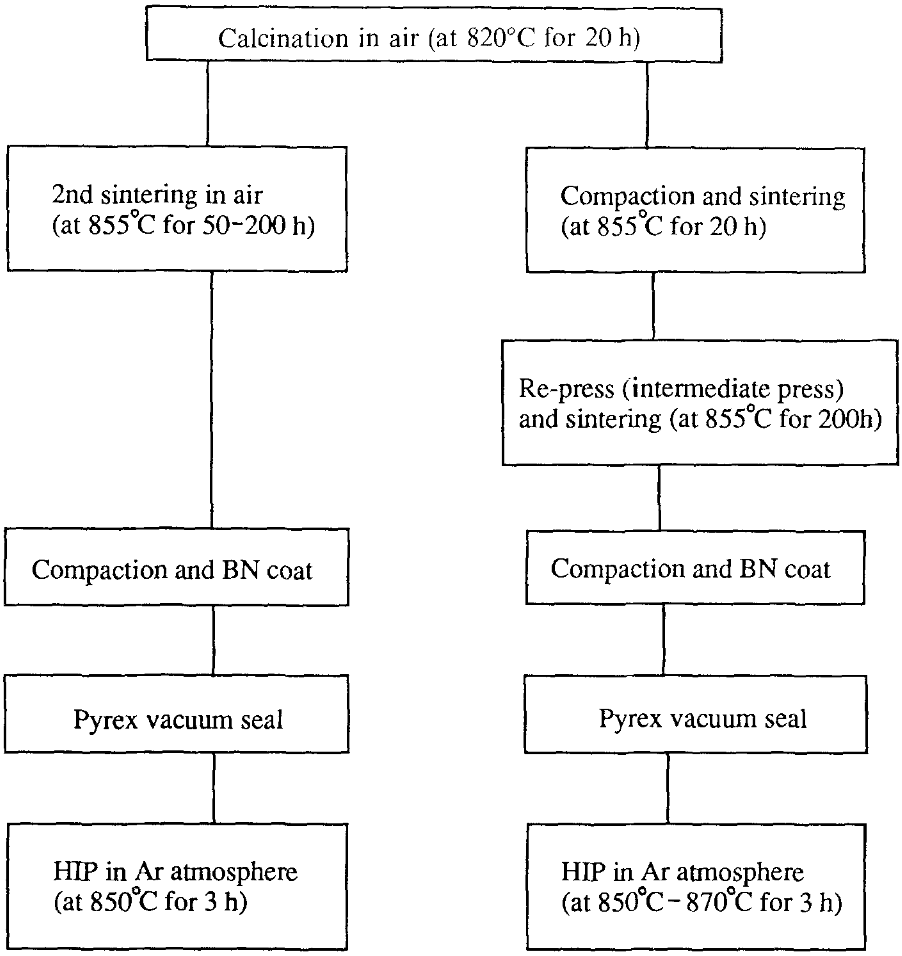

Figure 1 Sample preparation procedure for HIP sample.

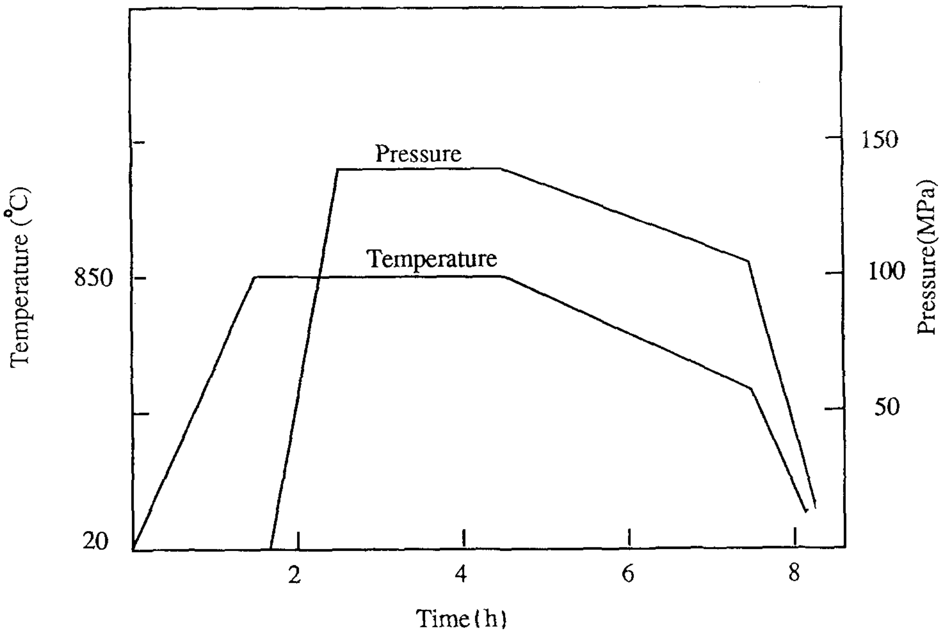

Figure 2 A typical example of an HIP cycle.

the samples were individually encapsulated in an evacuated Pyrex tube. The sealed samples were placed in an IPS Eagle 6 hot isostatic pressure furnace. A graphite furnace and Ar atmosphere were used for the HIP process.

A typical HIP cycle is shown in Fig. 2. The densification was performed at a temperature of 850 °C and a pressure of 138 MPa for a duration of 3 h. The HIP-treated samples were cooled slowly at a rate of 100 °C h^{-1}. Some surface reaction between the Pyrex

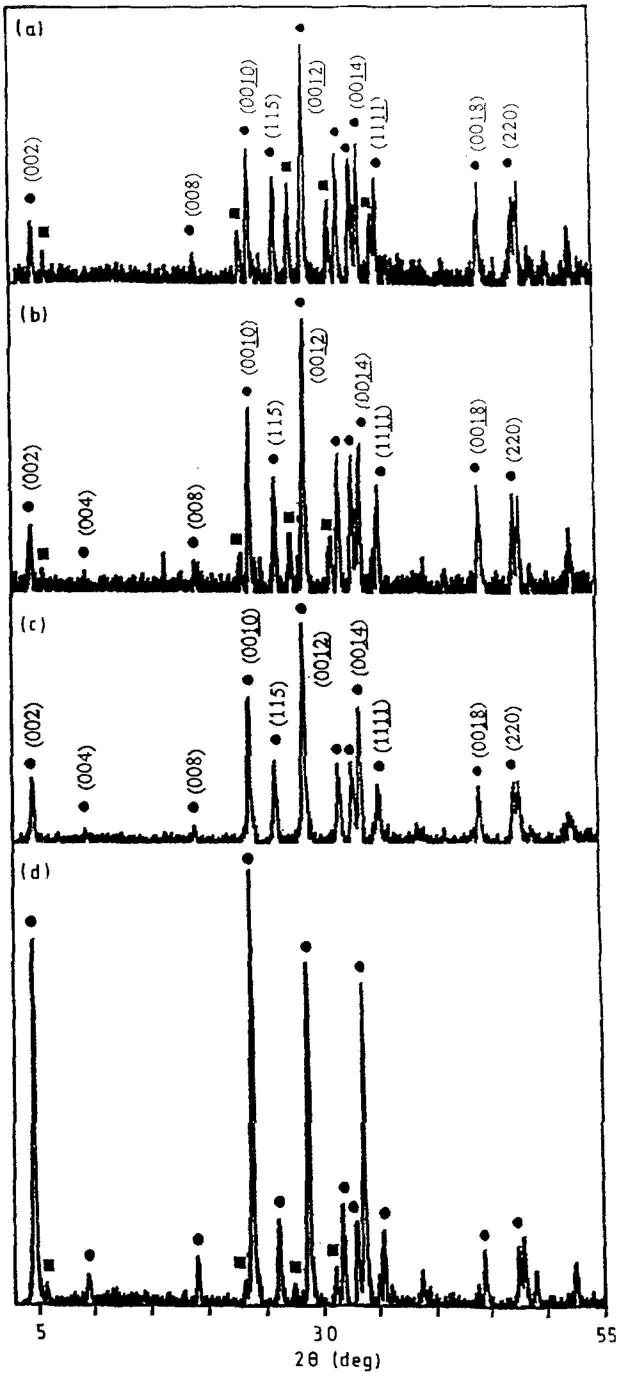

Figure 3 X-ray diffraction data for HIP processing at (a) 870 °C, (b) 860 °C and (c) 850 °C, and (d) for powder samples prepared by intermediate pressing before the HIP process. (●) High-T_c (2223), (■) low-T_c (2212).

glass and BN-coated surface (which was easily removed by grinding) was, however, observed.

The crystal structure was identified by using a Scintag XDS-200 X-ray diffractometer equipped with a computerized data collection system. Density and electrical resistivity were measured respectively by using the buoyancy method (ASTM B328-73) and a four-probe d.c. method with a T-type thermocouple for temperature measurement. Microstructural and compositional studies were also performed by using a Hitachi S-2500C scanning electron microscope (SEM) equipped with a Link spectrometer for energy dispersive X-ray analysis (EDAX).

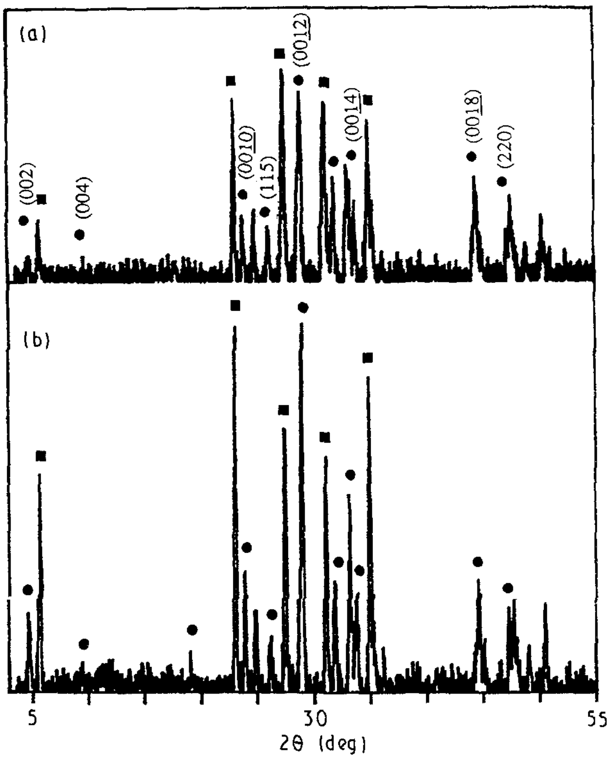

Figure 4 X-ray diffraction data (a) for HIP processing at 850 °C and (b) for powder samples prepared by conventional sintering before the HIP process. (●) High-T_c (2223), (■) low-T_c (2212).

3. Results and discussion

The X-ray diffraction results of Fig. 3a–c are for samples after the HIP process at various temperatures and Fig. 3d pertains to powder samples prepared by intermediate pressing before the HIP process. The diffraction peaks corresponding to high-T_c and low-T_c phases were identified by utilizing the diffraction patterns published by Endo *et al.* [12]. The strong relative intensity of the (0 0 2) reflection for the 2223 phase, as shown in Fig. 3d, results from the intermediate pressing process [11].

It is observed that peak intensities corresponding to the high-T_c phase are maintained and those of peaks corresponding to the low-T_c phase are diminished substantially after HIP treatment at 850 °C, as shown in Fig. 3c. This suggests that HIP-treated samples consist of nearly 100% high-T_c phase. However, as the HIP temperature increased to 870 °C which is near the decomposition temperature of the high-T_c phase [13], the relative intensities of the high-T_c peaks began to diminish and the intensities of the low-T_c peaks began to increase, as shown in Fig. 3a. There is, however, no noticeable peak broadening which is often found for low temperature and high pressure synthesis [14]. This result, then, suggests that crystalline imperfections are not introduced by hot isostatic pressing. A sample sintered for about 200 h without intermediate pressing contains primarily the low-T_c (2212) phase, as shown in Fig. 4b. If such a sample is HIP-processed, the resulting sample contains mostly the low-T_c phase with a very small amount of 2223 phase, as shown in Fig. 4a.

The densities of HIP-treated samples as measured by the buoyancy method were 6.06 g cm^{-3} for HIP at 850 °C, 6.09 g cm^{-3} for HIP at 860 °C and 6.15 g cm^{-3} for HIP at 870 °C. These values are 94, 94.4 and 95.3% of the theoretical density, respectively. In contrast, specimens sintered conventionally in air had densities of 3 to 4 g cm^{-3}, i.e. 46.5 to 62% of theoretical density. This significant improvement in densification is probably due to enhanced diffusion and/or void elimination under high pressure.

Fig. 5 shows the temperature dependence of resistivity for a sample HIP-treated at 850 °C (intermediate pressing + HIP) (Fig. 5a) and a sample given conventional sintering + HIP (Fig. 5b). The resistivity for the first sample decreased monotonically with decreasing temperature and reached the zero resistivity state at 105 K. Although the other sample (Fig. 5b) containing a large volume percentage of the low-T_c phase exhibited a drop in the resistivity around 110 K (similar to the first sample), its superconducting transition was broad and $T_{c,zero}$ value was about 87 K. From these results, it was tentatively concluded that the broad transition was related to the initial presence of a large percentage of the low-T_c phase.

Fig. 6a shows the microstructure on the fracture surface of a conventionally sintered specimen, sintered at 850 °C for 3 h. Fig. 6b shows the fracture surfaces of the sample HIP-treated at 850 °C for 3 h. The conventionally sintered specimen shows a rather porous structure which consists of plate-like as well as some spherical grains. The fracture morphology suggests that the grains are weakly connected. On the other hand, the fracture surface of the HIP-treated specimen shows that the grain size of the fully grown 2223 phase is much larger than those of conventionally sintered samples. The microstructure also shows a dense packing of thin plate-like grains. This remarkable growth of plate-like grains during hot isostatic pressing is also responsible for pore elimination and densification. Improved densification related to grain growth can be explained by the enhanced diffusion due to stress gradients across boundaries which act as both sinks and sources of vacancies. Although a hydrostatic pressure is applied, shear deformation can undoubtedly occur due to the high elastic anisotropy of the crystal and due to the presence of dissimilar phases of varying elastic compliance.

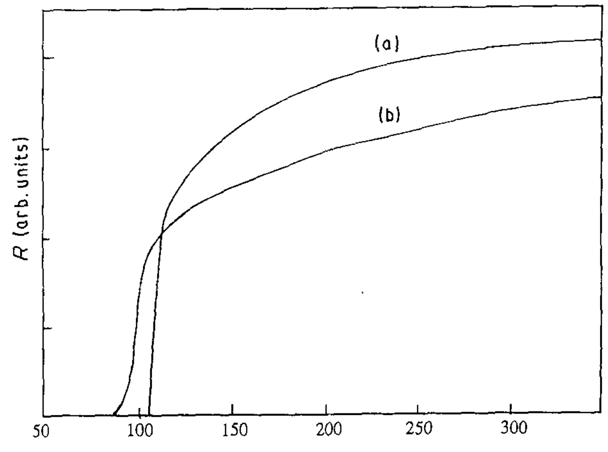

Figure 5 Temperature dependence of resistivity for HIP-treated samples: (a) intermediate pressing + HIP, (b) conventional sintering + HIP.

Fig. 7 shows the microstructure on the fracture surface of a specimen hot isostatically pressed at 870 °C for 3 h. It is observed that the grain size of the 2223 phase increases extensively. Some low-T_c phase particles were found in addition to particles of a non-superconducting phase or phases. It has been reported that the low-T_c phase starts to form as soon as the high-T_c phase begins to decompose at around 870 °C [13]. The dark grey and darker phases as seen in Fig. 7

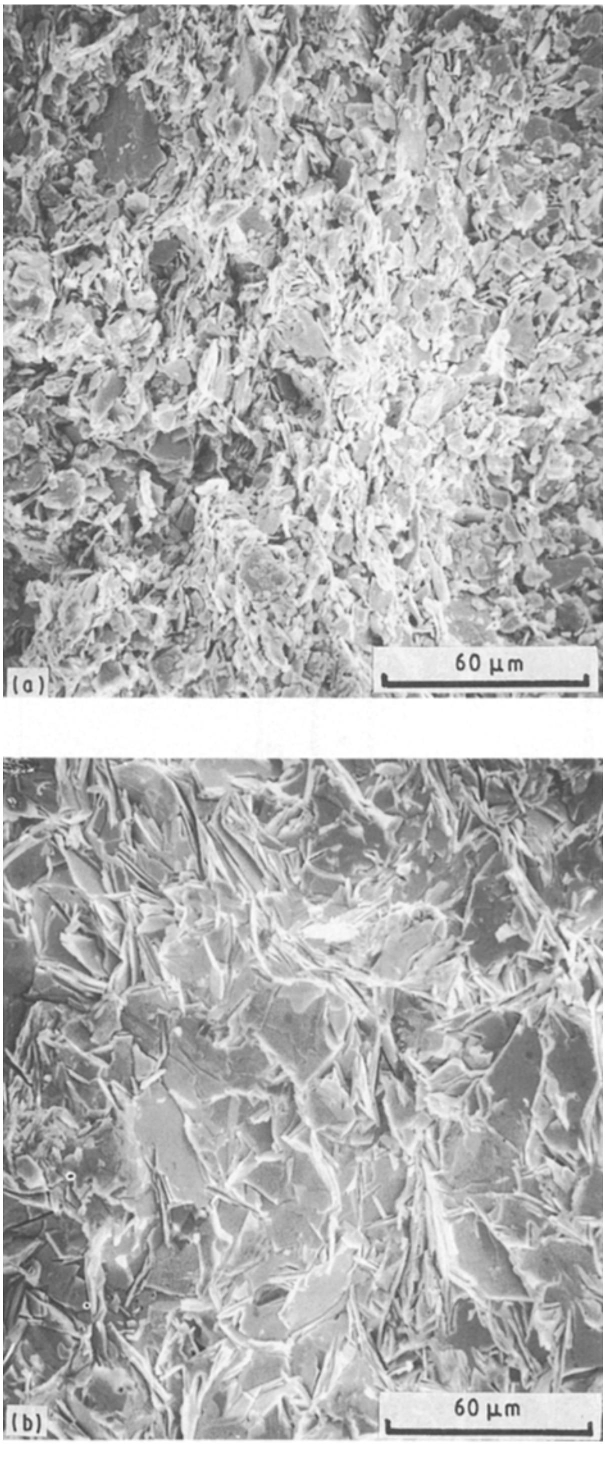

Figure 6 SEM micrograph of (a) normally sintered sample and (b) sample of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ isostatically pressed at 850 °C for 3 h.

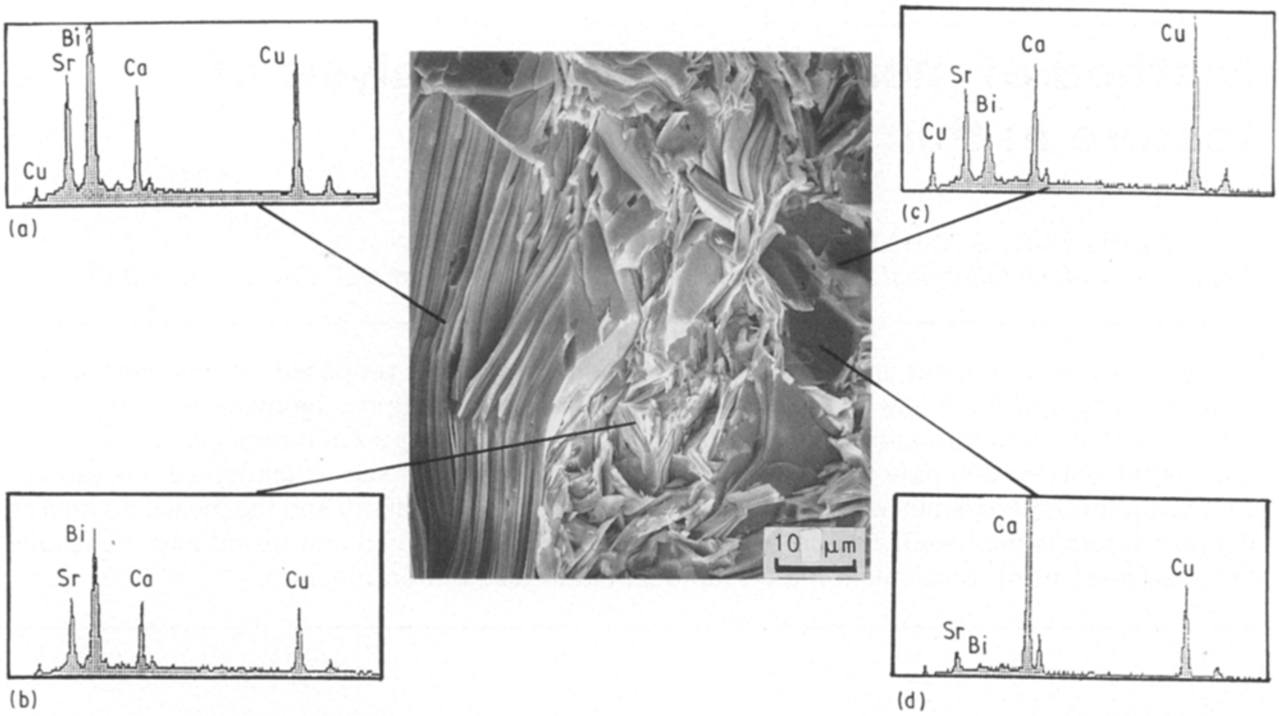

Figure 7 EDAX and SEM micrograph of HIP-treated sample of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_Z$ at 870 °C. The spectra (a) to (d) correspond to 2223 phase, 2212 phase, (Ca, Sr)-rich phase and Ca-rich phase, respectively.

are identified as 2223 and (Ca, Sr) -rich phases, respectively. These conclusions are based on EDAX analysis. Fig. 7a and b show the compositions of the high-T_c and low-T_c phases, respectively. It is shown that the Ca and Cu contents of the low-T_c phase were lower than those in the high-T_c phase.

4. Conclusions

The most significant result of the present study is that it demonstrates that hot isostatic pressing, along with intermediate pressing, can be used to consolidate Bi(Pb) SrCaCuO superconducting compounds to obtain nearly the theoretical density while maintaining the high-T_c phase. The relative stability of the high-T_c phase in Bi(Pb)SrCaCuO compounds during HIP indicates the feasibility of hot work processing (such as extrusion) to obtain superconducting strips and other extended forms.

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