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Effect of silver in $Y_1Ba_2Cu_3O_{7-x}$ samples

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Two techniques for preparing Y–Ba–Cu–O/Ag specimens are presented: (a) solid-state reaction, and (b) normal precursors dissolved in hot concentrated nitric acid and dried in air. The samples are characterized by scanning electron microscopy (SEM), scanning Auger, X-ray diffraction, optical microscopy and electrical resistivity measurements. In comparison with a normal 1–2–3 superconductor it was found that the normalized resistance $[R(T)/R(280\ \text{K})]$ decreases for both preparation methods. The material retained a high initial temperature of superconductivity, T_c, for a maximum of 6% w/o Ag_2O during solid-state reaction and 6.5% w/o Ag_2O for samples dissolved in hot concentrated nitric acid and dried in air.

1. Introduction

Since the original announcement of superconductivity at 90 K in Y–Ba–Cu–O [1], there has been a frantic race to develop materials with superior properties by adding to and substituting for the individual elemental components. A variety of alternative rare earths have been substituted for yttrium, nearly all leading to superconductive transitions in the 90–95 K range [2–4]. On the other hand, various transition metal additives appear to uniformly decrease T_c [5–7].

Another class of additives, gold and silver, appear not to react at all with Y–Ba–Cu–O during the sintering process [8, 9]. Due to their inertness, Au and Ag have been suggested as passivating layers for surfaces of, or cladding sheets for wire made from the copper oxide based superconductors [10, 11]. Silver has been found to be one of the few materials that does not degrade the superconductivity properties of the 1–2–3 material [12]. In addition, it facilitates oxygen diffusion into the bulk [13], and lowers the normal state resistivity and contact resistance of the composite. Surface passivation of Y–Ba–Cu–O type superconductors is required because of detrimental reactions that occur with atmospheric CO_2 and H_2O. Silver has been found to improve corrosion resistance against moisture and CO_2 [14]. A further problem associated with the high T_c superconductors results from the polycrystalline nature and connected porosity of the material, in both thin film and bulk form. The low critical currents in bulk materials, and all but the best epitaxially grown thin films, could be a result of intergranular weak links occurring at grain boundaries due to interaction with atmospheric contaminants via surface connected porosity.

2. Experimental procedure

Two different solid-state preparation methods were used: (a) the standard method [15], with 2–10 w/o Ag_2O added to the already prepared $Y_1Ba_2Cu_3O_{7-x}$ samples, and (b) a chemical method consisting of dissolving the appropriate amounts of Y_2O_3, $BaCO_3$ and CuO with 2–10 w/o Ag_2O in concentrated HNO_3. The solvent was then evaporated at a temperature of 40 °C, for 3 h. Powders were then calcined at 900 °C for 24 h in air, ground and pressed into pellets 1.25 cm in diameter. The pellets were subsequently annealed at 900 °C in oxygen for 24 h and allowed to cool inside the oven.

X-ray analysis was performed in a GEXRD6 diffractometer using CuK_α radiation at 40 KV and 20 mA. The microstructure of the grains was studied with a JEOL JSM-5300 microscope. The surface composition was determined by Auger spectroscopy using a scanning Auger microscope, Perkin–Elmer PHI-595. The system had a base pressure of 266×10^{-8} Pa, with an electron beam at 3 KeV and 150 nA.

3. Results and discussion

Superconductivity of the samples was determined by means of the Meissner effect at 77 K, and by a.c. electrical resistivity measurements (four probe method). Fig. 1 shows the normalized resistance, $R(T)/R(280\ \text{K})$, as a function of temperature for samples 1–4 (0, 2.5, 5.6 and 6.0 w/o Ag_2O), prepared by solid-state reaction. The normalized resistance, taking the 0.0 w/o as the reference point, decreases gradually for the same range of Ag_2O concentrations. Above 6 w/o, samples are not superconducting.

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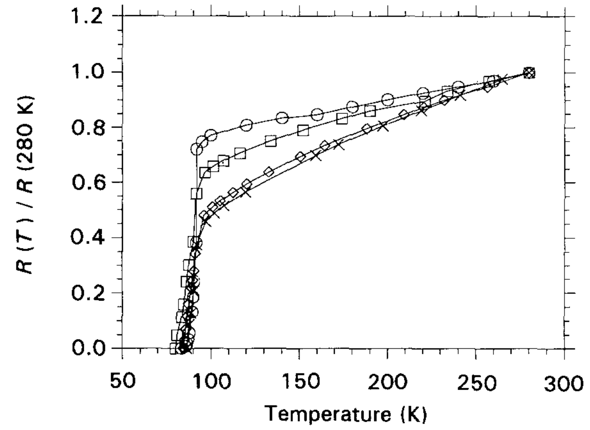

Figure 1 Normalized resistance $R(T)/R(280\ \mathrm{K})$ versus temperature for samples 1–4, prepared by solid-state reaction. (○) 0.0%, (□) 2.5%, (◇) 5.6%, (✳) 6.0% w/o Ag_2O, respectively.

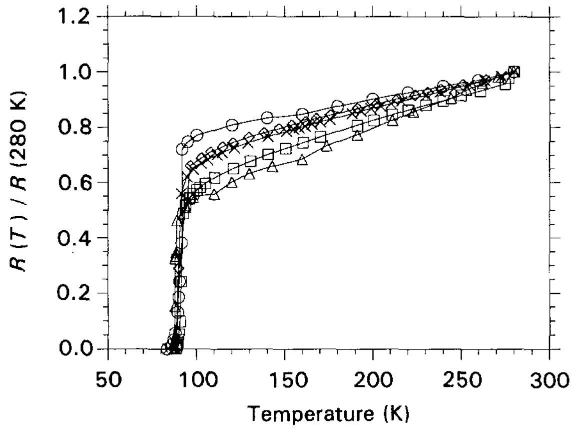

Figure 2 Normalized resistance $R(T)/R(280\ \mathrm{K})$ versus temperature for samples 1–5, prepared by dissolution in concentrated hot nitric acid and air dried. (○) 0.0%, (□) 2.5%, (◇) 5.6%, (✳) 6.0%, (△) 6.5% w/o Ag_2O, respectively.

Fig. 2 shows the normalized resistance as a function of temperature for samples 1–5 (0, 2.5, 5.6, 6 and 6.5 w/o Ag_2O), prepared by dissolution in hot nitric acid and air dried. Above 6.5 w/o the samples are not superconductors.

The temperature at zero resistance, T_0, was observed to vary between 87 and 92 K. This may be due to slight changes in oxygen concentration in the 1–2–3 material by the addition of Ag_2O.

Figs 3 and 4 show optical micrographs for a sample with no Ag added and a sample with 5.9 w/o Ag_2O, prepared by solid-state reaction. The arrow in Fig. 4 indicates the presence of grains with different morphology than the ones observed in Fig. 3, suggesting that they might be silver or silver oxide grains. This assumption is confirmed by analysis with Auger spectroscopy obtained from specific regions as indicated in Fig. 5. Auger spectra were recorded at different points, and the standard multiple-technique analytical computer system (MACS) software for this particular instrument was used to obtain a semiquantitative analysis of the spectra. Under this condition the resolution of the instrument in the stationary point mode was 0.3 μm.

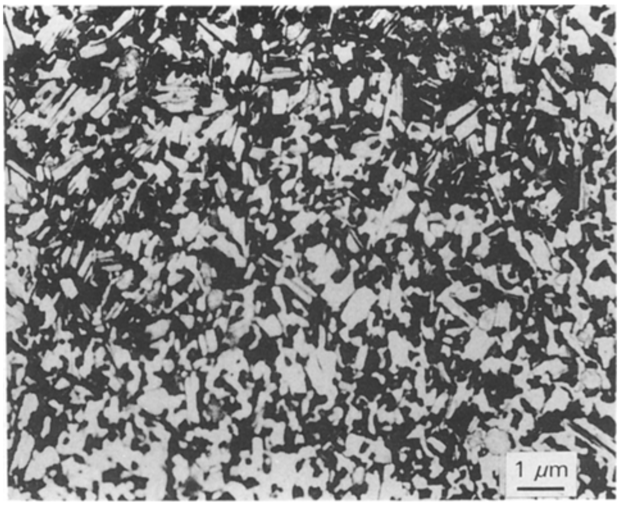

Figure 3 Optical micrograph for a sample with 0.0 w/o Ag_2O prepared by solid-state reaction.

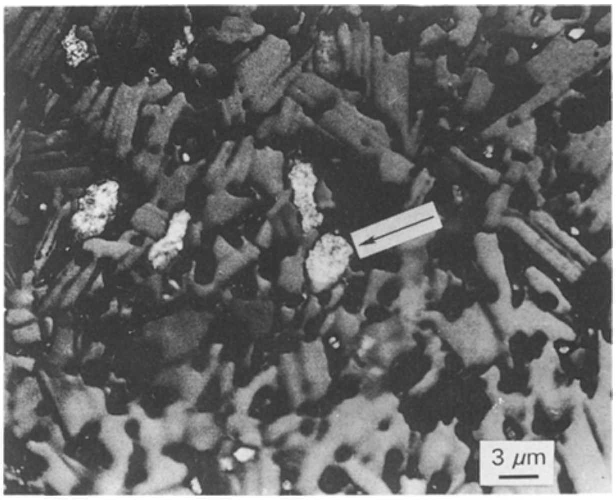

Figure 4 Optical micrograph for a sample with 5.9 w/o Ag_2O prepared by solid-state reaction.

An Auger spectrum is shown in Fig. 5, where each of the elements which appear on the surface of the sample are identified. Indicated in parentheses is the relative concentration of the element at that particular place. Notice the high concentration for silver (24.9 wt %). This, added to the O concentration (46.13 wt %) indicates the possibility that the silver is oxidized. Also, by this analysis, it is possible to infer that silver preferentially clumps and fills voids, or is segregated. This assumption is confirmed by SEM micrographs of the analysed region. Fig. 6a and b shows SEM micrographs of one of those regions where the analysis was performed; the arrow indicates the location of the analysis. Note the existence of clear regions identified as silver rich grains by Auger analysis, as well as some darker spots compared with some grey spots produced by the matrix, regions which are cavities produced by the sintering process.

Fig. 7a and b shows optical micrographs for a sample with 5.0 w/o Ag_2O prepared by dissolution in hot concentrated nitric acid. Comparing with Fig. 4

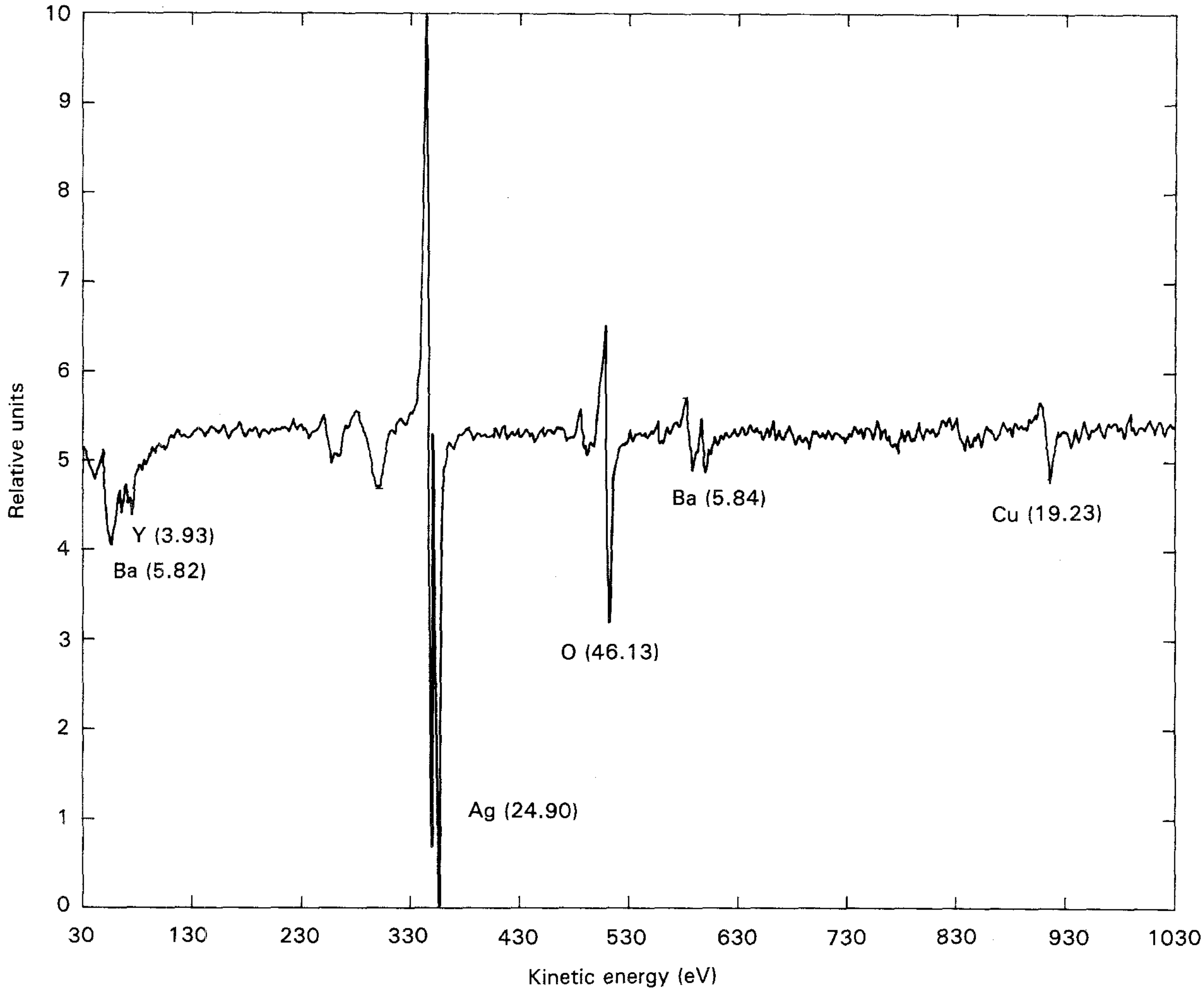

Figure 5 Auger spectra of the sample $Y_1Ba_2Cu_3O_{7-x}$ with 5.9 w/o Ag_2O, prepared by solid-state reaction. Indicated in parentheses is the relative concentration of the element.

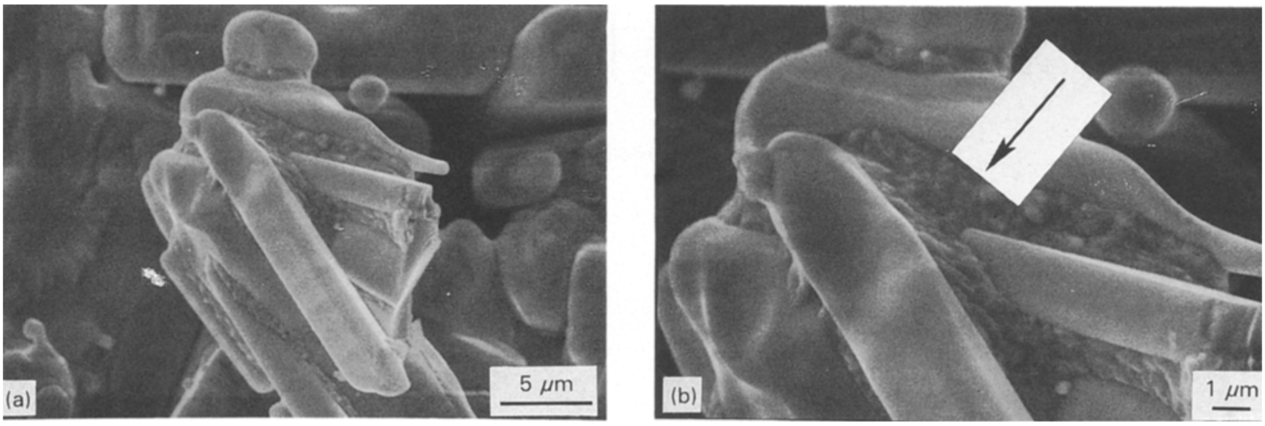

Figure 6 (a) and (b) show SEM micrographs of a sample of $Y_1Ba_2Cu_3O_{7-x}$ with 5.9 w/o Ag_2O, prepared by solid-state reaction. The arrow indicates where the Auger analysis was performed.

one can, in this case, observe a difference in morphology. The grains are no longer the plate-like structure of the 1–2–3 phase, but instead are rounded on the edges and smaller. Also, it was not possible to locate silver clumps; instead silver was scattered throughout the material. This conclusion is confirmed in Fig. 8, where an Auger analysis is shown. The arrow in Fig. 7a indicates where the Auger analysis was performed. It should be pointed out that the Auger analysis was performed in several regions of the material, and in most of the regions the silver content was extremely low or not observable. It was concluded that with this preparation method, silver is preferentially located between grains and, in some cases, fills the voids of the material. Fig. 9a and b, shows X-ray diffractograms for samples containing 5 w/o Ag_2O

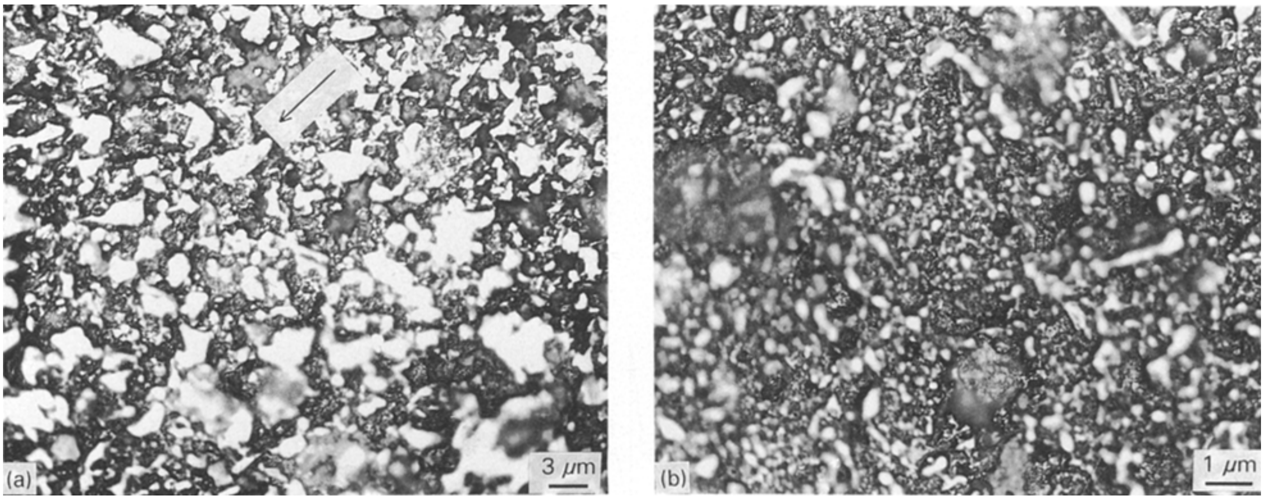

Figure 7 (a) and (b) show optical micrographs for a sample with 5.9 w/o Ag_2O prepared by dissolution in concentrated hot nitric acid and air dried.

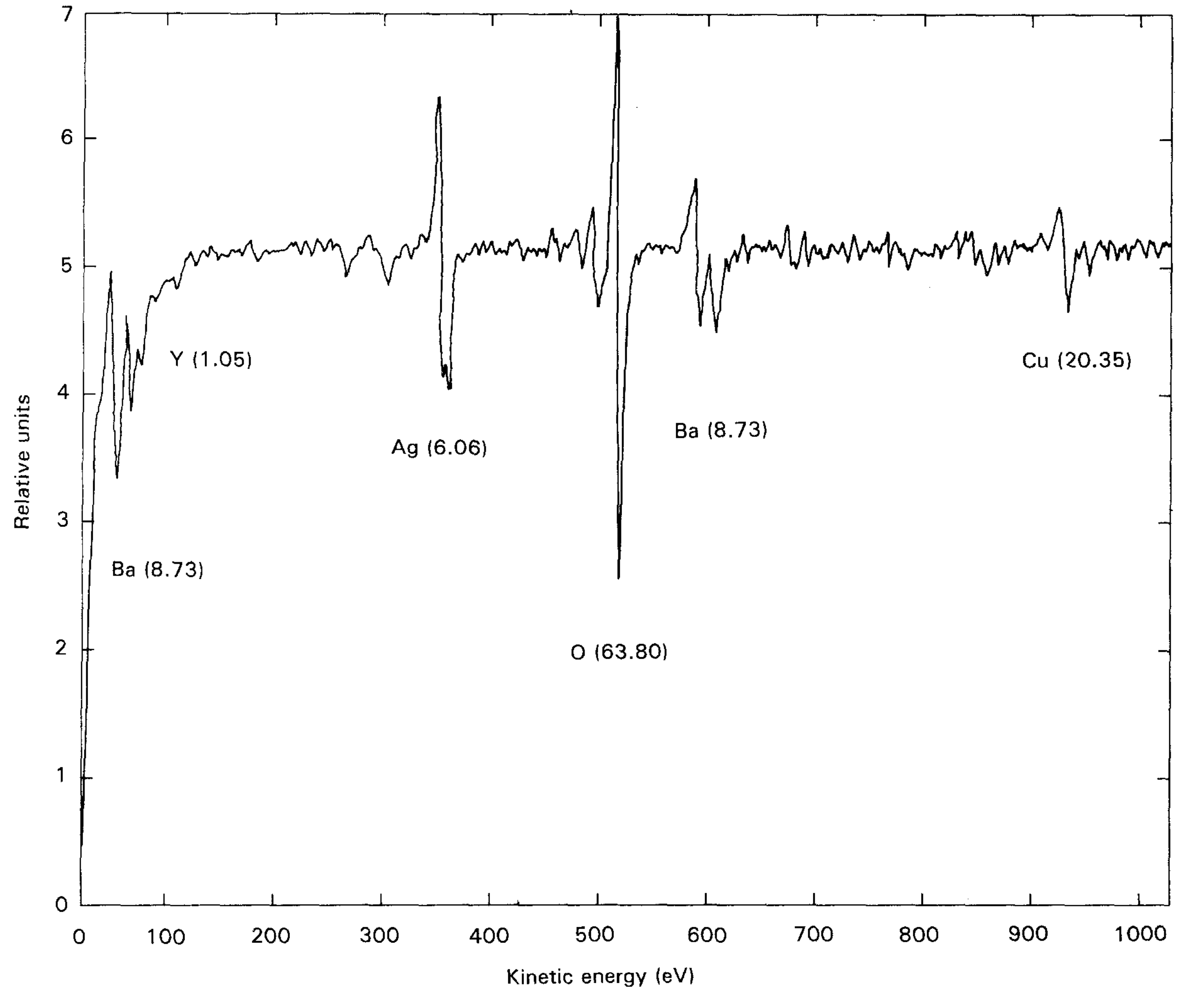

Figure 8 Auger analysis for a sample with 5.9 w/o Ag_2O prepared by dissolution in nitric acid. The arrow in Fig. 7a is where this Auger analysis was performed.

prepared by solid-state reaction and 6 w/o Ag_2O prepared by dissolution in hot nitric acid, respectively.

In Fig. 9a it is possible to identify most of the lines with the orthorhombic 1–2–3 phase and those indicated by arrows with the Ag_2O phase, in agreement with the Auger analysis. It is also possible to identify the $Y_2Ba_1Cu_1O_x$ (2 1 1) phase, indicated by circles, and small quantities of CuO which are labelled; this is so small that, in this case, it could be confused with the noise level. Fig. 9b shows an X-ray diffractogram similar to Fig. 10a, with different intensities for some of the peaks. It is also possible to identify the lines which

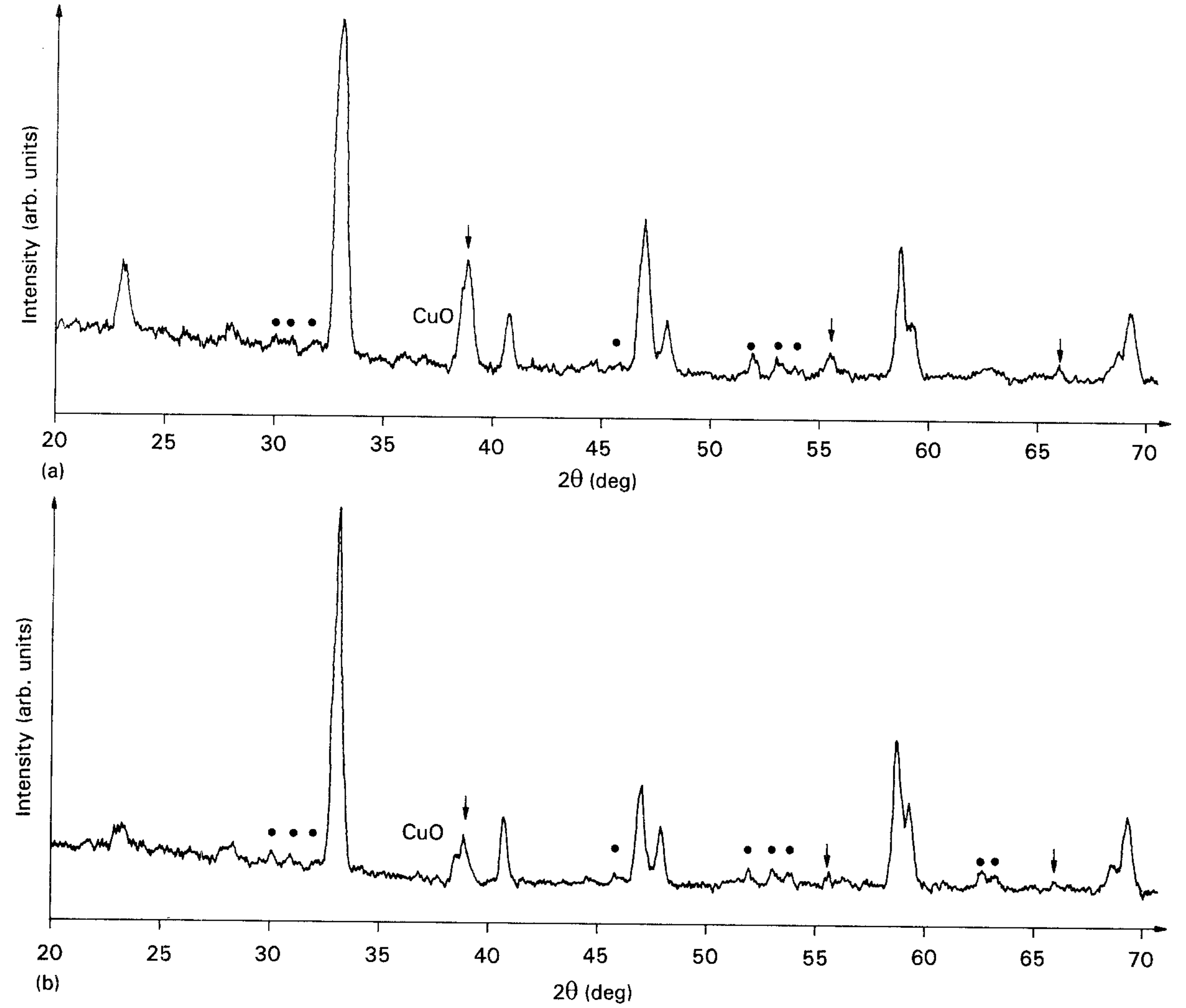

Figure 9 X-ray diffractograms for samples containing (a) 5.9 w/o Ag_2O prepared by solid-state reaction, and (b) 6 w/o Ag_2O prepared by dissolution in nitric acid and air dried. Peaks for CuO are labelled, those for $Y_2Ba_1Cu_1O_x$ (211) are indicated by circles, those for Ag_2O are indicated by arrows, and the main peaks belong to the $Y_1Ba_2Cu_3O_{7-x}$ (1 2 3) phase.

correspond to the 1–2–3 phase, and some lines indicated by arrows corresponding to Ag_2O. It is also possible to identify the (2 1 1) phase, indicated by circles; as well as CuO, which is labelled. It is worth mentioning that the Ag_2O peaks were not as large as those of Fig. 9a, since for preparation by dissolution in nitric acid the Ag_2O spreads throughout the superconductor. This assumption is confirmed by Auger analysis.

4. Conclusions

It has been observed that upon adding Ag to the regular $Y_1Ba_2Cu_3O_{7-x}$ superconductor, by two different preparation methods, the normalized resistance decreases. Ag could be observed as metallic precipitates, the amount of which increased with increasing amount of Ag_2O.

Conclusive evidence that silver segregates to the grain boundaries of the material, as suggested in other reports [16], has not been found; rather, it segregates between the grains in the bulk of the materials.

Due to the high solubility of oxygen in silver, Ag may aid the annealing process by transporting oxygen throughout the bulk.

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