

Properties of Ag-Doped $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_{4-x}\text{Ag}_x\text{O}_y$ (2234) Oxides Prepared by S.S.R. Method

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Abstract

The effect of Ag-doping $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_{4-x}\text{Ag}_x\text{O}_y$ compounds ($x=0.0-1.0$), prepared by conventional Solid-State-Reaction (SSR) technique, was studied using x-ray diffraction (XRD) and electrical resistivity. The high- T_c fraction of the 2223 phase, formed from the nominal composition of 2234, decreases with increasing Ag content. From lattice parameter calculations it follows that Ag-doping the unit cell phase of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ is limited to the value of $x \leq 0.1$. The zero resistance critical temperature ($T_{c,zero}$) was determined from the resistivity curves for all samples. The value of $T_{c,zero}$ decreases slightly to 106 K for $x \leq 0.4$ and when the nominal silver content increases up to $x=0.7$ or more $T_{c,zero}$ strongly decreases to 72 K. The critical current density J_c at 77 K decreases dramatically as silver content increases. This result is discussed on the basis of precipitation of low- T_c 2212 and other impurity phases in $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_{4-x}\text{Ag}_x\text{O}_y$ compounds.

1. Introduction

Silver has been successfully used to fabricate high-temperature superconductor-metal composites in various forms such as silver-cored wires, silver-substrate films and silver-sheathed wires or tapes. However, published results of the results of silver on the superconductivity of BiPbSrCaCuO compounds are very inconsistent. For instance, S. X. Dou et al. [1] reported that Ag doping strongly decomposes the BPSCCO system and destabilizes the superconducting phase, resulting in a strong depression of T_c , J_c and lattice parameters when samples are treated in air or under high oxygen partial pressure. Ren and Wang [2] also reported that Ag doping depressed the critical transition temperature (T_c) of BiPbSrCaCuO (2223) bulk samples from 107 K to 62-86 K. Investigation by Ishida et al. [3,4,5] showed an increase in the transition temperature T_c for Ag doping

up to 10 vol. % and then a decrease with more silver. Oota et al. [6] found that the Ag doping neither caused a decomposition of the high- T_c phase nor depressing of the value of the T_c . Guo et al. [7] also found that the Ag doping caused neither changes in the values of T_c nor the composition of high- T_c phase. Conflicting results have also been reported about the influence of silver on critical current density (J_c) and J_c behaviour in magnetic fields [2,4-7]. Therefore, further detailed investigation is needed to understand the behaviour of silver in BiPbSrCaCuO superconductors.

In previous papers, we discussed the effect of Ag-doping on the magnetic behavior of BiPbSrCaCuO superconductors [8]. In the present paper, we discuss the effect of Ag doping on the crystal structures and the electrical properties of superconducting BiPbSrCaCuO ceramics.

2. Experimental details

Samples with a nominal composition of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_{4-x}\text{Ag}_x\text{O}_y$ ($0.0 \leq x \leq 1.0$) were prepared using conventional solid-state reaction technique. Chemical powders of Bi_2O_3 (purity of 99.9 %), PbO (purity of 99.9 %), SrCO_3 (purity of 98 %), CaCO_3 (purity of 99.5 %), CuO (purity of 99.9 %) and AgNO_3 (purity of 99.9 %) were used as starting materials. The powders were thoroughly mixed and ground in the appropriate amounts by a grinding machine for 2h. After milling, the mixed powders were calcined in air at 790°C for 20h and then cooled to room temperature with the furnace turned off. The calcined materials were reground finely and pressed into pellets of 13mm in diameter at 300 MPa. The pellets were sintered in air at 825°C for 120h and then furnace cooled to room temperature. The samples were pulverized, pressed at 300 MPa and sintered in air at 825°C for another 10, then cooled down to room temperature at a rate of 1°C/min. For comparison, samples without Ag doping were also prepared by the same processing route. All samples were heat treated in alumina crucible.

X-ray diffraction was performed in a Rigaku D/Max-III C x-ray diffractometer to identify the phases, using CuK_α radiation at 40 kV and 30 mA, and a scanning rate of 5 °/min in the 2θ range of 5 to 70° at room temperature.

Zero resistance transition temperature (T_c) and critical current density (J_c) were used to characterize superconducting properties of the samples. The electrical resistivity was measured on bar-shaped specimens with a standard four-probe DC technique with silver point contacts. Zero field critical current was measured at 77 K in liquid nitrogen and the critical current density was determined from the current-voltage curve using a 1 $\mu\text{V}/\text{cm}$ criterion.

3. Results and discussion

Systematic x-ray diffraction studies were carried out on samples at room temperature to explain the interaction between Ag and the superconductor. The x-ray diffraction patterns for undoped samples (a) and Ag-doped samples (b, c, d, e) are shown in Fig. 1. Figure 1(a) shows that the undoped sample consists mostly of the high- T_c phase 2223. In addition, peaks for Ca_2PbO_4 , $\text{Ca}_2\text{Cu}_7\text{Sr}_3\text{O}_x$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ are detected

at $2\theta=17.64^\circ$, $2\theta=31.96^\circ$ and $2\theta=27.80^\circ$, 31.22° , respectively.

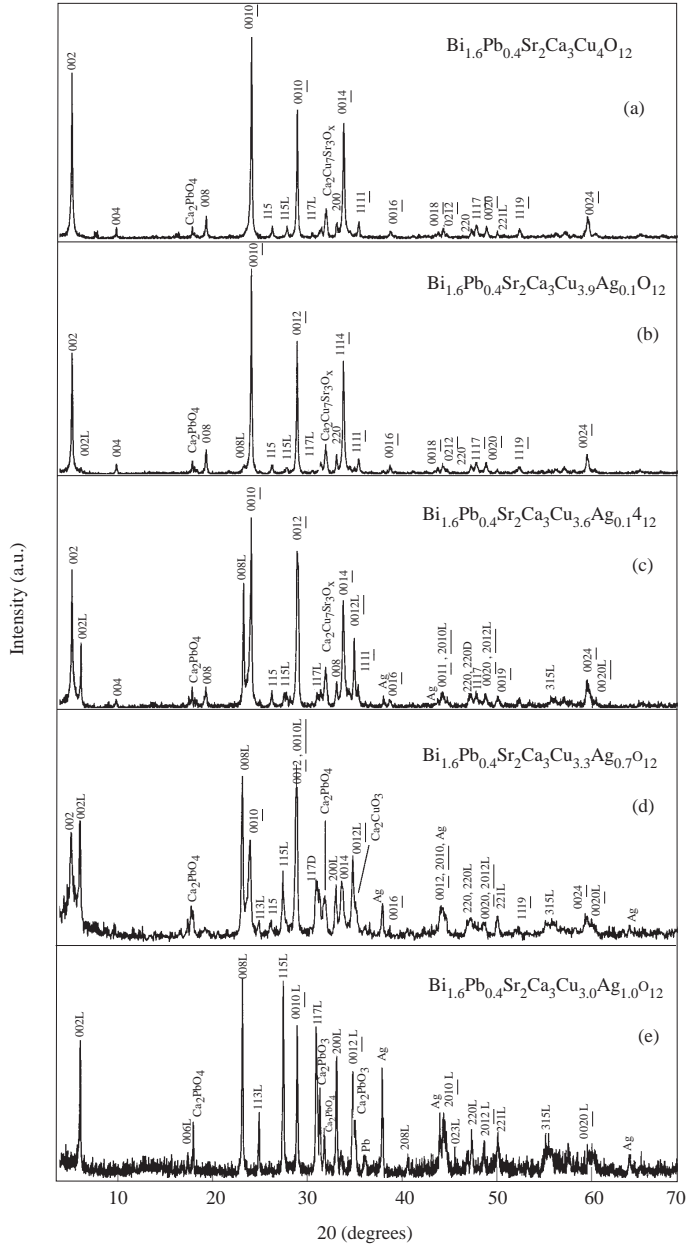


Figure 1. Room temperature x-ray diffraction patterns for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_{4-x}\text{Ag}_x\text{O}_y$ compounds ($x=0.0-1.0$), prepared by a conventional Solid-State-Reaction (SSR) technique.

X-ray diffraction patterns for the Ag-doped samples in Fig.1 (b, c, d, e) indicate that increasing Ag doping results in an appearance of 2212 low- T_c phase. As the Ag content increases, the amount of 2212 phase increases as seen from the dominant peak ratios between the high T_c phase (2223) and low- T_c phase (2212). At the same time, the Ca_2CuO_3 and Ca_2PbO_3 phases appear at $2\theta=31.35^\circ$ and $2\theta=35.35^\circ$, respectively. The peak for the free (isolated) Ag becomes visible in samples with the Ag concentration x equal to 0.4. With addition of Ag, the peak positions for the high- T_c and low- T_c phases are shifted by almost one degree or so (compare Figs. 1a and 1d). For the largest Ag content ($x=1.0$, Fig. 1e), the reflections of the Bi(2223) phase have completely disappeared. The Bi(2212), Ca_2PbO_4 and Ca_2PbO_3 and Ca_2CuO_3 phases are dominant. Also, the free (isolated) Pb peak becomes apparent.

The lattice parameters deduced from XRD patterns given in Fig. 1 are shown in Fig. 2. One can immediately see that the lattice parameter a remains unchanged with Ag addition, while in the lattice parameter c only a slight change can be observed with x up to 0.1 and then remains constant. This result confirms that the solubility of silver is strongly limited ($x<0.1$) and therefore that the remaining silver is segregated in the grain boundaries in metal phase. In order to get definite conclusions about the solubility of silver in BiPbSrCaCuO superconductors, further work on processing Ag-doped 2223 samples is in progress.

The high- T_c volume fraction for all samples were estimated from the intensity ratios of various high- T_c and low- T_c x-ray reflections using the following equation [9]:

$$m = \%2223 = \frac{I_{115}^H + I_{002}^H}{I_{115}^H + I_{002}^H + I_{115}^L + I_{002}^L}$$

denote. Here, I_{115}^H and I_{002}^H denote the peaks intensities of (115) and (002) in 2223, and I_{115}^L and I_{002}^L denote the XRD peaks intensities of (115) and (002) in 2212, respectively. The resulting values only illustrate the variation of the relative proportion of the Bi(2223) phase and do not yield its real amount in the sample. Figure 3 shows the variation of high T_c values as a function of silver content. The real intensity and intensity in cps, plotted as a function of silver content, are shown in Fig. 4a and Fig. 4b, respectively. It can be seen from Fig. 3 and Fig. 4 that the volume fraction of the high- T_c phase and the intensity of high- T_c phase reflection (002) decreases when the silver content is increased and the high- T_c phase fraction becomes undetectable for silver content $x=1$.

Figure 5 shows that the temperature dependence of the electrical resistivity of the samples. The resistivity curve of the undoped samples has a 2223 phase with a zero resistivity temperature (T_c) of 110 K. Ag-doped samples with $0 \leq x \leq 0.4$ have one-step resistivity transitions. The temperature of zero resistivity, however, decreases slightly with Ag concentration for $x \leq 0.4$ (~ 106 K). Sample with Ag concentration $x=0.7$ have two-step resistive transition, suggestive of the presence of two phases, the 2223 and 2212 phases. As can be seen in Fig.1 (d), the peak intensities at $2\theta=4.7^\circ$ for the high- T_c phases and $2\theta=5.8^\circ$ for the low- T_c phase are almost comparable, in agreement with its resistivity measurement of Fig. 5 ($x=0.7$). The resistivity of the sample with $x=1.0$ in Fig. 5 has a single 2212 superconducting transition with zero resistivity of 72 K.

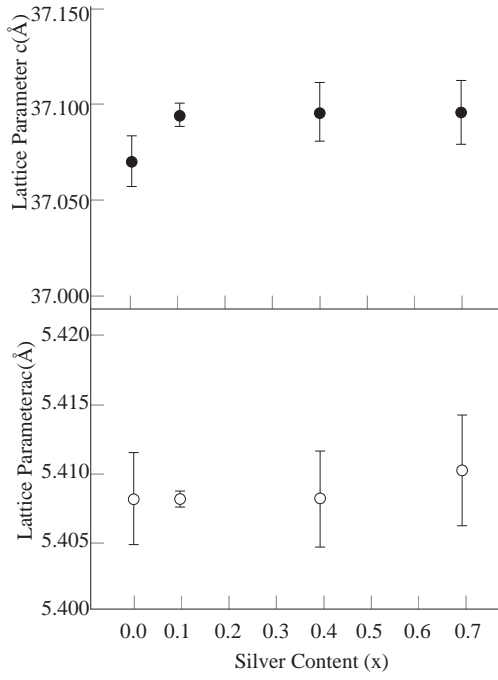


Figure 2. The variation of lattice parameters a and c as a function of silver content (x).

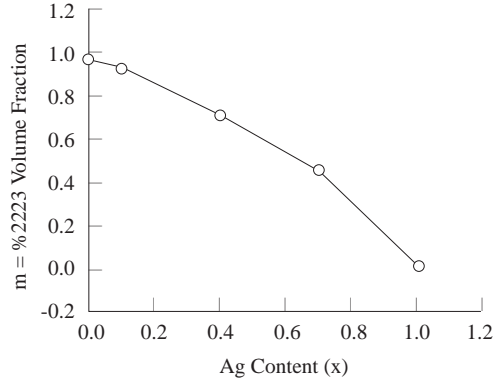


Figure 3. Shows the volume fraction of high- T_c phase as a function of silver content (x).

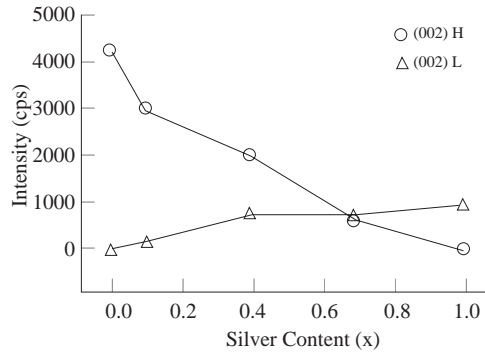
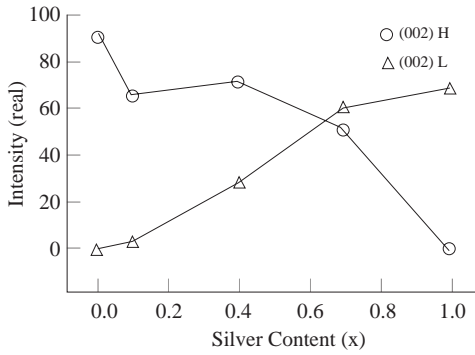


Figure 4. Shows (a) the real intensity and (b) intensity in cps as a function of silver content (x).

Although all the samples with low dopant concentrations contain some amounts of the 2212 phase, as seen from the XRD, they have a one-step resistive transition. Because the volume fraction of the 2223 phase is sufficient to form a continuous network of grains with most weak links interconnecting the islands of only this phase. Upon lowering

the temperature, the current by passes the islands of the 2212 phase and goes through paths traversing the grains of the 2223 phase coupled together via some weak links. A sufficiently thin layer of the 2212 phase can play a role as the weak link.

The 2234 starting composition is excess in Ca and Cu, therefore, the excess Ca and Cu elements play an important role in the formation of impurity phases during the solidification process. The existence of the impurity phases in the superconductors decrease the values of T_c . Bock et al. [10] found that the single phase 2212 exhibited $T_{c(0)}=84$ K, while sample exhibited a mixture of 2212 and other impurity phases displayed T_c values between 60 K and 70 K. There is good agreement between present values and those of Bock et al. [11] in samples containing of high Ag content ($x=1.0$).

Fig. 6 shows the critical current density J_c against Ag content. In the figure, the critical current density is shown for samples with no silver (control sample), and with silver ($x=0.1$ and $x=0.4$). The data indicates that the critical current density decreases markedly as silver concentration increases. The critical current density for sintered samples is usually a measure of the weak links between grains, and as such is often a function of the processing conditions, rather than being an intrinsic property of the material. The decrease in J_c is most likely due to the precipitation of the low- T_c 2212 and other impurity phases which cause an increase in the number of weak links in the silver-added samples. Because the low- T_c phase has lower current carrying capacity than the high- T_c phase at 77 K, the critical current density decreased quickly with increasing low- T_c phase fraction.

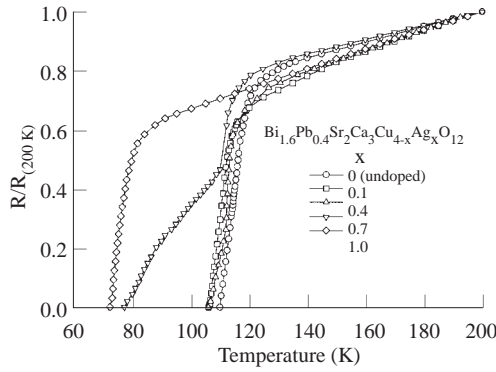


Figure 5. Shows the temperature dependence of the electrical resistivity of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_{4-x}\text{Ag}_x\text{O}_y$ compounds ($x=0.0-1.0$).

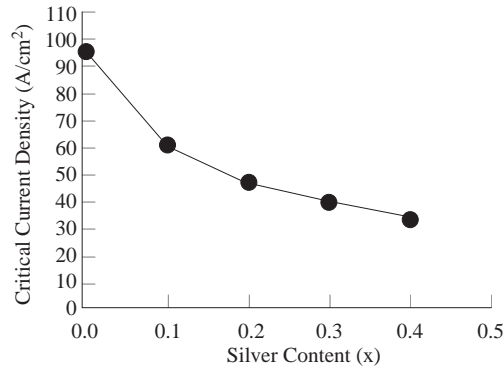


Figure 6. Shows the variation of critical current density measured by a standard four point method as a function of silver content (x).

The effect of Ag doping seems to depend greatly on sample processing. The observed difference in T_c and J_c values between our results and the results reported by other investigators may be due to the method used for silver addition in the compound, the difference in the composition of the parent materials and heat treatment procedures.

4. Summary

The small expansion of the c parameter suggests that the solubility of Ag into the structure of the Bi,Pb (2223) system is very low. The Ag doping has a considerable influence on the precipitation of the impurity phases which results in increasing the amounts of liquid phase in samples. It was found that the tetragonal matrix phase of 2223 decomposes to the low- T_c phase 2212 with increasing the silver content ($x=1$) in samples. For the undoped samples the impurity phases are 2212, Ca_2PbO_4 , and $\text{Ca}_2\text{Cu}_7\text{Sr}_3\text{O}_x$ phases, while for the doped samples they are 2212, Ca_2PbO_4 , $\text{Ca}_2\text{Cu}_7\text{Sr}_3\text{O}_x$, Ca_2CuO_3 and Ca_2PbO_3 phases. The amount of the 2212 phase increases with Ag addition. These impurity phases influence significantly the superconductivity of the Bi,Pb (2223) system.

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