

**PHASE COMPOSITION AND
SUPERCONDUCTING PROPERTIES OF
(Pb_{0.6}Sn_yCu_{0.4-y})Sr₂(Y_{1-x}Ca_x)Cu₂O_z**

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Abstract. The effect of Sn doping in (Pb_{0.6}Sn_yCu_{0.4-y})Sr₂(Y_{1-x}Ca_x)Cu₂O_z for $0 \leq y \leq 0.3$ and $0 \leq x \leq 0.7$ was investigated. It was established that a nearly pure 1212 phase could be obtained at $0 \leq y \leq 0.1$ and $0 \leq x \leq 0.3$. The obtained XRD patterns as well as the results of the EDX and ICP-AES analyses showed that the Sn-substitution was possible in the (Pb,Cu)-1212 phase. Superconductivity was observed at $0.4 \leq x \leq 0.7$. The onset of the diamagnetic transitions varied from 10 to 30 K. The influence of the strong Pb deficiency on the superconducting properties of the samples was discussed.

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1. Introduction

Soon after the discovery of the nonsuperconducting lead-based 1212 cuprate $(\text{Pb,Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_7$ [1] many superconductors with transition temperatures T_c from 17 K [2] to 105 K [3] were obtained by using different substitutions. Maignan et al [4] pointed out that the rocksalt layer of the 1212 phase could accommodate a tremendous number of elements. It was established that the difference in the valence state of the elements in the rocksalt layer stabilized the phase 1212 [5]. Lee and Han [6] summarized that the cationic sizes of the substituting elements in the rocksalt layers varied from 0.72 Å for Mg to 1.18 Å for Sr. The tin ionic radius (0.69 Å) was smaller than that of Mg but higher than that of Cu(II) (0.62–0.65 Å) and could allow a partial substitution of the copper sites in the rocksalt layers. Moreover its higher valence state, Sn(IV), could be used for stabilization of the (Pb,Cu)-1212 superconductor [5]. It was established that Sn stimulated the Hg-1212 phase formation [7] and even could form a tin-based 1212 structure [8]. Ichimaru et al [9] showed that the $(\text{Pb}_{2/3}\text{M}_{1/3})\text{Sr}_2\text{YCu}_2\text{O}_z$ material was multiphase at $\text{M} = \text{Sn}$ but no data on the superconducting properties were reported. In a previous work we observed superconductivity at 17 K and a magnetoresistance effect of about 60% at $H = 120$ kOe and $T = 4.2$ K in multiphase $(\text{Pb}_{0.7}\text{Sn}_{0.3})\text{Sr}_2(\text{Y}_{0.6}\text{Ca}_{0.4})\text{Cu}_2\text{O}_z$ [10].

The purpose of the present work is to elucidate whether a substitution is possible in the Sn-doped (Pb,Cu)-1212 system as well as to investigate the superconducting properties of different $(\text{Pb}_{0.6}\text{Sn}_y\text{Cu}_{0.4-y})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$ samples.

2. Results and Discussion

The investigated samples with nominal compositions $(\text{Pb}_{0.6}\text{Sn}_y\text{Cu}_{0.4-y})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$ ($0 < y < 0.3$ and $0 < x < 0.7$) were prepared by a solid state reaction in air from starting materials PbO, SnO₂, SrCO₃, Y₂O₃, CaCO₃ and CuO with a purity over 99.9%. They were homogenized, pressed into pellets and fired at 800–840 °C for 20 h. After homogenization new pellets were formed from the resulting material. They were sintered at 850–950 °C for 30–120 hours and quenched in air. X-ray diffraction (XRD) was used to examine the samples using a TUR-M62 diffractometer. An EDX on SEM analysis was performed on the pellets using a Jeol Superprobe 733 microscope at an acceleration voltage of 25 keV. An inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on powdered samples transferred to the solutions by using an ICP spectrometer “Plasma 40” of Perkin-Elmer. The susceptibility of the samples was measured as a function of temperature

$\chi(T)$ using a Lake Shore 7000 Series AC susceptometer-DC magnetometer at a frequency of 133 Hz and zero magnetic field.

The investigation of the XRD patterns of $(\text{Pb}_{0.6}\text{Sn}_y\text{Cu}_{0.4-y})\text{Sr}_2\text{YCu}_2\text{O}_z$ for $y = 0.05, 0.1$ and 0.2 showed that only the $y = 0.05$ sample was nearly single phased. At higher tin concentrations an impurity SrSnO_3 phase appeared. This result suggests a low solubility limit of Sn in the (Pb,Cu)-1212 phase as in $\text{YBa}_2\text{Cu}_3\text{O}_y$ [11].

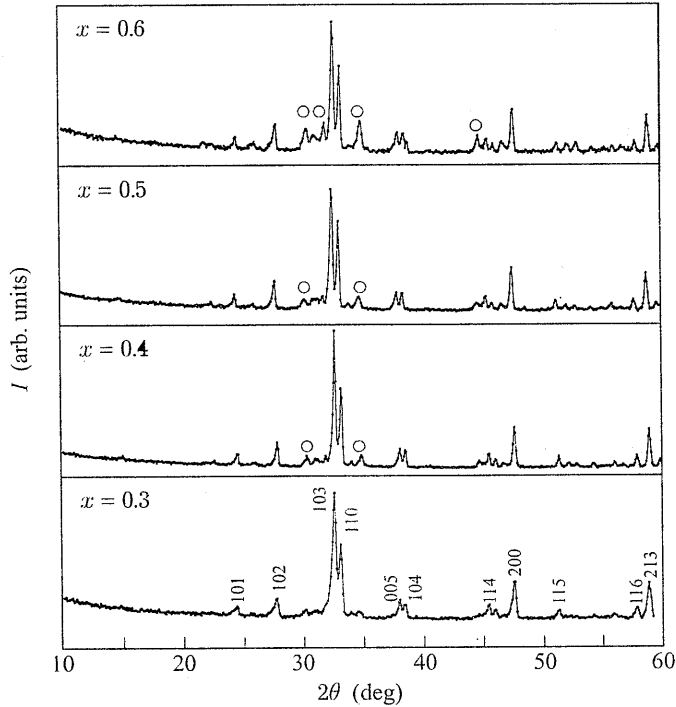


Fig. 1. XRD patterns for $y = 0.1$ and $0.3 \leq x \leq 0.6$ samples
○ — impurities

Figure 1 shows the XRD patterns for $y = 0.1$ and $0.3 \leq x \leq 0.6$ samples. It may be seen in the figure that the phase 1212 is dominating and the $x = 0.3$ sample is nearly single phased. The $x = 0.4, 0.5$ and 0.6 samples contain an impurity phase, identified as SrCu_2O_3 . In Fig. 2 the XRD patterns for $y = 0.3$ and $x = 0, 0.5$ and 0.6 samples are given. It may be seen that all the samples are multiphase with a dominating 1212 phase at this concentration of the Sn. The impurities are SrSnO_3 and SrCu_2O_3 . The decrease of the phase purity with increase of the calcium content x is a common feature of all the investigated

1212 systems. The results from Figs 1 and 2 determine the parameters for obtaining nearly single phase samples: $0 \leq y \leq 0.1$ and $0 \leq x \leq 0.3$.

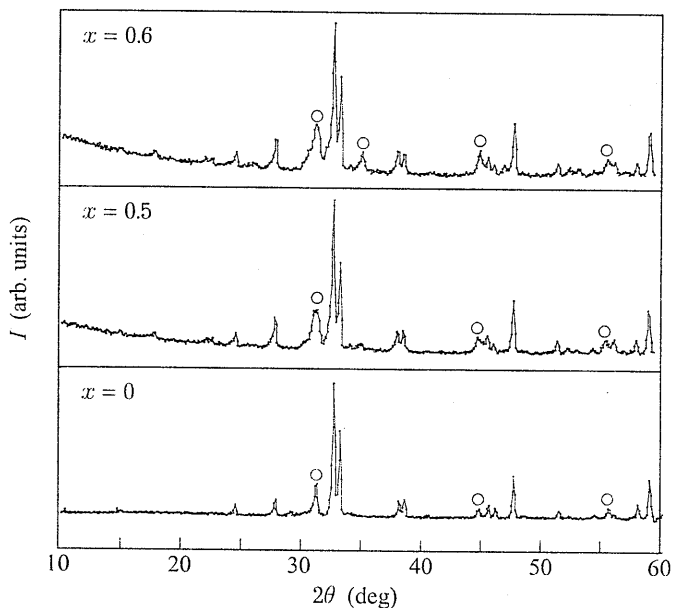


Fig. 2. XRD patterns for $y = 0.3$ and $x = 0, 0.5$ and 0.6 samples
○ — impurities

In order to obtain the quantities of the different elements, an EDX on SEM and an ICP-AES analyses have been performed to a nearly single phase sample with nominal composition $(\text{Pb}_{0.55}\text{Sn}_{0.1}\text{Ca}_{0.1}\text{Cu}_{0.33})\text{Sr}_2(\text{Y}_{0.73}\text{Ca}_{0.27})\text{Cu}_2\text{O}_z$. We have chosen a single phased sample in order to prove the presence of Sn in the phase as well as to obtain a better reliability between the EDX and ICP data and the chemical composition. If it is assumed that the Sr^{2+} sites are occupied solely by these ions, and that the overall occupancy of the (Y,Ca) sites must be unity, the chemical composition of the sample is determined to be $(\text{Pb}_{0.4}\text{Sn}_{0.1}\text{Ca}_{0.02}\text{Cu}_{0.16})\text{Sr}_2(\text{Y}_{0.76}\text{Ca}_{0.24})\text{Cu}_2\text{O}_z$ according to EDX and $(\text{Pb}_{0.42}\text{Sn}_{0.11}\text{Ca}_{0.23}\text{Cu}_{0.36})\text{Sr}_2(\text{Y}_{0.77}\text{Ca}_{0.23})\text{Cu}_2\text{O}_z$ according to ICP-AES analysis. It may be seen that the two analyses confirm the presence of Sn in the sample but also denote a loss of Pb in comparison with the nominal composition. In order to check whether tin is not present at the grain boundaries as in the case of some additives in YBCO [12, 13] an EDX on SEM analysis has also been performed on a nearly single phased $x = 0.2, y = 0.1$ sample. The grain size of this sample is 2–4 μm and the diameter of the electron probe 0.6–

0.7 μm . The result of this analysis on 5 different crystals is given in Table 1. The obtained data indicate the presence of Sn in the 1212 phase. The results of the XRD, EDX on SEM and ICP-AES analyses show that the Sn substitution is possible in the (Pb,Cu)-1212 system but the substitution level is too small.

Table 1. Chemical compositions of different microcrystals in the $(\text{Pb}_{0.6}\text{Sn}_{0.1}\text{Cu}_{0.3})\text{Sr}_2(\text{Y}_{0.8}\text{Ca}_{0.2})\text{Cu}_2\text{O}_z$ nearly single phase sample, according to the EDX on SEM analysis

Crystal	Size (μm)	Composition
1	4	$(\text{Pb}_{0.42}\text{Sn}_{0.08}\text{Ca}_{0.09}\text{Cu}_{0.16})\text{Sr}_2(\text{Y}_{0.92}\text{Ca}_{0.08})\text{Cu}_2\text{O}_z$
2	3	$(\text{Pb}_{0.38}\text{Sn}_{0.08}\text{Ca}_{0.08}\text{Cu}_{0.3})\text{Sr}_2(\text{Y}_{0.9}\text{Ca}_{0.1})\text{Cu}_2\text{O}_z$
3	2	$(\text{Pb}_{0.42}\text{Sn}_{0.09}\text{Ca}_{0.06}\text{Cu}_{0.1})\text{Sr}_2(\text{Y}_{0.87}\text{Ca}_{0.13})\text{Cu}_2\text{O}_z$
4	3-4	$(\text{Pb}_{0.42}\text{Sn}_{0.07}\text{Ca}_{0.1}\text{Cu}_{0.13})\text{Sr}_2(\text{Y}_{0.9}\text{Ca}_{0.1})\text{Cu}_2\text{O}_z$
5	4	$(\text{Pb}_{0.43}\text{Sn}_{0.07}\text{Ca}_{0.06}\text{Cu}_{0.16})\text{Sr}_2(\text{Y}_{0.89}\text{Ca}_{0.11})\text{Cu}_2\text{O}_z$

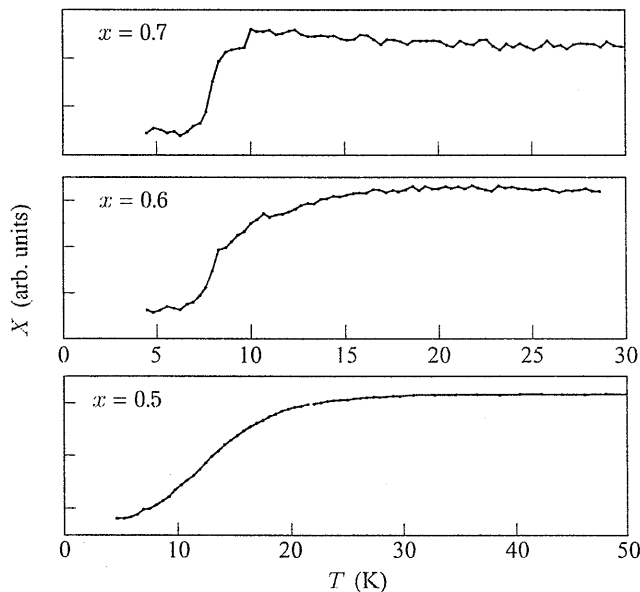


Fig. 3. Temperature dependence of the susceptibility $\chi(T)$ of $x = 0.5$, 0.6 and 0.7 samples for $y = 0.1$

The susceptibility measurements showed that the $0 \leq x \leq 0.3$ samples are not superconducting down to 4.2 K at every y . Also the unsubstituted $y = 0$ samples are not superconducting under these preparation conditions. Figure 3 shows the dependence of the real part of the susceptibility vs temperature $\chi(T)$ for the $y = 0.1$ and $x = 0.5, 0.6$ and 0.7 samples. A broad incomplete transition can be seen for the $x = 0.5$ sample with a deviation from the straight line at

about 30 K. The $x = 0.6$ and 0.7 samples have an onset of the diamagnetic transitions at 17 K and 10 K respectively. Also the diamagnetic transition is better expressed for the $x = 0.6$ sample than that for the $x = 0.5$ one as in the case of the (Pb,Ca)-1212 phase [14].

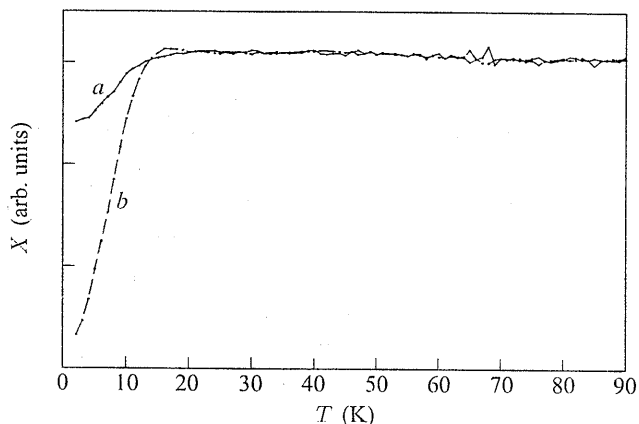


Fig. 4. Temperature dependence of the susceptibility $\chi(T)$ of $x = 0.5$ (curve *a*) and 0.6 (curve *b*) samples for $y = 0.3$.

Figure 4 shows the dependence of $\chi(T)$ for the $y = 0.3$ and $x = 0.5$ and 0.6 samples. It may be seen in the figure that the $x = 0.5$ sample is superconducting at $T_{\text{on}} = 20$ K and the $x = 0.6$ one — at 16 K. The $x = 0.7$ sample is still superconducting at $T_{\text{on}} = 25$ K but the impurity phases are dominating. It has been established that the T_c of the obtained samples is very sensitive to the synthesis temperature and that the latter is strongly dependent on x . This could be explained by the increase of the loss of Pb at higher synthesis temperatures. The loss of Pb is compensated by an increase of the extra oxygen atoms in the rocksalt layers. It is known that oxygen in the (Pb,Cu)O layers due to a random arrangement tends to trap holes and prevents their transfer into the CuO_2 layers which carry the superconducting current. This phenomenon limits the T_c of the unsubstituted system to around 45–67 K [15]. A partial substitution of Sn in the CuO_2 layers could further reduce the T_c . Naqvi and Boyd [16] have succeeded to obtain an 82 K superconductor in the (Pb,Cu)-1212 system by using a more complicated method of preparation. The obtained low values of T_c show that the oxygen content in the Sn-doped samples is not optimized. Another problem is the very low superconducting volume fraction. This could be explained by the small grain size of the material relative to the penetration depth and possibly by a decomposition reaction at the grain surface resulting in a material with a very granular structure [17]. A Pb loss also occurs as can be seen from the EDX and ICP-AES data. The lack of superconductivity in

the $0 \leq x \leq 0.3$ samples, the presence of a maximum of T_c as well as the strong dependence of the superconductivity on the lead content suggest that the diamagnetic properties are due to the dominating 1212 phase and not to any minor impurity.

3. Conclusion

The effect of Sn doping in $(\text{Pb}_{0.6}\text{Sn}_y\text{Cu}_{0.4-y})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$ for $0 \leq y \leq 0.3$ and $0 \leq x \leq 0.7$ was investigated. The obtained XRD patterns as well as the results of the EDX and ICP-AES analyses showed that the Sn substitution was possible in the (Pb,Cu)-1212 system and a nearly pure phase could be obtained at $0 \leq y \leq 0.1$ and $0 \leq x \leq 0.3$. Superconductivity was observed at $y = 0.1$ and $0.5 \leq x \leq 0.7$ as well as at $y = 0.3$ and $0.4 \leq x \leq 0.7$. The onset of the diamagnetic transitions varied from 10 K to 30 K. The low values of T_c were explained by assuming an increase of the extra oxygen atoms in the rocksalt layers due to the strong Pb deficiency.

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