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NOVEL SUPERCONDUCTING PHASES OF TL-BASED COMPOUNDS

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1. Introduction

The interest in novel superconducting compounds has been attracted, recently, by the Pb-containing High Temperature Superconductors (HTS) [1-5]. The larger part of work has been done on Bi-Pb type HTS [6,7]. The Tl-based HTS, howeever, are also of considerable importance because of their highest critical parameters (T_c, H_c) [8,9]. Due to the dangerous properties of Tl the research in this area is progressing more slowly. The list of the stable phases of Tl-Ba-Ca-Cu-O HTS is still incomplete. The Tl-Pb HTS were studied mostly in the compound Tl-Pb-Sr-Ca-Cu-O [10] and less in the family Tl-Pb-Sb-Ca-Ba-Cu-O [11]. The substitution of Tl with Pb is intended to stabilize some phases with high T_c. We found phases with T_c = 82, 90, 102 and 121 K. Here we report the measurements of the $I_c(T)$ of the 102 K phase. We also discuss briefly the influence of the composition on the lattice parameters and the a.c. susceptibility relation to the grain size and microstructure.

2. Experimental

The nitrates solution of the metals Tl, Pb, Sb, Ba, Ca, Cu of starting composition $Tl_{0.75}Pb_{0.2}Sb_{0.05}Ca_2Ba_3Cu_4$ was dried and decomposed at 780°C. Pellets were prepared under 1-2 kbars pressure and annealed at different temperatures from 820°C to 915°C. The highest critical temperature phase was found to be the 121 K. It was prepared by a 3 min annealing at 891°C in oxigen atmosphere. The lattice parameters of this tetragonal phase are a = b = 3.84 Å and c = 31.96 Å. The average composition of the pellets of this type found by SEM analysis was $(Tl,Pb)_1 - Ca_2 - Ba_{4.1} - Cu_{5.6} - O$, the Tl-Pb ratio being 4.4. We should mention here that a slight change in the composition lead to different c-parameter of the tetragonal elementary cell. For example the composition $(Tl + Pb)_1 - Ca_{2.8} - Ba_{2.8} - Cu_{4.4} - O$ with the ratio Tl:Pb equal to 3.17 has a cell length of 32 Å. The X-ray powder diffraction pattern is practically the same as the one of the first mentioned compound but the peak at low angles being quite well pronounced is slightly displaced. We mention here this observation in order to illustrate the similarity of the Tl-Pb system to solid solutions compounds.

We turn next to another phase with lower T_c = 102 K but the same starting composition prepared by annealing first at 820°C for 3 min in oxigen atmosphere. After quenching and grinding the pellet was annealed for 6 min at 915°C. The result was an remarkably homogeneous sample with sharp transition at T_c = 102 K. This phase was studied by SEM and in the *µm* range it has the microstructure shown on Fig. 1.

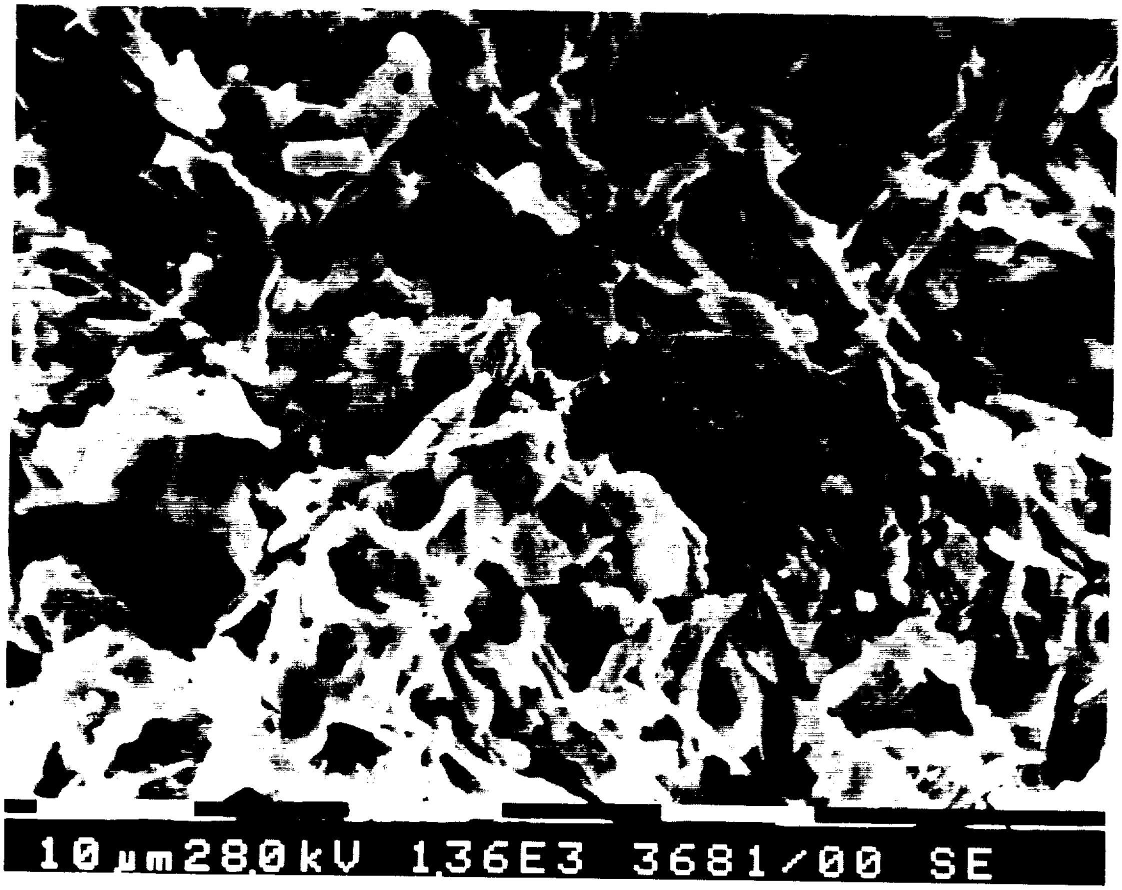

Fig. 1.
SEM microstructure of the 102 K ceramic sample. Large voids are seen and crystals are absent

This crystals free structure is closely related to the a.c. susceptibility of the sample measured at different magnetic fields.

3. A.C.Susceptibility

The real χ' and imaginary χ'' parts of the magnetic susceptibility were measured simultaneously at different temperatures upon warming. The a.c. field amplitude was between 24 A/m and 800 A/m, the frequency being 10 Hz.

The sample was in the form of a prism (2 × 4 × 10 mm). In order to minimize the demagnetization effect, the a.c. field was chosen to be parallel to the length of the sample. Corrections for the demagnetization were performed [12]. On Fig. 2a and Fig. 2b the temperature dependence of the susceptibility χ' and χ'' are presented.

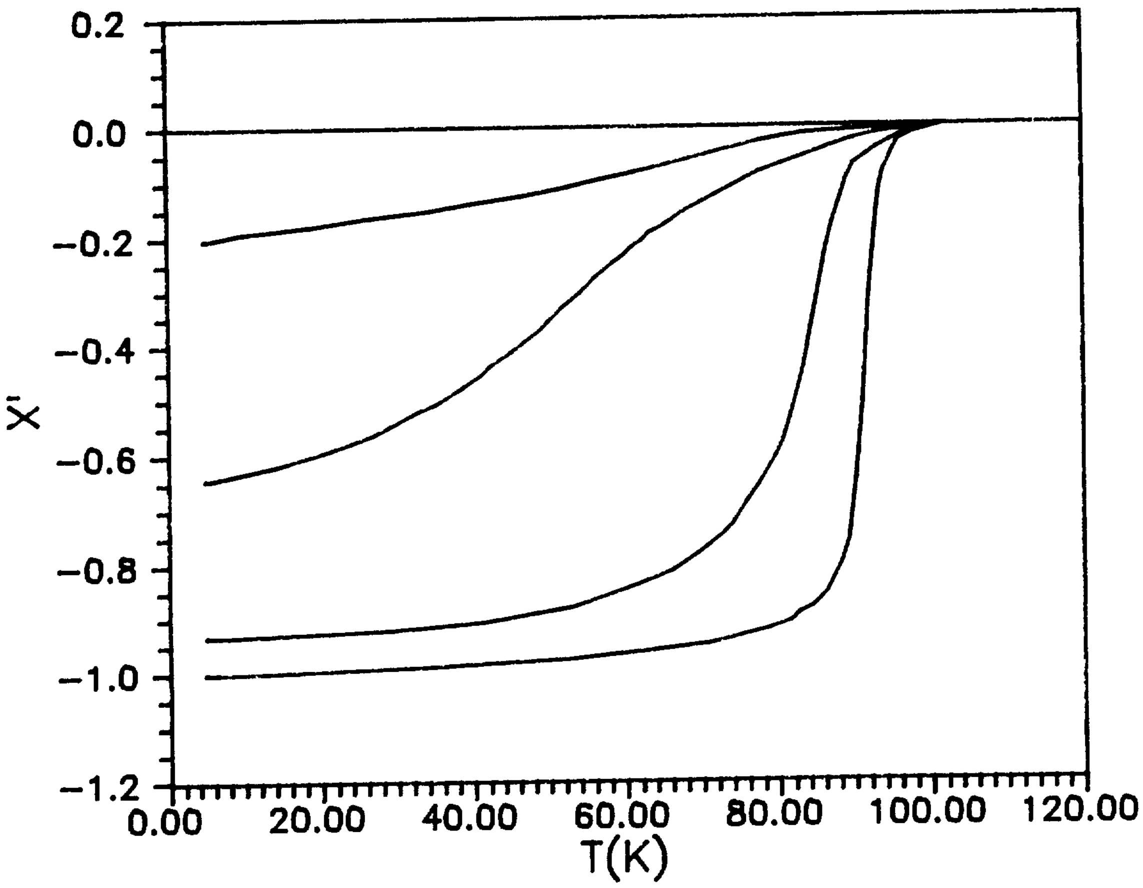

Fig. 2a.
Temperature dependence of χ' measured at fields 24 A/m - curve *a*; 240 A/m - curve *b*; 2400 A/m - curve *c* and 8000 A/m - curve *d*

The complete diamagnetic shielding is demonstrated by the value -1 of χ' (or $\chi'' = 0$) below 60 K at low magnetic fields. At higher fields, however, the situation is entirely different.

The $\chi'(T)$ curves are well above the low field one with complete absence of common part. Two stage behaviour in χ' is not seen also, in contrast with the typical ceramic HTS like *YBaCuO*.

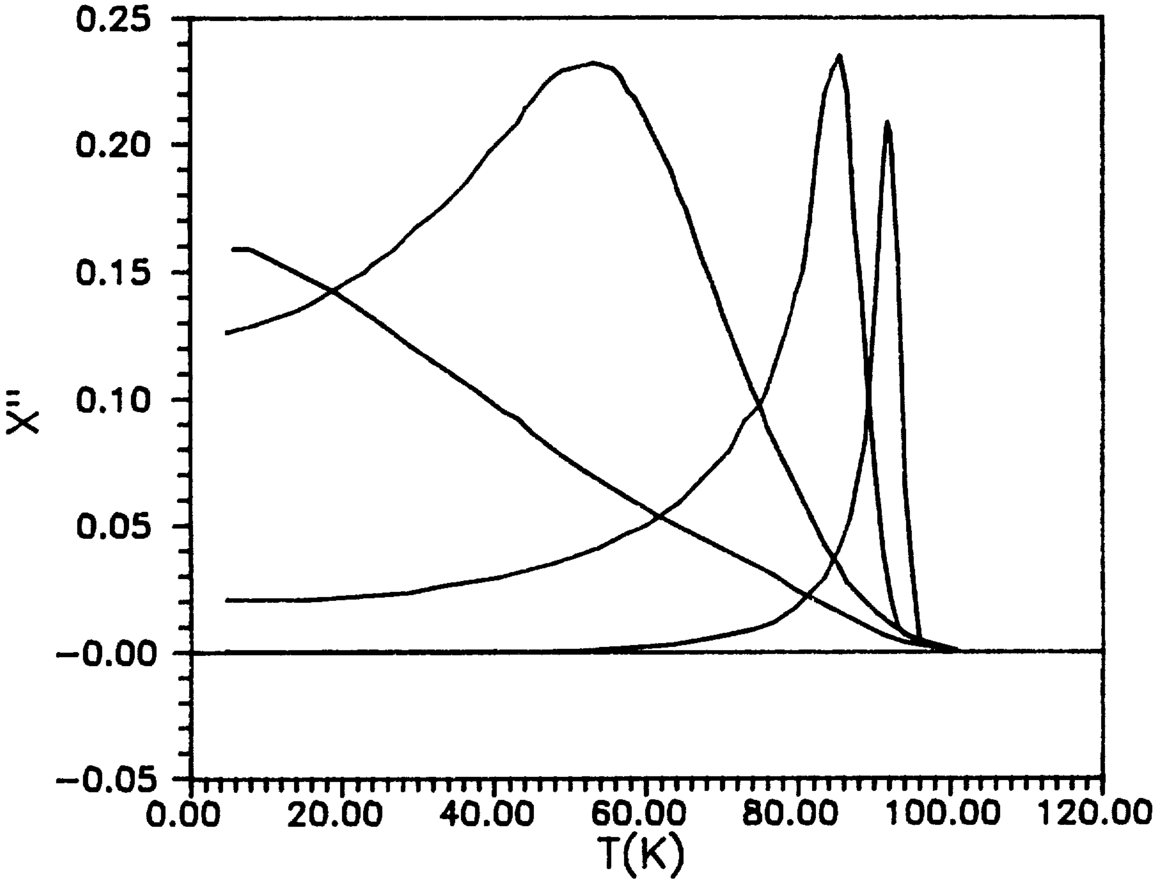

Fig. 2b.
Temperature dependence of χ'' measured at the same fields as χ' (Fig. 2a)

The second peak in χ'' is also absent in agreement with the $\chi'(T)$ dependence. The maximum value of χ'' (in fields between about 24 A/m and about 2400 A/m), at which the magnetic field penetrates completely the coupling matrix is in agreement with the larger part of the data reported for ceramic samples [13]. It is worth mentioning that strong field dependence of the χ'' maximum suggesting usually Josephson type grains coupling was not observed, at least in the fields range of measurement. In principle, the observed behaviour can happen in the case when the contributions to the susceptibility of the grains and the coupling matrix are not well temperature-separated. To our knowledge this situation is not valid in our case.

The a.c. susceptibility data were used recently by several authors to estimate the transport critical current. Based on Kim's critical state model a method for determining the temperature dependence of the intergranular critical current has been developped by Chen et al.[12]. Using this method and neglecting the volume fraction of the grains the temperature dependence of the transport critical current $I_c(T)$ has been reconstructed of Fig. 3 from the measured susceptibilities.

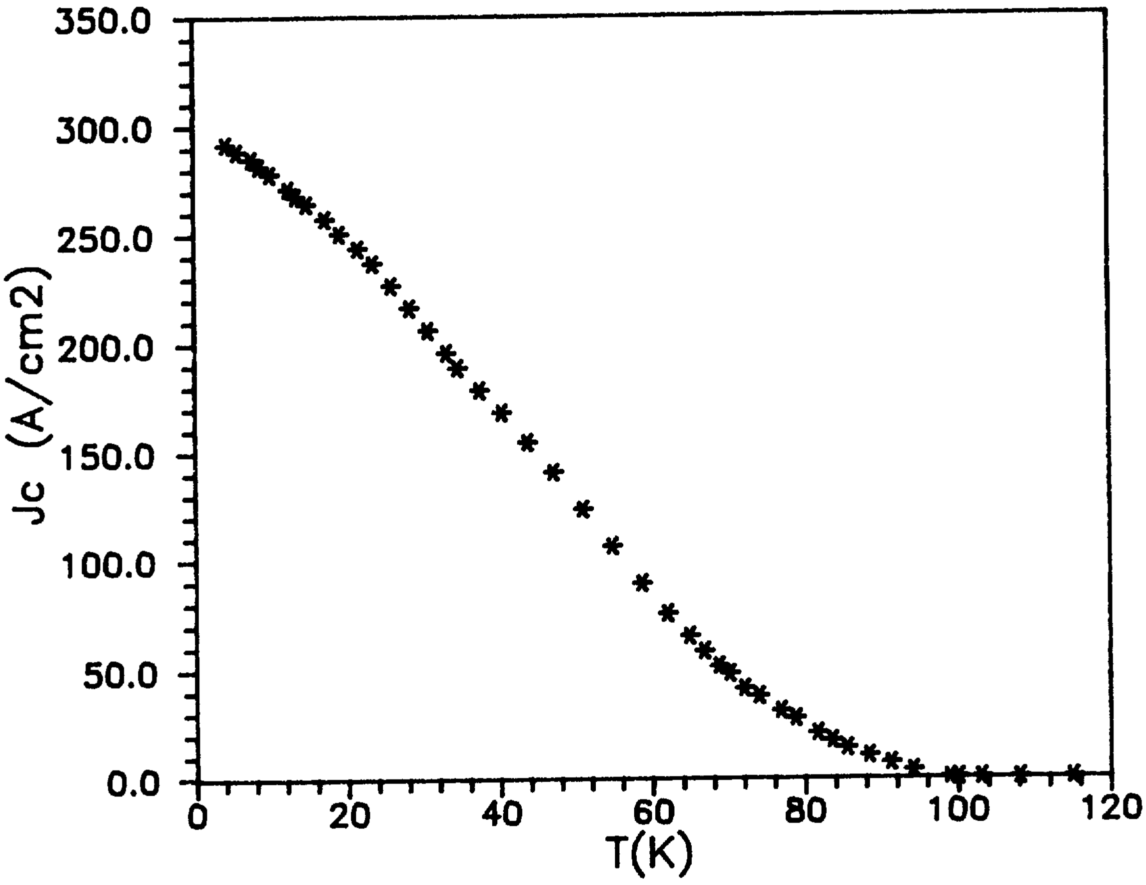

Fig. 3.
Critical current temperature dependence of the 102 K phase.

4. Results

In conclusion we briefly enumerate the results reported here. First we mention the observed variety of phases of the superconducting compound $Tl-Pb-Sb-Ca-Ba-Cu-O$. Among them we concentrated our affention here on the 102 K phase, which being homogeneous appears to have monocrystalline-like microstructure, complete diamagnetic shielding and specifie behaviour of the complex susceptibility (Fig. 2 a,b). Finaly, we mention the reconstruction of the critical current temperature dependence $I_c(T)$ shown on Fig. 3 from the measured susceptibilities.

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