(Tl$_{0.5}$Pb$_{0.5}$)(Sr$_{1-x}$Ba$_x$)$_2$(Ca$_{1-y}$Gd$_y$)Cu$_2$O$_z$ 1212 Superconductors

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Abstract. Thallium-free precursors for bulk superconductors with the overall composition (Tl$_{0.5}$Pb$_{0.5}$)(Sr$_{1-x}$Ba$_x$)$_2$(Ca$_{1-y}$Gd$_y$)Cu$_2$O$_z$ ($x = 0.0, 0.05, 0.1, 0.15, 0.2, 0.25, y = 0.0, 0.05, 0.1, 0.2, 0.3, 0.4$) were prepared via wet chemical gel techniques. The respective amounts of Tl$_2$O$_3$, PbO and Gd$_2$O$_3$ were co-milled to the precursor and the mixture was subjected to a heat treatment first at 850 °C followed by sintering at 925 °C in order to optimize the superconducting properties of the bulk material. X-ray diffraction showed that samples with $x$ and $y$ equal to or smaller than 0.2 were nearly phase-pure. While changes in the $x$ value had little effect on the properties of the materials, a Gd stoichiometry of 0.2 yielded the best results in this series. Critical temperatures around 100 K were obtained for samples with the composition (Tl$_{0.5}$Pb$_{0.5}$)(Sr$_{1-x}$Ba$_x$)$_2$Ca$_{0.8}$Gd$_{0.2}$Cu$_2$O$_z$.

1. Introduction

The Tl-1212 phase has a very similar structure to the YBCO-123 superconductor. YBCO, generally abbreviated as 123, is actually a 1212C phase [1]. Difficulties in the preparation of the undoped compound with high phase purity and some reluctance to work with thallium compounds limited the research on this superconducting compound. Substitution of rare earth cations into Ca$^{2+}$ sites [2-6] but also into the Sr$^{2+}$ sites [1-9] and partial replacement of Tl$^{3+}$ by either Pb$^{4+}$ [10, 11], Bi$^{3+}$ [12, 13] or Cr$^{3+}$ [14-16] considerably facilitated the synthesis of Tl-1212. Critical temperatures around 100 K may be achieved for the doped Tl-1212 phase. The preparative conditions for doped Tl-1212 phases are less stringent than for other cuprate superconductors and optimal oxygen stoichiometry is achieved rather easily. Compared to the Tl-1223 phase the Tl-1212 phase exhibits a wider processing window and extended phase stability. This makes this material an interesting superconducting compound for both bulk phase applications and for superconducting films [17, 18] justifying further research on this class of superconductors.

Very few publications deal with Gd doped thallium superconductors. Soon after the discovery of Tl-based superconductors, compounds of the type RE-Tl-Sr-Ca-Cu-O (RE: Y, La,Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were prepared [19]. The authors claimed a $1:2:2:2:3$ structure in this preliminary study and reported a sharp drop in resistance in the range of $80 – 90$ K. X-ray diffraction data were not included in this publication. Septenary oxides with the formal composition (Tl$_{0.5}$Pb$_{0.5}$)Sr$_2$(Ca$_{0.8}$RE$_{0.2}$)Cu$_2$O$_x$ were prepared with the rare earth cations (RE) being La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb in order to fabricate superconducting material with a YBa$_2$Cu$_3$O$_y$ structure [4]. Magnetic and superconducting properties for Tl(Sr$_{1.6}$RE$_{0.3}$)CaCu$_2$O$_{7.5}$ (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were published [7].
2. Experimental

2.1. Preparation of superconducting bulk material
Respective amounts of the nitrates of Sr, Ba, Ca and Cu were dissolved in water. The solution was evaporated to dryness and post-dried at 130 °C and 1 mbar. Calcination was carried out in a chamber furnace at 900 °C in air for 50 h. Appropriate amounts of PbO, Tl₂O₃ and Gd₂O₃, respectively, were added in a milling step in a Retsch micro-mill with a zirconia pestle and mortar for 30 minutes. The resulting powders were uni-axially compacted with a pressure of 1 GPa into cylinders of 10 mm diameter and about 1 mm thickness. The discs were wrapped in silver foil. After detailed studies on the heat treatment procedure, the following sintering technique was applied. The samples were first heated to 850 °C at a rate of 3 K min⁻¹ and kept at this temperature for 10 hours. The samples were then heated to 925 °C at a rate of 1 K min⁻¹ and the temperature was maintained for 1 hour. The cooling rate was 5 K min⁻¹.

2.2. Characterization equipment and analysis
X-ray diffraction (XRD) measurements with Ni-filtered Cu-Kᵢ radiation were carried out on an X'Pert instrument (Panalytical) and on a Geigerflex D-max II a (Rigaku, Japan). The XRD data were analyzed on basis of a tetragonal unit cell. Micrographs were obtained on a scanning electron microscope (Jeol JSM 6400, Japan). Energy dispersive X-ray fluorescence analysis (EDX) was performed on a Röntec system (Röntec, Germany). Critical temperatures were obtained employing the 1 µV cm⁻¹ criterion. Critical current densities at 77 K were determined by dc-transport measurements.

3. Results

The XRD spectra as exemplified in figure 1 showed that the samples were practically phase pure. The temperature dependence of samples of the optimal composition proved that $T_c(0)$-values of 100 K with a sharp transition could be achieved (figure 2). Samples with a Gd stoichiometry other than 0.2 usually showed drawn out two-step transitions.

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**Figure 1.** X-ray diffractogram of a $(\text{Ti}_{0.5}\text{Pb}_{0.5})(\text{Sr}_{0.8}\text{Ba}_{0.2})_2(\text{Ca}_{0.8}\text{Gd}_{0.2})\text{Cu}_2\text{O}_y$ sample (a) and the reference spectrum for $\text{TiSr}_2\text{CaCu}_2\text{O}_7$ (b) [20] indexed as tetragonal unit cell. Ni-filtered Cu-Kᵢ radiation

**Figure 2.** Temperature dependence of the relative resistance of a $(\text{Ti}_{0.5}\text{Pb}_{0.5})(\text{Sr}_{0.95}\text{Ba}_{0.05})_2(\text{Ca}_{0.8}\text{Gd}_{0.2})\text{Cu}_2\text{O}_y$ sample
The lattice parameters for samples with different Sr/Ba ratios showed an increase in the $a$ and $c$ parameters with increasing barium content (Figure 2). This may be expected by the substitution of the Sr$^{2+}$ ions by the larger Ba$^{2+}$ ions. Changes in the substitution on the Ca$^{2+}$ ions by the Gd$^{3+}$ ions, however, led to a decrease of the $c$ axis and to an increase in the $a$-axis (Figure 3). The ionic radius of Gd$^{3+}$ is smaller than the one of Ca$^{2+}$, thus a decrease in the $c$-axis upon partial replacement of Ca$^{2+}$ by Gd$^{3+}$ may be expected. The increase in the $a$-axis upon rare earth substitution into the Tl-1212 phase has been observed before and was accounted for by changes in the Cu – O bond distances due to hole filling [5].

Figure 3. Lattice parameters of bulk phase (Tl$_{0.5}$Pb$_{0.5}$)(Ba$_x$Sr$_{1-x}$)$_2$CaCu$_2$O$_z$ sintered first at 850 °C for 10 hours and then at 925 °C for 1 hour. ($\bigcirc$) $a$-axis, ($\square$) $c$-axis

Figure 4. Lattice parameters of bulk phase (Tl$_{0.5}$Pb$_{0.5}$)(Ba$_{0.2}$Sr$_{0.8}$)$_2$(Ca$_{1-y}$Gd$_y$)Cu$_2$O$_z$ sintered first at 850 °C for 10 hours and then at 925 °C for 1 hour. ($\triangle$) $a$-axis, ($\bigotimes$) $c$-axis

While the Sr/Ba ratio had little influence on the critical temperature, the replacement of Ca$^{2+}$ by Gd$^{3+}$ had a maximum in the $T_{c(0)}$ values for a Gd stoichiometry of 0.2 (figures 5 and 6).

Figure 5. Critical temperatures ($T_{c(0)}$) of bulk phase (Tl$_{0.5}$Pb$_{0.5}$)(Ba$_x$Sr$_{1-x}$)$_2$CaCu$_2$O$_z$ sintered first at 850 °C for 10 hours and at 925 °C for 1 hour

Figure 6. Critical temperatures ($T_{c(0)}$) of bulk phase (Tl$_{0.5}$Pb$_{0.5}$)(Ba$_{0.2}$Sr$_{0.8}$)$_2$(Ca$_{1-y}$Gd$_y$)Cu$_2$O$_z$ sintered first at 850 °C for 10 hours and at 925 °C for 1 hour

Thermogravimetric analysis of the sintered superconductors showed that the superconductor once formed is stable up to 950 °C in air. Critical current densities of bulk materials depend strongly on the fabrication procedure. Our studies indicated a maximum in the $j_c$ values for a Gd stoichiometry of 0.2. Critical current densities between 2 000 and 3 000 A cm$^{-2}$ were achieved for the best samples. These values are rather high considering that the specimens were non-aligned polycrystalline bulk material.
Electron microscopy of the samples indicated partial re-crystallization of the superconducting material for samples sintered at 925 °C.

4. Summary
Lead and gadolinium doping facilitated the formation of the Tl-1212 superconducting phase. The preparation of the oxidic precursor by a wet chemical technique followed by special heat treatment of the co-milled powders yielded practically phase pure material. Critical temperatures ($T_{c(0)}$-values) of 100 K may be achieved. The Sr/Ba ratio had practically no effect on the superconducting properties. The best superconducting properties were obtained for a Gd stoichiometry of 0.2.

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