Short Communication

Preparation of Superconducting $Tl_2Ba_2CaCu_2O_{8+y}$ by a Fast Solid-State Reaction at 955 °C

A. Nørlund Christensen[a] and B. Lebech[b]

[a]Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark and [b]Department of Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark

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Since the discovery[1] of superconducting compounds in the Tl–Ba–Ca–Cu–O system with transition temperatures T_c close to 100 K, three superconducting compounds with related crystal chemistry have been found:[2]

$Tl_2Ba_2CuO_{6+y}$	$T_c = 80$ K
$Tl_2Ba_2CaCu_2O_{8+y}$	$T_c = 110$ K
$Tl_2Ba_2CaCu_3O_{10+y}$	$T_c = 120$ K

These compounds have layered structures, similar to the layered structures of the corresponding compounds in the Bi–Sr–Ca–Cu–O system.[3-6]

In this communication the preparation of $Tl_2Ba_2CaCu_2O_{8+y}$ is reported. The model of the structure (Ref. 5) was used to compare observed and calculated intensities.

Preparation of $Tl_2Ba_2CaCu_2O_{8+y}$. As thallium compounds are toxic and relatively volatile, the syntheses were carried out in sealed ampoules. The compound was made from the following chemicals: Tl_2O_3 (BDH), $CaCO_3$ (Merck p.a.), BaO_2 (Riedel) and CuO (Merck p.a.). CaO was made from $CaCO_3$ kept at 900 °C for 24 h in an Al_2O_3 crucible. $BaCuO_2$ was made from pellets of a stoichiometric mixture of BaO_2 and CuO. The pellets were pressed at a force of 10 ton and kept in an Al_2O_3 crucible at 950 to 990 °C for 24 h. A stoichiometric mixture of Tl_2O_3, CaO and $BaCuO_2$ was then pressed into pellets at a force of 15 ton. The pellets were placed in gold ampoules that were sealed by arc welding, and the ampoules were then placed in an Al_2O_3 boat in a hot-tube furnace at 955 °C in an oxygen flow. As the boat was loaded into the quartz tube in the furnace the temperature dropped by ca. 50 °C, but then increased gradually to 955 °C. The ampoules were heated for 30 min and kept at the maximum temperature, 955 °C, for at least 5 min. After this heat treatment the Al_2O_3 boat was removed from of the furnace, and the gold ampoules were allowed to cool in air. The oxygen flow was intended to transport any Tl_2O_3 that might leak from the ampoule to a wash bottle with dilute sulfuric acid. It is important to use sealed ampoules to reduce sublimation of Tl-containing compounds. In a test experiment with pellets not sealed in an ampoule it was observed that a considerable sublimation took place from the pellets of the Tl_2O_3–CaO–$BaCuO_2$ mixture at 955 °C. Attempts to make the compound $Tl_2Ba_2CaCu_2O_{8+y}$ in sealed ampoules from a stoichiometric mixture of Tl_2O_3–$BaCO_3$–$CaCO_3$–CuO at 940–955 °C failed, as the reaction product contained a considerable quantity of unreacted $BaCO_3$ and CuO. Attempts to make $BaCuO_2$, "$BaCu_3O_4$" and "$Ba_2Cu_3O_5$" from pellets of stoichiometric mixtures of $BaCO_3$ and CuO at 935–955 °C also failed. The reaction products contained only minor traces of $BaCuO_2$ and considerable quantities of unreacted $BaCO_3$ and CuO.

Diffraction measurements. X-Ray patterns of the reaction products were measured on a Stoe diffractometer, equipped with a curved position-sensitive detector covering a 2θ angle of 40°. By measuring in two positions of the detector a 2θ range of 80° may be covered. The diffractometer used $CuK\alpha_1$ radiation ($\lambda = 1.540598$ Å), and was calibrated with a standard of $Ag_6Ge_{10}P_{12}$ ($a = 10.312$ Å). Samples from four preparations were investigated, and all had $Tl_2Ba_2CaCu_2O_{8+y}$ as the main product, with minor traces of $Tl_2Ba_2CuO_{6+y}$ and unidentified phases. One of the samples did not show reflections from $Tl_2Ba_2CuO_{6+y}$ or $Tl_2Ba_2Ca_2Cu_3O_{10+y}$ among the few impurity reflections, and this sample was used in the neutron diffraction (see below). Samples that had been melted or partly melted contained larger quantities of $Tl_2Ba_2CuO_{6+y}$ in comparison with sintered samples. This indicates that $Tl_2Ba_2CaCu_2O_{8+y}$ most likely melts incongruently, and that on freezing of the melt the main solid phase formed is $Tl_2Ba_2CuO_{6+y}$.

The neutron diffraction powder pattern of $Tl_2Ba_2CaCu_2O_{8+y}$ was measured at room temperature in the 2θ range 5–95° in steps of 0.053° using $\lambda = 2.303$ Å neutrons and the multidetector powder diffractometer at DR3, Risø, Denmark.[7] The model of the structure[5] was then refined by the

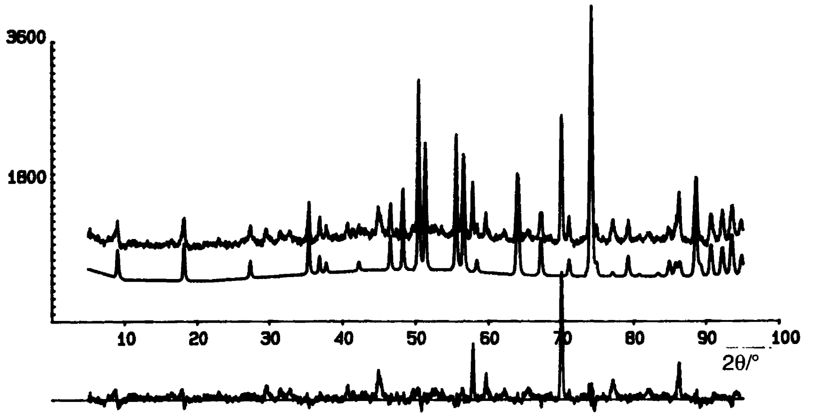

Fig. 1. Profile fit of neutron powder diffraction data. Upper curve observed and lower curve calculated profile. Differences are given in the lower part of the figure. The two sharp reflections at 2θ=59 and 70° are the (111) and (200) reflection from Al. The remaining peaks in the difference plot are from unidentified impurities, and none of these reflections can be ascribed to $Tl_2Ba_2CuO_{6+y}$ or $Tl_2Ba_2Ca_2Cu_3O_{10+y}$.

profile refinement method[8] using the program EDINP.[9] The atomic cross-sections were (all in 10^{-12} cm units from Ref. 10): Tl, 0.889; Ba, 0.525; Ca, 0.490; Cu, 0.7718 and O, 0.5805. Atomic coordinates for the model and values of the parameters refined are listed in Table 1, and Fig. 1 shows the observed and calculated patterns and a difference plot.

Discussion. Below is listed a selection of reports on the synthesis of $Tl_2Ba_2CaCu_2O_{8+y}$. Liang *et al.*[11] heated pellets of a mixture of Tl_2O_3, BaO, CaO and CuO in air at 790–800 °C for 8 h. Hewat *et al.*[12] made $Tl_2Ba_2CaCu_2O_{8+y}$ from Tl_2O_3, BaO_2, CaO and CuO mixtures. Pellets of the mixtures were heated in an O_2 flow at 750 °C for 2 h followed by 860 °C for 24 h. The pellets were then reground, repressed and heated in an O_2 flow at 880 °C for 16 h followed by 700 °C for 4 h and 550 °C for 2 h. The product was almost phase pure $Tl_2Ba_2CaCu_2O_{8+y}$. Shimakawa *et al.*[13] made the compound from a stoichiometric mixture of Tl_2O_3, BaO, CaO and CuO. Pellets of the mixture were wrapped in platinum or gold foils and heated at 890 °C for 10 h. X-Ray powder patterns showed the samples to be a pure phase. Sequeira *et al.*[14] pre-reacted a mixture of $BaCO_3$, $CaCO_3$ and CuO corresponding to the composition "$CaBa_2Cu_2O_5$" (this is not a compound) at 850 °C for 24 h, followed by grinding, and heating at 925 °C for 48 h with several intermediate grindings. This reaction product was mixed with Tl_2O_3, and pellets wrapped in a Pd–Ag alloy foil were heated at 925 °C for 15 min. A neutron powder diffraction pattern of a sample prepared in this way showed minor reflections from an impurity phase.

The samples of $Tl_2Ba_2CaCu_2O_{8+y}$ made in the present investigation were obtained from pellets of a mixture of Tl_2O_3, CaO and $BaCuO_2$ in sealed gold ampoules placed in a hot furnace at approximately 900 °C, heated for 30 min from 900 to 955 °C, and kept at that maximum temperature for at least 5 min. The sample of $BaCuO_2$ was made from a mixture of BaO_2 and CuO at 950–990 °C for 24 h. The formation of $Tl_2Ba_2CaCu_2O_{8+y}$ from the mixture of Tl_2O_3, CaO and $BaCuO_2$ at 955 °C was fast, and the samples contained only minor quantities of impurity phases. Compared with the preparations reported in Refs. 11–14, the reaction temperature used in this investigation was higher than that reported previously, and the reaction time could consequently be reduced to a few minutes at 955 °C. The sample thus prepared showed a strong Meissner effect when cooled in liquid N_2 and showed a transition to a diamagnetic state at 100 K when measured on a Faraday balance.

Model calculations of the structure of $Tl_2Ba_2CaCu_2O_{8+y}$ on X-ray[13] as well as on neutron powder data[12,14,15] indicate a non-stoichiometry on the metal atom sites in the structure. This tendency was also observed in this investigation. The most precise structure investigation of $Tl_2Ba_2CaCu_2O_{8+y}$ by neutron powder diffraction is that by Hewat *et al.*[12] It has been suggested that the observed non-stoichiometry could be due to transfer of Tl to the Ca site.[12,13]

Table 1. Parameters for the $Tl_2Ba_2CaCu_2O_{8+y}$ structure.[a]

Atom	Site	Occupancy	*x*	*y*	*z*	$B/Å^2$ [b]
Tl	4*e*	3.44(12)	1/2	1/2	0.2120(9)	2.2
Ba	4*e*	3.60(28)	0	0	0.1232(12)	2.2
Ca	2*a*	1.96(12)	0	0	0	2.2
Cu	4*e*	3.52(12)	1/2	1/2	0.0532(9)	2.2
O1	8*g*	7.08(12)	0	1/2	0.0529(5)	2.2
O2	4*e*	4	1/2	1/2	0.1453(16)	2.2
O3	16*n*	4.16(16)	0.620(7)	1/2	0.2807(14)	2.2

[a] $a = 3.8549(4)$, $c = 29.388(3)$ Å. $u = 0.176(9)$, $v = -0.128(6)$, $w = 0.086(3)$, $T = 0.100(6)$. [b] Overall isotropic temperature factor parameter not refined.

The peak shapes are assumed to be the convolution of Gaussian and Lorentzian functions. *u*, *v* and *w* are profile parameters for the Gaussian, and *T* a profile parameter for the Lorentzian profile shape. The observed profiles are fitted with a profile where the full width at half maximum is calculated as $(u\tan^2\theta + v\tan\theta + w)^{1/2} + T/\cos\theta$. Zero = 0.0218(6)° (the zero-point offset of the diffractometer). $R = 6.2\,\%$ (unweighted *R*-value: $R = \Sigma|I_{obs} - I_{calc}|/\Sigma I_{obs}$). $R_w = 7.1\,\%$ (weighted *R*-value: $R_w = [\Sigma(y_{obs} - y_{calc})^2\, W/\Sigma y_{obs}{}^2 W]^{1/2}$, where the *y* values are the profile intensities with the background y_b subtracted, and $W = 1/(y_{obs} + y_b)$. $R_e = 4.2\,\%$ (expected *R*-value from counting statistics).

An accurate density determination on single crystals of $Tl_2Ba_2CaCu_2O_{8+y}$ would be most helpful in solving this problem.

In the present preparation, it was observed that a stoichiometric mixture of Tl_2O_3, CaO and $BaCuO_2$ to produce $Tl_2Ba_2CaCu_2O_{8+y}$ resulted in the formation of a compound with minor quantities of $Tl_2Ba_2CuO_{6+y}$ as an impurity phase, indicating that the tendency of non-stoichiometry on the Tl, Ba and Cu sites of $Tl_2Ba_2CaCu_2O_{8+y}$ may be more pronounced than the tendency for non-stoichiometry on the Ca sites. Also, the refinements of the occupancies of the metal atom sites support this hypothesis (see Table 1) if it is assumed that Ca in site 2*a* is not substituted with Tl.

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