10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

PS-10.01.20 DIFFERENT WAYS TO CONTROL THE POLYMORPHISM IN Tl-2201. By Carin Ström, Sten-Gunnar Eriksson and Jörgen Albertsson*, Department of Inorganic Chemistry, GU/CTH, S-412 96 Göteborg, Sweden.

The thallium based superconductor $Tl_{2-x}Ba_{2-y}Sr_yCuO_{6-\delta}$ has been synthesized by a closed-container method. Materials with a variety of thallium, oxygen and strontium contents have been investigated. A Guinier film technique, in combination with a photoscanning system, has been used to determine phase purity and lattice parameters. High resolution X-ray powder diffraction data from the X7B beam line at NSLS, Brookhaven National Laboratory, USA, and neutron diffraction data from POLARIS, ISIS, England, has been analysed by Rietveld refinement methods. T_c and other superconducting properties have been studied by ac susceptibility measurements using a SQUID magnetometer. The polymorphism reported here was induced either by changing the thallium or oxygen contents or by strontium substitution at the barium site.

A decrease in the thallium content results in a transition at $2\text{-}x \approx 1.85$ from the orthorhombic phase described by Parise, Gopalakrishnan, Subramanian & Sleight [*J. Solid State Chem.* (1988). **76**, 432-436] to the tetragonal phase described by Hewat *et al.* [*Physica C* (1988). **156**, 375-381]. The space groups are *Abma* and *I4/mmm*, respectively. In the orthorhombic region the *c* axis shows a linear increase with growing thallium deficiency with an abrupt decrease after the O–T transition. The thallium deficiency has a positive but not dramatic effect on T_c. $Tl_2Ba_2CuO_{6-\delta}$ and $Tl_{1.85}Ba_2CuO_{6-\delta}$ becomes superconducting at 60 and 76 K, respectively. There is no detectable change in T_c if the transition from tetragonal to orthorhombic symmetry is induced by a minor (≈ 1%) increase in the thallium content.

The transition is also induced by a small uptake of oxygen effectuated by annealing the samples in oxygen at 300 °C for 48 h. Here the resulting changes are dramatic. T_c is lowered by about 50 K and there is a large decrease in the *c* axis. Upon strontium substitution in $Tl_2Ba_2CuO_{6-\delta}$, the lattice symmetry changes from orthorhombic to tetragonal at $y \approx 0.45$. The *c* axis decreases linearly at first but has a discontinuity close to the transition. The material becomes non-superconducting at $y \approx 0.6$.

The polymorphism in Tl-2201 is determined by the atomic ordering in the Tl_2O_4 layers. Only minor changes in the Cu–O bond distances occur with changes in the thallium and the oxygen content. The structural changes are not only located in the Tl_2O_4 layers in the strontium substituted materials. The copper coordination, described by a Jahn-Teller distorted octahedron, is compressed.

PS-10.01.21 A SINGLE CRYSTAL NEUTRON STUDY OF THALLOUS NITRATE PHASE-III. By P.U.M. Sastry*, H. Rajagopal, A. Sequeira and R. Chidambaram, Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India.

Among the nitrates of larger cations (Tl^+, Rb^+, Cs^+), $TlNO_3$ exhibits interesting structural phase transitions with symmetry changes from orthorhombic(phase-III) to rhombohedral(II) and to cubic(I) as a function of temperature. X-ray structure of phase-III is known but structures of phases II and I and the detailed mechanism of these transformations are not known. In order to probe the nature of these transitions, a neutron study of $TlNO_3$ is undertaken. The structure of phase-III (at R.T.) has been refined to an R (on F) value of 0.039 based on intensities of 230 independent reflections recorded at a wavelength of 1.216 A°, using the 4-circle neutron diffractometer (T-1011) at *DHRUVA* reactor. The refined neutron structure is in good agreement with that of X-rays (Fraser W.L. *et al*; Acta. Cryst., 1975, B31, 365). The Tl-ions have large thermal motions with an equivalent isotropic B-value of 2.86 $(A^\circ)^2$, while the average B-values of N and O atoms are 1.74 $(A^\circ)^2$ and 3.32 $(A^\circ)^2$ respectively. Rigid body analysis shows large in-plane librational amplitudes for both the nitrate ions. A stereoscopic picture (Fig 1) of the unit cell of phase-III viewed along a diagonal of the pseudo-cubic Tl-lattice indicates large deviations of NO_3 ions from the 3-fold symmetry expected for phase-II.

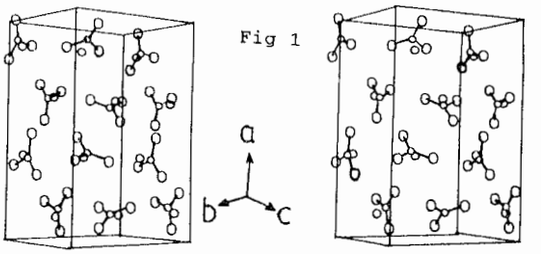
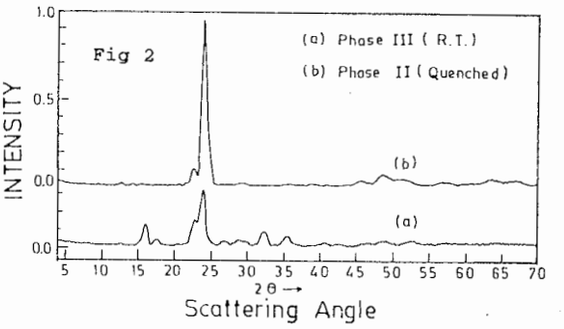


Fig 1

Interestingly, the neutron powder diffractogram (Fig 2) of phase-II shows drastic changes from that of phase-III. The pattern is consistant with a rhombohedral cell (a = 10.5 A°, c = 7.6 A°) but calls for a significant rearrangement of NO_3 ions from phase-III positions.



The structure of phase-II is being refined. Detailed structures of the two phases and the relation between them will be discussed.

PS-10.01.22 INVESTIGATION ON THE STRUCTURAL CHARACTERISTICS OF CRYSTAL $Bi_2Sr_2CaCu_2O_y$ USING X-RAY DIFFRACTION OF VARIOUS TARGETS By Shi Lei*, Zhou Guien, Huang Yunlan, Jia Yunbo and Zhang Yuheng, Structure Research Laboratory, University of Science and Technology of China, Academia Sinica, Hefei, Anhui 230026, P.R. China.

