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

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PS-10.01.20 DIFFERENT WAYS TO CONTROL THE POLY-MORPHISM IN TI-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  $Tl_{2,x}Ba_{2,y}Sr_yCuO_{6.5}$  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  $2-x \approx 1.85$  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 I-4/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<sub>2</sub>Ba<sub>2</sub>CuO<sub>6-5</sub> and Tl<sub>1.83</sub>Ba<sub>2</sub>CuO<sub>6-5</sub> 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 ( $\approx$  1%) increase in the thallium content.

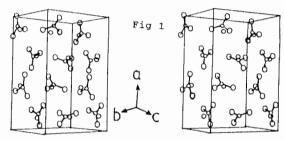
The transition is also induced by a small uptake of oxygen effectuated by annealing the samples in oxygen at 300 °C for 48 h. Here the resulting changes are dramatic.  $T_c$  is lowered by about 50 K and there is a large decrease in the c axis. Upon strontium substitution in  $\text{Tl}_2\text{Ba}_2\text{CuO}_{6-\delta}$ , 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 TI-2201 is determined by the atomic ordering in the  $\mathrm{Tl_2O_4}$  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  $\mathrm{Tl_2O_4}$  layers in the strontium substituted materials. The copper coordination, described by a Jahn-Teller distorted octahedron, is compressed.

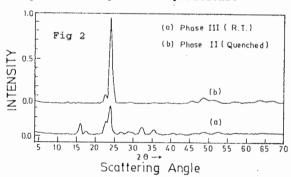
PS-10.01.21 A SINGLE CRYSTAL NEUTRON STUDY OF THALLOUS NITRATE PHASE-III. By P.U.M. Sastry', H. Rajagopal, A. Sequeira and R. Chidambaram, Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India.

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<sub>3</sub> 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°)², while the average B-values of N and 0 atoms are 1.74 (A°)² and 3.32 (A°)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<sub>3</sub> ions from the 3-fold symmetry expected for phase-II.



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 (  $a=10.5~\mbox{\AA}^{\circ}$ ,  $c=7.6~\mbox{\AA}^{\circ}$ ) 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 $_2$ Sr $_2$ CaCu $_2$ O $_y$ 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.