

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 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 $Tl_{2-x}Ba_{2-y}Sr_zCuO_{6.5}$ 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 *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 . $Tl_{2-x}Ba_2CuO_{6.5}$ and $Tl_{1.8}Ba_2CuO_{6.5}$ 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.

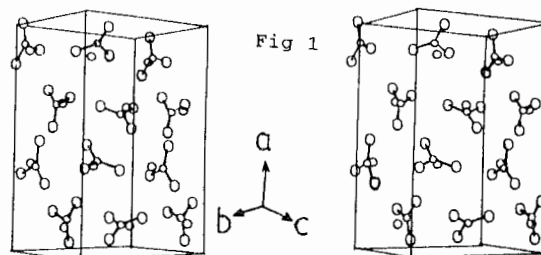
The transition is also induced by a small uptake of oxygen effectuated by annealing the samples in oxygen at 300 °C for 48 h. Here the resulting changes are dramatic. T_c is lowered by about 50 K and there is a large decrease in the *c* axis. Upon strontium substitution in $Tl_2Ba_2CuO_{6.5}$, the lattice symmetry changes from orthorhombic to tetragonal at $y = 0.45$. 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.

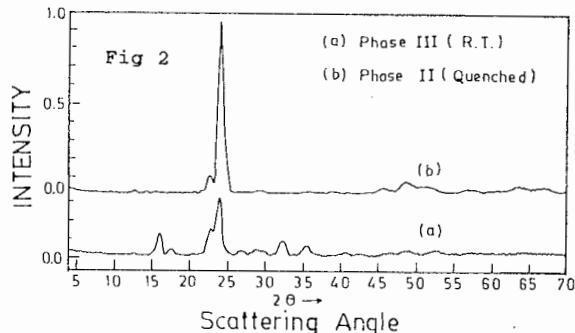
PS-10.01.21 A SINGLE CRYSTAL NEUTRON STUDY OF THALLOUS NITRATE PHASE-III. By P.U.M. Sastry*, H. Rajagopal, A. Sequeira and R. Chidambaram, Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India.

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 Å, 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 $2.86 (\text{Å}^2)$, while the average B-values of N and O atoms are $1.74 (\text{Å}^2)$ and $3.32 (\text{Å}^2)$ 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.



Interestingly, the neutron powder diffractogram (Fig 2) of phase-II shows drastic changes from that of phase-III. The pattern is consistent with a rhombohedral cell ($a = 10.5 \text{ Å}$, $c = 7.6 \text{ Å}$) 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.

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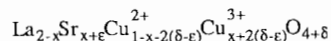
The Bragg diffraction layers caused by characteristic radiation and Laue diffraction caused by continuous radiation of crystal $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (called 2212 phase) have been distinguished by a normal x-ray source with both characteristic and continuous radiation. The structural characteristics of crystal $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ has been studied by the change of x-ray tubes (Cu, Fe, Mo and W targets) with different characteristic K α radiation. An important structural characteristics found of the crystal is that "Bi-atomic concentrated" bands (Bi_2O_3) don't enter into the lattice of oxygen-deficient perovskite entirely, and form a three-dimensional period coexisting with a two-dimensional lattice.

PS-10.01.23 HREM INVESTIGATION AND CRYSTAL CHEMISTRY OF (101) AND (101) EXTENDED DEFECTS OF $\text{M}_{2+\delta}\text{CuO}_{4+\delta}$ PHASES ($\text{M}_2 = \text{La}_{2-x}\text{Sr}_x$). By J. Galy, M.J. Casanove, A. Alimoussa and C. Roucau, CEMES-LOE / CNRS, 29 rue J. Marvig, BP 4347, F31055 Toulouse Cedex, France.

The crystal chemistry understanding of the defects in the high-Tc superconducting oxide phases is of tremendous importance due to their impact on their conductivity, critical temperature.... Too often these phases are formulated with a stoichiometry characterized by an excess or deficiency of oxygen affected to crystallographic sites which are not relevant to the well established rules of crystal chemistry or chemistry.

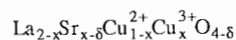
The aim of this lecture is to detail a structural and chemical interpretation of extended planar defects accounting for the non-stoichiometry of the high Tc superconducting $\text{M}_{2+\delta}\text{CuO}_{4+\delta}$ phases, denoted LSCO, with $\text{M}_2 = \text{La}_{2-x}\text{Sr}_x$.

Investigation by HREM techniques of (101) defects in thin LSCO crystalline films will be presented. The detailed crystal chemistry explaining the atomic structure within the defect is supported by numerical calculation simulating the HREM images. In the case of over stoichiometry it will be shown how the (101) defect drives us to the formula



with $0 \leq \epsilon \leq \delta$.

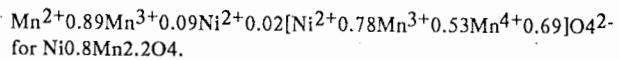
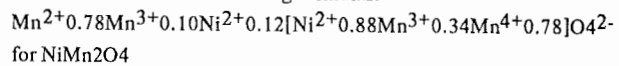
A brief description of the incidence of $(\bar{1}01)$ defects on sub-stoichiometric M_2CuO_4 phases will also be shown; they drive to a formula



PS-10.01.24 CATION VALENCE DISTRIBUTION AND ELECTRICAL CONDUCTIVITY MECHANISM IN NICKEL MANGANITES. By J.L. Baudour*, H. Elbadraoui, Lab. Recherche sur les Matériaux à Finalités Spécifiques (E.A.1356) Toulon France. F. Bouree, Lab. Léon Brillouin, Saclay, France. A. Rousset, R. Legros Lab. de Chimie des Matériaux Inorganiques Toulouse, France. B. Gillot, Lab. de Recherche sur la Réactivité des Solides, Dijon, France.

Nickel manganites $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ crystallize into a cubic spinel structure. A major problem is the determination of the valencies and cation distribution among both the tetrahedral (A sites) and octahedral (B sites) sublattices of the spinel structure. An important controversy exists on this subject and many alternative proposals have been suggested from electrical, magnetic, x-ray, neutron diffraction studies and theoretical treatments.

The combination of the neutron diffraction and Mn^{2+} oxidation experiments by thermogravimetry (Baudour, J.L., Bouree, F. et al., Physica B, 1992, 180 & 181, 97-99; Gillot, B., Baudour, J.L., Bouree, F. et al., Solid State Ionics, 1992, 58, 155-161.) on NiMn_2O_4 and $\text{Ni}_0.8\text{Mn}_2.2\text{O}_4$ specimen prepared under the same thermal conditions leads to the following formulas:



By extrapolating the above results we can deduce the cationic distribution in $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ for $0.6 < x < 0.8$ in agreement with thermogravimetry results and with the variation of the lattice parameter which is extremely sensitive to this distribution. The electrical properties are described by a hopping mechanism of charge carriers between Mn^{3+} and Mn^{4+} on octahedral sites via localized states rather than by the band conduction model via delocalized states. A short range order between nickel and manganese atoms in the B sites is examined from neutron diffraction results and the correlation coefficients are determined.

The hopping activation energy governing the conduction mechanism exhibits a minimum for the $\text{Ni}_0.8\text{Mn}_2.2\text{O}_4$ composition. This is discussed in relation with the structural properties.

PS-10.01.25 DEGRADATION OF HIGH-Tc YBCO CERAMIC IN ATMOSPHERE. By Binay Kumar* & G.C. Trigunayat, Dept. of Physics & Astrophysics, Delhi University, Delhi-7; Amita Malik & G.L. Bhalla, SRI, 19 University Road, Delhi-7, INDIA.

Stability of HTSC against atmospheric conditions is crucial for practical applications. High-Tc YBCO samples were prepared by the ceramic route. They were characterized by XRD, SEM, TGA, oxygen content, and resistive measurements. YBCO samples were exposed to atmospheric conditions for 1, 1.5, 2, 2.5 & 3 months, and their properties were studied again. XRD studies disclosed non-superconducting compounds in the degraded samples, and the change of orthorhombic YBCO to tetragonal. SEM studies revealed cracks in superconducting grains and increase in the intergrain voids. Sharp decrease in O-content was observed for Tc around 94K & 80K, with a plateau around 86K in the curve of O-content vs Tc. Thermogravimetric analysis also revealed the presence of more volatile products in degraded YBCO.

Similar studies were carried out with polymer-coated YBCO ceramic as well. Fine coating (5 μm) of PMMA was achieved by plasma polymerization of monomers under high vacuum by radio frequency (13.56MHz) generator. The coated samples were found to be more stable against degradation by atmosphere.