

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

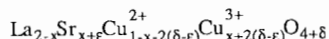
The Bragg diffraction layers caused by characteristic radiation and Laue diffraction caused by continuous radiation of crystal  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  (called 2212 phase) have been distinguished by a normal x-ray source with both characteristic and continuous radiation. The 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 $\alpha$  radiation. An important structural characteristics found of the crystal is that "Bi-atomic concentrated" bands ( $\text{Bi}_2\text{O}_3$ ) 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.

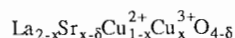
The aim of this lecture is to detail a structural and chemical interpretation of extended planar defects accounting for the non-stoichiometry of the high Tc superconducting  $\text{M}_{2+\delta}\text{CuO}_{4+\delta}$  phases, denoted LSCO, with  $\text{M}_2 = \text{La}_{2-x}\text{Sr}_x$ .

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

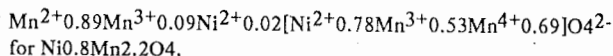
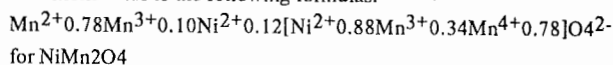
A brief description of the incidence of (101) defects on sub-stoichiometric  $\text{M}_2\text{CuO}_4$  phases will also be shown; they drive to a formula



**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  $\text{Mn}^{2+}$  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  $\text{NiMn}_2\text{O}_4$  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  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  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  $\mu\text{m}$ ) 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.