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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 Bi$_2$Sr$_2$CaCu$_2$O$_{y}$ (called c212 phase) have been distinguished by a normal x-ray source with both characteristic and continuous radiation. The structural characteristics of crystal Bi$_2$Sr$_2$CaCu$_2$O$_{y}$ has been studied by the change of x-ray tubes (Cu, Fe, Mo and W targets) with different characteristic x-ray radiation. An important structural characteristic found of the crystal is that "Bi-atomic concentrated" bands (4Bi$_2$O$_{10}$) don't enter into the lattice of oxygen-deficient perovskite entirely, and form a three-dimensional period consisting with a two-dimensional lattice.

PS-10.01.23 HREM INVESTIGATION AND CRYSTAL CHEMISTRY OF (101) AND (101) EXTENDED DEFECTS OF M$_2$CaCuO$_{4.5}$ PHASES (M$_2$ = La$_2$Sr$_2$). By J. Caly, M.J. Casanove, A. Almoussa and C. Roucou, CNRS-LGIE-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 M$_2$CaCuO$_{4.5}$ phases, denoted LSCO, with M$_2$ = La$_2$Sr$_2$.

Investigation by HREM techniques of (101) defects is 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

$$\text{La}_2\text{Sr}_2\text{CuO}_{4+\delta}$$

with $0 \leq \delta < 1$.

A brief description of the incidence of (101) defects on sub-stoichiometric M$_2$CaCuO$_{4.5}$ phases will also be shown; they drive to a formula

$$\text{La}_2\text{Sr}_2\text{CuO}_{4+\delta}$$


Nickel manganites Ni$_x$Mn$_2$O$_{4+\delta}$ crystallize into a cubic spinel structure. A major problem is the determination of the valences 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., Bourree, F. et al., Physica B, 1992, 180 & 181, 97-99; Gillor, B., Baudour, J.L., Bourree, F. et al., Solid State Ionics, 1992, 58, 155-161) on NiMn$_2$O$_4$ and Ni$_0.8$Mn$_{1.2}$O$_4$ specimens prepared under the same thermal conditions leads to the following formulas:

$$\text{Mn}^{2+}_{2.78}\text{Mn}^{3+}_{0.22}\text{Ni}^{2+}_{0.12}\text{Ni}^{3+}_{0.88}\text{Mn}^{3+}_{0.34}\text{Mn}^{4+}_{0.78}\text{O}_{4}$$

for NiMn$_2$O$_4$

$$\text{Mn}^{2+}_{2.94}\text{Mn}^{3+}_{0.06}\text{Ni}^{2+}_{0.21}\text{Ni}^{3+}_{0.78}\text{Mn}^{3+}_{0.53}\text{Mn}^{4+}_{0.69}\text{O}_{4}$$

for Ni$_{0.8}$Mn$_{1.2}$O$_4$.

By extrapolating the above results we can deduce the cationic distribution in NiMn$_3$O$_{4-x}$ for $0.4 \leq x \leq 0.8$ in agreement with thermogravimetry results and with the variation of the lattice parameters 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 the band conduction model via delocalized states. A short range order between nickel and manganese atoms is 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 Ni$_{0.8}$Mn$_{1.2}$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; Amit Malik & G.L. Bhalla, SRL, 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 intergran voids. Sharp decrease in O-content was observed for Tc around 54K & 80K, with a plateau around 80K 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.
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The degradation in YBCO ceramic can be explained in terms of the formation of non-superconducting products by the reaction of YBCO with CO₂, H₂O, etc. from the atmosphere, and in terms of breakage of weak intergrain links.


Structural superconducting single crystals: Nd₄₋ₓYₓBa₂Cu₃O₇₋ₓ (x = 0.34) (1), NdₓBa₂Cu₃O₇₋ₓ (x = 0.85)Ba₂Cu₃O₇₋ₓ (2) (1) (II), space group P4/mmm, a1, studied by X-ray diffraction method (diffractometer P2,T Siemens, MoKa). Parameters: a = 3.814(1) Å, c = 11.628 Å, for 235 observed reflections. Final value R = 0.068; (II) a = 3.885(1) Å, c = 11.605(2) Å, for 331 observed reflections. Final value R = 0.086. The superconductivity properties were measured by the field modulation microwave absorption method in low magnetic field, critical temperature Tc (I) = 10 K, (II) = 9 K, weak signal being seen to 90 K. The Al atom was shown to occupy only Cu(I) positions that increased the oxygen contents and connected with the tetragonal symmetry. The largest anisotropy of thermal parameters observed for "bridge" oxygen atoms could be interpreted as static disorder. The Tc were considered to correlate with plane Cu(2) hole density (Tokura, Torrance, Huang & Mazzi, 1986) calculated by the bond valence sum method. For superconductors with low Tc the hole density was shown to be very sensitive to the rare-earth site occupation factor. References: Tokura, Y., Torrance, J. B., Huang, T. C. & Mazzi, A. I. (1988). Phys. Rev. B38, 7156-7169.

PS-10.01.27 NEUTRON INVESTIGATION OF La₄Cu₃O₈ AND (NdCe)₂Cu₃O₈ SINGLE CRYSTALS. By A.M. Balagurran, S.N. Dabold, A. Balakrishna, N.N. Rybalov, E.V. Gomazatov, E.E. Ryder, V.A. Serebry, Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Obninsk Branch of Kurchatov Physical Chemistry Institute, Obninsk, Russia.

The purpose of this work was to study regularities of the structure defects caused by non-stoichiometry, to determine fine atomic and anion distribution. The investigations of regularities of the reciprocal lattice, the definition of twinning law, and the composition of twin were carried out by the time-night electron diffraction ON-2 with the help of position sensitive detector of the pulsed reactor BR-2 in Dubna. The neutron diffraction measurements for precise structure calculations were done on the 4-circle diffractometer Sympol P1N at the reactor VVR in Obninsk (β = 1.65 Å, sin θ = 0.1 Å).

There were two samples of La₄Cu₃O₈. The sample S1 was anacinet and quenched at 1150 °C, the sample S2 at 400 °C. Neutron experiments for these samples were done at 18 °C and 300 °C. The parameters of elementary cell are

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>3.814</td>
<td>3.814</td>
<td>11.628</td>
<td>145.234</td>
</tr>
<tr>
<td>S2</td>
<td>3.814</td>
<td>3.814</td>
<td>11.628</td>
<td>145.234</td>
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</tbody>
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L.S. refinement of atomic parameters at 300 °C gave R-factors 0.028 for 141 independent reflections for S1 and 0.028 for 141 independent reflections for S2 and next results. In position 6-atom parameters zic are for La = 0.31(98) and for 0.183(1) as for S1 and S2. Site occupations for all atoms in S1 and S2 are exact 1. But the parameters of thermal vibrations are systematically higher for all atoms in S1.

<table>
<thead>
<tr>
<th>Sample</th>
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<td>11.628</td>
<td>145.234</td>
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PS-10.01.28 STUDY ON THE TWINSING OF YBCO–123 PHASE SUPERCONDUCTOR BY USING DIFFERENTIAL INTERFERENCE MICROSCOPE. By Shen Jiashun Prof. and Wang Wenxui Prof., China University of Geosciences (Wuhan) Wuhan 430074, P.R. China.

A set of wonderful photos showing the (110) twinning of YBCO–123 phase were successfully taken by using differential interference microscope. The YBCO–123 phase crystal grew on the base of microcrystalline samples. Some of the (001) face of YBCO–123 crystal are roughly parallel to the stage of microscope. We select crystal with the same orientation accurately, so carefully to make it (001) face strongly coincide with the surface of stage, twinning section on the (001) face will show clearly in different interference colors. Changine wave length will cause interference color changed. Combined