

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

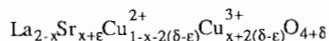
The Bragg diffraction layers caused by characteristic radiation and Laue diffraction caused by continuous radiation of crystal $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (called 2212 phase) have been distinguished by a normal x-ray source with both characteristic and continuous radiation. The structural 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 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 $\text{M}_{2\pm\delta}\text{CuO}_{4\pm\delta}$ 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.

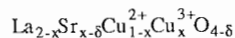
The aim of this lecture is to detail a structural and chemical interpretation of extended planar defects accounting for the non-stoichiometry of the high Tc superconducting $\text{M}_{2\pm\delta}\text{CuO}_{4\pm\delta}$ phases, denoted LSCO, with $\text{M}_2 = \text{La}_{2-x}\text{Sr}_x$.

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

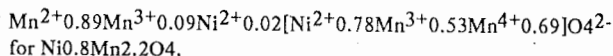
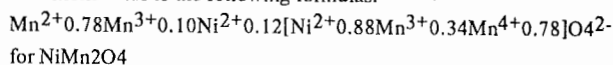
A brief description of the incidence of $(\bar{1}01)$ defects on sub-stoichiometric M_2CuO_4 phases will also be shown; they drive to a formula



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.

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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.

PS-10.01.26 THE STRUCTURE AND SUPERCONDUCTIVITY OF Nd_{1-x}Y_xBa₂(Cu,Al)₃O_{8+y} SINGLE CRYSTALS. By O.A. Usov*, N.F. Kartenko, I.V. Rozhdestvenskaya, S.I. Goloschapov, S.G. Konnikov, Yu.G. Nosov and V.N. Osipov, A.F. Ioffe Physico-Technical Institute, Academy of Sciences of Russia, Polytechnical str., 26, 194021 St.-Petersburg, Russia.
Isostructural superconducting single crystals: NdBa(2)Cu(2.86)Al(0.34)O(8.5) (I), Nd(0.35)Y(0.65)Ba(2)Cu(2.70)Al(0.30)O(7.0) (II), space group P4/mmm, Z=1, studied by X-ray diffraction method (diffractometer P2/1 Siemens, MoK α). Parameters: a=b=3.914(1), c=11.826 Å, for 323 observed reflections final R=0.058; (II) a=b=3.885(1), c=11.805(2) Å, for 331 observed reflections final R=0.089. The superconductivity properties were measured by the field modulated microwave absorption method in low magnetic field, critical temperature T(c): (I) 10 K, (II) 7 K, weak signal being seen to 50 K. The Al atom was shown to occupy only Cu(1) positions that increases the oxygen contents and connects with the tetragonal symmetry. The large anisotropy of thermal parameters observed for "bridge" oxygen atoms could be interpreted as static displacement. The T(c) were considered to correlate with plane CuO(2) hole density (Tokura, Torrance, Huang & Nazzari, 1988), calculated by the bond valence sum method. For superconductors with low T(c) 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. & Nazzari, A. I. (1988). Phys. Rev. B38, 7156-7159.

PS-10.01.27 NEUTRON INVESTIGATION OF La₂CuO₄ AND (Nd,Ce)₂CuO₄ SINGLE CRYSTALS. By A.M. Balagurov, S.N. Barilo, A.I. Beskrovnyi, N.N. Bydanov, K.V. Gamayunov, E.E. Rider, V.A. Sarin*, Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Obninsk Branch of Karpov Physical Chemistry Institute, Obninsk, Russia.

The purpose of this work was to study regularities of the structure defects caused by nonstoichiometry, to determine fine cationic and anionic distributions. The investigations of regularities of the reciprocal lattice, the definitions of twinning law, check of crystal quality were fulfilled on the time-of-flight diffractometer DN-2 with the help of position sensitive detector at the pulsed reactor IBR-2 in Dubna. The neutron diffraction measurements for precise structure calculations were done on the 4-circle diffractometer Syntex PIN at the reactor VVR in Obninsk ($\lambda = 1.167 \text{ \AA}$, $\sin \theta/\lambda = 0.81$).

There were two samples of La₂CuO₄. The sample S1 was annealed 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

		SP.GR.	a, Å	b	c	V, Å ³
18 °C	S1	C mca	5,369 (3)	13,144 (9)	5,389 (3)	380,3 (5)
	S2	C mca	5,363 (2)	13,147 (13)	5,398 (2)	380,6 (5)
300 °C	S1	I4/mmm	3,811 (2)		13,208 (8)	191,8 (3)
	S2	I4/mmm	3,810 (2)		13,214 (8)	191,8 (3)

L.S. refinement of structure parameters at 300 °C gave R-factors 0,025 for 141 independent reflections for S1 and 0,028 for 143 independent reflections for S2 and next results. In position (c,4mm) parameters z/c are for La 0,36119(6) and for O1 0,1833(1) as for S1 and S2. Site occupations for all atoms in S1 and S2 are exactly 1. But the parameters of thermal vibrations are systematically higher for all atoms in S1

		B eq., Å ²	B11	B22	B33
La	S1	1,10 (1)	1,22 (2)	B11	0,87 (3)
	S2	0,92 (2)	1,04 (3)	B11	0,68 (4)
Cu	S1	0,98 (2)	0,66 (3)	B11	1,62 (4)
	S2	0,79 (2)	0,48 (3)	B11	1,43 (4)
O1	S1	2,56 (3)	3,24 (5)	B11	1,20 (5)
	S2	2,33 (3)	3,01 (6)	B11	0,97 (6)
O2	S1	1,52 (3)	0,69 (4)	1,37 (4)	2,52 (5)
	S2	1,32 (3)	0,47 (5)	1,22 (5)	2,28 (6)

Two samples with the composition Nd_{2,05}Cu_{0,95}O_x (N1) and Nd_{1,90}Ce_{0,10}Cu_{0,92}O_x (N2) were investigated at 18 °C. The parameters of elementary cell are

		SP.GR.	a, Å	c	V, Å ³
N1		I4/mmm	3,9450 (8)	12,170 (3)	189,4 (1)
N2		I4/mmm	3,8480 (1)	12,093 (4)	188,5 (2)

L.S. refinement of structure parameters gave R-factor 0,027 for 139 independent reflections for N1 and 0,028 for 139 independent reflections for N2. The main results are

		x/a	y/b	z/c	B eq., Å ²	site occupation
Nd	N1	0,0	0	0,35098 (8)	0,63 (1)	1,002 (5)
	N2	0	0	0,3515 (2)	0,47 (5)	0,965 (5)
Cu	N1	0	0	0	0,68 (2)	1,00
	N2	0	0	0	0,57 (7)	1,00 (3)
O1	N1	0	0,5	0	0,94 (2)	0,993 (7)
	N2	0	0,5	0	0,96 (9)	1,00 (3)
O2	N1	0	0,5	0,25	0,85 (2)	0,995 (7)
	N2	0	0,5	0,25	0,74 (3)	0,985 (6)

Because the lengths of neutron scattering for Nd and Ce are different but for Nd and Cu are approximately equal we can propose from our experimental results and compositions the next crystal chemistry formula for N1: Nd₂(Cu_{0,95}Nd_{0,05})O_{3,91} and for N2: (Nd_{0,91}Ce_{0,09})₂(Cu_{0,92}Nd_{0,08})O_{3,94}

PS-10.01.28 STUDY ON THE TWINNING OF YBCO-123 PHASE SUPERCONDUCTOR BY USING DIFFERENTIAL INTERFERENCE MICROSCOPE. By Shen Jinchuan Prof. and Wang Wenkui Prof., China University of Geosciences(Wuhan), Wuhan 430074, P.R.China.

A set of wonderful photos showing // {110} twinning of YBCO-123 phase are successfully taken by using differential interference microscope. The YBCO-123 phase crystal grew on the base of microcrystalline corundum. Some of (001) face of YBCO-123 crystal are roughly parallel to the stage of microscope. We select crystal with such orientation and adjust carefully to make the (001) face strictly coincide with the stage plane. twinning striation on the (001) face will show clearly in different interference colors. Changing wave length will cause interference color changed. Combined