

**PS10.05.13 DIFFUSE SCATTERING STUDY OF  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  CRYSTALS.** Lei Shi<sup>1,2</sup>, Takuya Ohba<sup>1</sup>, Toru Hara<sup>1</sup>, Masahiko Tanaka<sup>3</sup>, Yuheng Zhang<sup>2</sup>, <sup>1</sup>Department of Materials Science and Engineering, Teikyo University, Utsunomiya 320, Japan, <sup>2</sup>Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China, <sup>3</sup>Photo Factory, KEK, Tsukuba 305, Japan

Although the crystal structures of Bi-based high-Tc superconductor, which is distinguished by incommensurate modulations, have been solved for several years, their implications for superconductivity are as yet uncertain. This indicates that the deviation from the average structure also should be considered, which may play an important role for the superconductivity. For this purpose the contour maps of the scattering intensity on  $b^*c^*$  plane for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  single crystals have been observed by both ordinary x-ray and synchrotron radiation. The characteristic feature were obtained in this experiments; that is, the intensity distribution around both the Bragg reflection and its satellites show a strong asymmetry. Both of them are elongated along the  $c$  axis, especially for the satellites which connect each other and almost form a rod shape. This reveals that the structure has a strong two-dimensional feature, which is coincide with the two-dimensional characteristics of physical transportation. Our observation also confirms the previous results that the modulated wavevector  $q=q_2b^*+c^*$  ( $q_2=2.0-2.1$ ).

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**PS10.05.14 RECOVERY OF SUPERCONDUCTIVITY IN THE WATER DEGRADED YBCO SAMPLES.** Sandeep Rekhi, G. L. Bhalla, G. C. Trigunayat, Department of Physics & Astrophysics, University of Delhi, Delhi-110 007, India

The recovery of superconductivity in the water degraded samples have been studied by first subjecting them to heat treatments and then estimating possible recovery of superconductivity in them through structural, electrical, magnetic, and morphological investigations. The results reveal the transformation of secondary phases formed during degradation into YBCO phase. The presence of some additional phases of YBCO, possibly arising from deficiency of the constituent elements resulting from degradation/lack of proper reaction between the secondary phases, are also observed. The heat treatment carried out in a sample after pulverising it led to full recovery of superconductivity in it. A possible mechanism for the observed recovery of superconductivity has been suggested.

**PS10.05.15 REAL STRUCTURE AND PHOTOLUMINESCENCE SPECTRA OF COPPER OXIDE HIGH-Tc SUPERCONDUCTOR SINGLE CRYSTALS AND CERAMICS.** T.V.Smimova and P.V.Zinoviev, B.Verkin Institute for Low Temperature Physics & Engineering, Kharkov, UA 310164, Ukraine

The present work is aimed at studying correlation between peculiarities of the real structure ( $RS$ ) of HTSC and evolution of the photoluminescence spectra ( $PS$ ) and establishing the nature of spectral bands of superconducting cuprates.  $PS$  of single crystals with different oxygen content and coarse-grained ceramics of  $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$  have been studied. The oxygen index  $\delta$  in single crystals was defined by the Raman spectra and XRD.  $PS$  of single crystals with  $\delta = 0.1$  and  $\delta = 0.9$  in the blue-green region exhibit, in fact, a single band with a maximum in the vicinity of 2.8 eV, whereas those of single crystals with non-stoichiometric oxygen exhibit also the band with a maximum near 2.4 eV. In superconducting ( $T_c \sim 92$  K) coarse-grained ceramics samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$  the main contribution to the  $PS$  is from the band with a maximum near 2.8 eV. The contribution from the band near 2.4 eV increases upon mechanical grinding and light exposure of the samples. The effect of  $RS$  and light exposure is associated with processes of the oxygen vacancies formation.

**PS10.05.16 IN SITU HIGH TEMPERATURE ELECTRON DIFFRACTION STUDIES ON THE MODULATED STRUCTURES IN (Bi, Pb)-BASED SUPERCONDUCTORS.** Michael Czank\*, Wulf Depmeier\* and Nicolai D. Zhigadlo\*, \*Mineralogisches Institut, Univ. Kiel, D-24098 Kiel and \*\*Inst. of Solid State and Semicond. Physics, Belorussian Acad. of Sciences, Minsk 220072

In addition to the known incommensurate modulations and phase transitions in the superconductor phases  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x}$  (2212 phase) and  $(\text{Bi}_{1-y}\text{Pb}_y)\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x}$  (2223 phase) [e.g. 1-3], we observed new modulations over a range of temperatures (293-800K).

The 2212 phase is incommensurately modulated ( $q_1=0.21b^*$ ) at room temperature. With in situ heating additional satellites with  $q_2=0.46a^*$  and  $q_3=0.46b^*$  to all  $h-k=2n$  reflections gradually appear above  $\sim 630$ K. The new phase is quenchable, but  $q_2$  and  $q_3$  have additional very small components in  $b^*$  and  $a^*$ , respectively. The 2212 phase decomposes above  $\sim 700$ K. No twinning, as reported [1 and 3] was observed.

In the 2223 phase two different crystal types are present: a) Grains having only one modulation ( $q=0.137b^*$ ), where the satellites are attached to all  $h,k$  reflections. b) Grains with two modulations ( $q_1=0.21b^*$  and  $q_2=0.137b^*$ ), where  $q_1$  is mainly associated with  $h=2n$  and  $k=2n$ , while  $q_2$  has the strongest satellite intensities with  $h-k=2n$  and  $h,k=2n+1$ . In all crystals above  $\sim 630$ K the  $2a \times 2b$  superstructure gradually appears. The modulations coexist until the phase decomposes above  $\sim 720$ K. We found twinning on (010) and on (100) at room temperature. Dark-field images show twin lamellae. Twins disappear gradually above  $\sim 630$ K. Diffuse streaks along [110] and  $[\bar{1}\bar{1}0]$  are present in some crystals at room temperature and appear in others at higher temperature. Their intensities increase with temperature and finally new satellites with  $q=0.26a^* + 0.26b^*$  develop. These modulations are also quenchable.

Heating experiments in air support the assumption that the various modulations are connected to distortions and/or ordering within the different structural layers.

#### References:

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**PS10.05.17 OXYGEN DEFECT STRUCTURE IN  $\text{La}_2\text{MO}_{4+\delta}$  ( $M = \text{Cu, Ni, Co}$ ).** W. Paulus<sup>1,2</sup>, A. Cousson<sup>1</sup>, G. Heger<sup>2</sup>, A. Revcolevschi<sup>3</sup>, G. Dhalenne<sup>3</sup>, S. Hosoya<sup>4</sup>, V. Kvardakov<sup>5</sup>. <sup>1</sup>CE-Saclay, Lab. Léon Brillouin, F-91191 Gif-sur-Yvette; <sup>2</sup>RWTH Aachen, Inst. of Crystallography, Jägerstr. 17-19 D-52056 Aachen, Germany; <sup>3</sup>Lab. of Solid State Chemistry, Univ. Paris-Sud, F- 91405 Orsay, France; <sup>4</sup>Univ. of Kofu, Institute of Inorganic Synthesis, Kofu 400, Japan; <sup>5</sup>Kurchatov Institute Russian Science Centre, 123182 Moskau, Russia.

$\text{La}_2\text{MO}_4$  ( $M = \text{Cu, Ni, Co}$ ) are isostructural ( $\text{K}_2\text{NiF}_4$ -type structure) and can incorporate oxygen on interstitial sites forming  $\text{La}_2\text{MO}_{4+\delta}$ . The amount of the extra oxygen is limited to  $\delta = 0.08, 0.16$  and  $0.25$  for the Cu, Ni and Co homologous compounds respectively. With the formation of the oxygen-rich phases, strong changes in the physical properties are observed, e.g. the semiconductor  $\text{La}_2\text{CuO}_{4.00}$  becomes metallic and superconducting with a  $T_c$  max. of 44K when oxygenated to  $\delta = 0.08$ . For the Ni and Co compounds no superconducting behaviour was observed for any oxygen stoichiometry. In all cases, however, a continuous vanishing of all  $a\sqrt{2} \times a\sqrt{2} \times c$  superstructure reflections goes along with the uptake of oxygen. These superstructure reflections are related to the tilting of the  $\text{MO}_6$  octahedra observed for stoichiometric  $\text{La}_2\text{MO}_{4.00}$  compounds in the orthorhombic phase at ambient temperature. The purpose of our studies is to understand the structural disorder induced by the uptake of extra oxygen in order to estimate the influence on phase transitions and electrical properties. We report here on our temperature-dependent neutron diffraction studies carried out on single crystals of  $\text{La}_2\text{CoO}_{4+\delta}$  and discuss the results in relation with those obtained for  $\text{La}_2\text{NiO}_{4+\delta}$  and superconducting  $\text{La}_2\text{CuO}_{4+\delta}$ .