April 2012

Covalent bonds in superconducting rapid cooled alloys: $(Bi_{1.7}Pb_{0.3}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta})_2$, n=1 to 9 detected by local atomic enhanced XRD

J. Kmiec
San José State University

K. Tyson
San José State University

Juana Acrivos
San José State University

D. Gulamova
Academy of Sciences of Uzbekistan

J. Chigvinadze
E. Andronikashvili Institute of Physics

Covalent bonds in superconducting rapid cooled alloys: $(Bi_{1.7}Pb_{0.3}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta})_{2,\ n=1\ to\ 9}$ detected by local atomic enhanced XRD

San José State University
@ Mills College
April 28 2012

J Kmiec*, K Tyson*, JV Acrivos*, DD Gulamova**, and JG Chigvinadze***
*San José State University, San José, CA 95192-0101, USA, ** Physics of Sun (Institute of Materials Science Academy of Science, 700084, Tashkent, Uzbekistan,
*** E. Andronikashvili Institute of Physics, 0177 Tbilisi, Georgia. Work supported by H C Dreyfus Foundation, US National Lab DOE-SLAC, NSF Ukraine

Abstract: High temperature layer superconducting cuprates (HTLSC) alloys: $(Bi_{1.7}Pb_{0.3}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta})_{2,n=1-9}$ called (2_s:2:n-1:n) prepared in Uzbekistan from melts in concentrated sun flux, followed by rapid cooling, SFQA technology that preserves melt tiling by confinement of conduction layer: $|(CuO_2)_{1/2}|Ca|(CuO_2)_{1/2}]_{n-1}|$ in the hard shell ||, of the n=1 phase, $[(CuO_2)_{1/2}|SrO|Bi_{1.7}Pb_{0.3}O|Bi_{1.7}Pb_{0.3}O|SrO|(CuO_2)_{1/2}]_2$. Disproportion leads to different n-phase mixing, and periodic lattice distortions (PLD) through bond resonance covalent crystal axes: $2(r_{Cu^{+2}}+r_{O^{-2}})=4.2Å > \underline{a=3.82Å} > d(CuO)+2^{-3/2}d(O_3)) = 3.2Å \approx (c_n-c_1)/2(n-1)$. Individual phase local bonds Cu-Ca, Cu-Sr, Cu-O-Cu are ascertained by X-Ray diffraction near Cu K-edge followed by Cu-Ca bond scattering. The HTLSC density, ρ decrease as n increases obtains $T_{c,n}$ ~180 K, identified due to n=8 phase on the surface of bulk n=4. Thus, bond resonance leads to higher n phases on surface and predicts: $T_{c,n} \Rightarrow$298K as n⇒50, if the superconducting skin depth is within c_{50}, of a few μm even in mixed n phases.

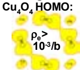
Introduction: Conductivity in HTLSC

depends on $\rho_{electron}$, grain boundaries, GB.

Covalent vs Ionic

1. HRTEM 2212: 1998 WY LIANG et al.

2. Non-bonding HTLSC Cu_4O_4 HOMO:



JV Acrivos, O Stradella, 1993

3. $SrTiO_3$ Σ13:[015]GB 2001, K vanBenthem

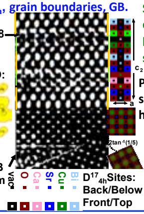


Figure 1: Covalent 2212 / ionic $SrTiO_3$ e density, high resolution electron HRTEM[1] conduction layers: $|CuO_2|Ca|_{n-1}$ within shell: |SrO|BiO|OBi|OSr| .

Phase diagrams show ≠ n-phases[2d]. high n on surface. XRD cartoon near Cu K-edge shows CuCa bond back scattering id for T_{cn}~180K is n=8.

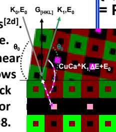
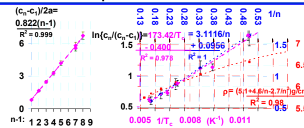


Figure 3: Activity of free $2e^- \Leftrightarrow e_2^=$ in confined layers, $\ln\{V_n/V_{n-1}\} = \ln\{c_n/(c_n-c_1)\}$ versus 1/n, $1/T_{c,n}$:

$$-\Delta G^{\neq}_n/k_BT = \ln\{c_n/(c_n-c_1)\} = 173.42/T_{c,n} - 0.4001.$$

{a, b, c_1, $(c_n-c_1)/2(n-1)$}={3.82Å, a±$u_{n,b}$, 24.6Å, 0.822 a}, u = PLD amplitude that gives rise to XRD structure (fig. 2)



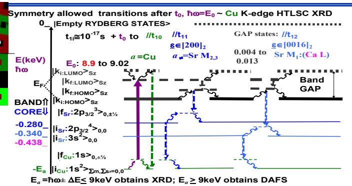


Figure 4: Energy level diagram for enhanced XRD in Q_0, Q*.

Cu-M bonds are identified by M core ΔE energies (fig. 4) to be Cu-Sr, Cu-Ca, Cu-O-Cu in mixtures of n phases.

The mixing of different n-phases has been considered a detriment to prepare HTLSC. But the formation of lower density, higher n-phases on the surface, within the skin depth suggest superconducting transport

In SFQA melts, disproportion mixes n phases:

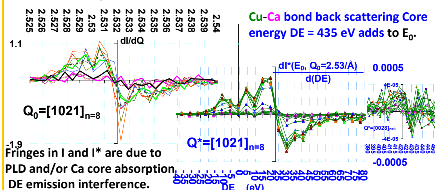
$$:2^*[2_s:2:n-1:n] \Leftrightarrow [2_s:2:n-2:n-1] + [2_s:2:n:n+1], \quad dP/dT = \Delta_\phi H/(T\Delta_\phi V), \quad (1)$$

Pressure, P waves are controlled by the Clapeyron relation (1). In XRD near the Cu K-edge, states a are excited by N ħω photons at K_0 incidence and scattered to K_1, $Q_0=K_{1,E_0}-K_{0,E_0}$. But Cu-M bonds contribute through M states, $a_{\neq}$ core ΔE, to obtain $Q^*=K_{1,E_0+\Delta E}-K_{0,E_0+\Delta E}$ when:

$$0|aa_{\neq}\mathbf{Q}_{HOMO}> + N\,\hbar\omega \leftrightarrow (N-1)\,\hbar\omega + <a(-1s)a_{\neq}\mathbf{Q}_{HOMO}\mathbf{Q}^*_{LUMO}| \quad (2)$$

is followed in t≤10^{-17}s by depletion of M $a_{\neq}$ core states / emission / absorption / backscattering from $|\mathbf{Q}_{HOMO}>$, $|(\mathbf{Q}^*)_{LUMO}>$, ε_0, ε_s ∈ **Q**,**Q***. The Cu-M bond contributions are identified by DE

RESULTS: Figure 2: K_0 incident X-rays at E_0=8940 to 9025eV scatter to K_1, obtain I vs $Q_0=K_1-K_0$ compare to enhanced atomic XRD, I* vs $Q^*=Q_0[1+\Delta E/E_0\cos(CuCa\hat{}K_1)]$ when K_0 X-rays, at constant at E_0, aligned for Q_0 excite Cu 1s. Bond along Cu-Ca path adds Ca core DE=435eV to E_0, obtains Q* Bragg reflection id of surface phase.



Fringes in I and I* are due to PLD and/or Ca core absorption DE emission interference.

[HKL]$_n$ assignments identify n=1 to 9 possible phases due to the degeneracy of reflections in the alloys. XRD reflections reveal chemical activity by the scattering paths along Cu-M bonds, also involved in the growth free enthalpy, ΔG≠, which in turn also determine the alloy transport and superconductivity properties.

Discussion: 1. Resonance is indicated by the crystal axes average of purely ionic and covalent bonds. **2.** The CuO non bonding Cu_4O_4 HOMO indicates [10L] GB formation in rapid cooled sun flux melts leads to n-mixing. GB formation in oxides induce rotations that are detected by local Cu atomic enhanced XRD of pairs of Q_0, Q* from mixed n phases formed in melts, with strong local Cu-Ca, Cu-Sr, Cu-O-Cu bonds that are impossible to determine by XAS in mixed phases. **3.** Interaction between the extended electronic states, $|Q_0>$, $|Q^*>$, decrease Gibbs free enthalpy of formation, ΔG≠ which is related to $T_{c,n}$ (fig. 3) and may be due to tiling in melts exposed to sun radiation.

Conclusion: The SFQA alloys grown by novel fast cooling, preserves melt tiling, mix different n phases, and show GB formation typical of the parent $SrTiO_3$ promise useful applications with increased $T_{c,n}$ ≈150 to 180K in low density high n- phases formed on surface of alloys.

ACKNOWLEDGEMENTS: Support for truly interdisciplinary, international work at San José State and DOE National Laboratory SLAC-SSRL, USA; Tiblisi, Georgia and Tashkent, Uzbekistan by the Science and Technology Centre in Ukraine (STCU) #4266 and Georgian National Science Foundation (GNSF) grant 08-477-4-260 and the Camille and Henry Dreyfus Foundation and DOE, and for published and unpublished HRTEM by YW Liang[1] is gratefully acknowledged.

References: [1] (a) W. Zhou, D.A. Jefferson and W.Y. Liang, "*Research Review, High Temperature Superconductivity*" Cambridge University, WY Liang, editor (1998), p.15; (b) W.Y. Liang and Y. Yin unpublished (1998); (c) K van Benthem, RH French, W Sigle, C Elsasser, M. Rühle, *Ultramicroscopy*, 86, 303, (2001); (d) J.V. Acrivos, *Physics and Chemistry of Electrons and Ions in Condensed Matter, J.V. Acrivos, N.F. Mott and A.D Yoffe*, ed, NATO ASI Series C130, 479 (1983); [2] JG Chigvinadze, AA Iashvili, TV Machaidze, *Phys. Letts. A* 300, 524 (2002); [3](a) DD Gulamova, DE Uskenbaev, G Fantozzi, JG Chigvinadze, O.V. Magradze. Zh. Tekhn. Fiz. 79, 98 (2009); (b) T Scopigno et al., *Physica B* 318, 341(2002); (c) JV Acrivos, *Microchemical Journal* 99,239–245(2011); P Strobel, JC Toledano et al., Physica C 201, 27 (1992)