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Fast melt cooled superconducting alloys: $(Bi_{1.97}Pb_{0.03}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta})_2$ n/n' n≤24 intergrowth

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Abstract: High temperature layer superconducting cuprate (HTLSC) alloys: $(Bi_{1.97}Pb_{0.03}Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta})_2$ called (2_s:2:n-1:n) have been grown from n-oxide stoichiometric melts in concentrated sun flux, followed by rapid cooling SFQA technology that preserves the melt tiling after annealing at 845±5°C**. Synchrotron XRD at the DOE SLAC-SSRL near the Cu K-edge has identified the mixing of n ≠ n' alloys as observed by many in thin films last century. An ideal D^{17}_{4h} Space Group structure obtains $\{a_n, b_n, c_n\}$ = {3.815 Å, a_n+u_{bn}, $2d_P(n+3)+u_{cn}$} where d_P is a perovskite sandwich, $(CuO_2)_{1/2}$|_Ca|$(CuO_2)_{1/2}$, thickness, and u_n are the amplitudes of periodic lattice distortions, PLD also observed last century*. Many electron interactions lead to covalent bonds indicated by $2(r_{Cu^{+2}}+r_{O^{-2}})$ =4.2Å > a = 3.82Å >d(CuO)+$2^{-3/2}d(O_3)$). Thus n-nano clusters grow n-1 perovskite sandwiches confined within a hard shell $(CuO_2)_{1/2}$|OSr|$Bi_{1.97}Pb_{0.03}$O|O$Bi_{1.97}Pb_{0.03}$|SrO|$(O_2Cu)_{1/2}$. Disproportion reactions produce n'=Nn+3(N-1)≥n clusters that are supported by n cluster pillars (fig. 1). The increase in the transition temperature to the superconducting state was determined by axial-torsional vibration measurements in transverse magnetic fields that obtain T_c⇒190K as n increases in ppm emergent regions***. n, n' alloy mixtures identify Cu-Ca, Cu-Sr, Cu-O-Cu strong bond scattering. Example shows that enhancement at $Q_0=[11(n+3)]_{n=4,(n'=12)}$=2.53/Å is also detected at $Q^*=[1116]_{12}$, $[1029]_{12}$ near Cu K-edge due to Cu-M bond back scattering that identify M=Ca, Sr, O, Cu (Table I, fig. 2).

Introduction: The quest is to ascertain how layer cuprates' T_c depends on chemical reactions in the melt subject to thermodynamics.

Our aim is to examine problems indicated by high resolution electron microscopy when the Gibbs free enthalpy of formation, $\Delta G_n^{\neq}$ governs the mixed n, n' layer growth, grain boundaries, GB (fig. 1) by using SFQA green technology methods to grow ceramics where low density, high T_c n'-alloys produced by chemical disproportions lead to pressure waves subject to the Clapeyron relation, e.g.,

2*[2_s:2:n-1:n] ⇔ [2_s:2:n-2:n-1] + [2_s:2:n:n+1], where $dP/dT=\Delta H_n/(T\Delta V_n)$ produces GB, PLD, cages, stabilizing polarized states: $2e^-$⇔$e_2^=$.

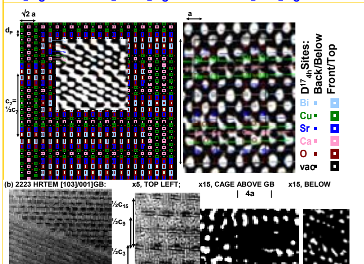

Figure 1: HRTEM[1] has identified intergrowth, and GB cages where polarons, bi-polarons $2e^-$⇔$e_2^=$ can catalyze transitions.

$F_Q=\Sigma_{unitcell,M,l} f_{Q,M,l}\,\alpha_{Q,M,l}$*; $\alpha_{Q,M,l}=\Sigma_l \exp(i(R_l+\delta_l)\bullet Q=\Sigma_{l,q,nsb=0,\pm1} J_{nsb}(u\bullet Q)\exp(i(Q+n_{sb}q)\bullet R_l+\phi))$											
$F_{Q,n}$(A139) $=\Sigma_M f_{M,Q}\,\alpha_{M,Q}$ ideal D^{17}_{4h} site amplitudes indicate degenerate n-alloy reflections lead to interference, PLD*											
<Q> ±≤ 1% $Å^{-1}$ **		$\Sigma\alpha^o_{Q,Cu,n\,CuO_2}$**		$F^o_{Q,n}$(A139)***		Sign($F^o_Q\Sigma\alpha^o_{Q,Cu,n\,CuO2}$**)		<e_E>=<S_E-S_{Eo}>/S_{Eo}****			
Symmetry	Center Ø at	CuO_2/Ca	BiO/OBi	CuO_2/Ca	BiO/OBi	CuO_2/Ca	BiO/OBi	jv_1	dg_15	dg_16	dg_18
nominal n								n=2+3	n=3	n=4	n=2
[0,0,n+3]	1.02	±4	±4	±1.4E2	±8E2, ±1.4E2	-	+, –				
[1,0,n+3]	1.94	0	0	±1.2E3	±1.4E2, ±4E2,	0	0	2.5	0.5	5.6	1
[1,1,n+3]	2.54	±4	±4	±3E2	-3E2, -4.8E2	-	+, –		0	4	na
[2,0,n+3]	3.45	-4	-4	±8E1	±8E2, ±6E2	–, + cancel	+, –		0	cc3.47	cc3.47
[2,1,n+3]	3.82	0	0	±1E3	E2, 3E2	0	0		0	1.5	5.4
[0,0,2n+6]	2.04	±4n	±4n	±8E2	$-1.7E3_{n=2}$	–, + cancel	+, OSC	0.08	0.6	4	0.28
[1,1,2n+6]	3.09	±4n	±4n	±1E3	$-2E3_{n=4}$	–, + cancel	+, OSC			3.5	0.7
[2,0,2n+6]	3.87	±4n	±4n	$1E2_{n=4}$	$-4E2_{n=4}$	–, + cancel	+		0	2	0.5
[00,3n+9]	3.05	±4	±4	±6E2	E2, 6E2	+	+, –		0	2	0.16
[1,0,3n+9]	3.47	0	0	±6E2	±6E2	0	0		0.2	6.5	0.6
[1,1,3n+9]	3.84	±4	±4	±4E2	-3E2, -4.8E2	+	+		0.2	1.5	0.44
[0,0,4n+12]	4.07	4n	4n	$4.6E2_{n=4}$	$4.6E2_{n=4}$	+	+			1.5	0.24
[2,0,0] reference	3.29	4n	4n	2.2E3	2.2E3	+	+			8	1

*A_M is the sample power loss to reach site R_l, $J_{nsb}(u\bullet Q)$ are 1st order Bessel functions with Q dependent argument [1b].
Ideal x,y sites are used with layer z/c_n fig. 1: z_n-Ø= BiO:¼/(n+3); SrO:5/8/(n+3); CuO_2:1/(n+3); Ca: 1.25/(n+3) determined by d_P/c_n=½/(n+3)

** Degenerate refelxions also appear for n=2 series [HKL=$2c_n$/a]; [HKL=(n+3)c_n/a]

$\Sigma\alpha^o_{Q,Cu,n}=2\sin(½\pi Ln/(n+3))/\sin(½\pi L/2/(n+3))$ in the absence of PLD

$\Sigma\alpha^o_{Q,Ca,n}=2\sin(½\pi L(n-1)/(n+3))/\sin(½\pi L/2/(n+3))$ in the absence of PLD

$\Sigma\alpha_{Q+nsbq,Cu,l}= 2J_{nsb}(u_{q,n}\bullet Q)(\exp[i(2\pi L+n_{sb}c_nq_{n,z})z_{1ø}]\Sigma_{m=0\ to\ n-1}\exp[-i(2\pi L+n_{sb}c_nq_z)md_P/c_n]$

$=2J_{nsb}(u\bullet Q)\sin\{(2\pi L+n_{sb}c_nq_{n,z})(n-1)/(n+3)/4\}/\sin\{(2\pi L+n_{sb}c_nq_{n,z})/4/(n+3)\}$

***$F^o_{Q,n}$(A139)= $\Sigma f^o_{M,Q}\alpha^o_{M,Q}$ determined from Cromer-Mann Tables at:http://www.ruppweb.org/xray/comp/scatfac.htm

****Average enhancement e at E=8960 to 8990 eV relative to real edge E_0=9000eV

Table I n,n' coincidence enhanced XRD amplitudes used in analysis.

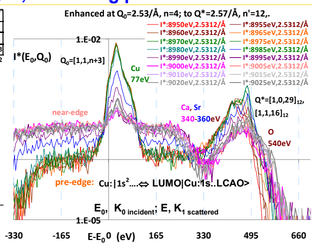

Figure 2: Enhanced XRD, shows that with K_0,E_0,Q_0 constant Cu 1s absorption, followed by scattering along Cu-M bond adds e.g., $\Delta E_{Ca-core}$=438eV. I* recorded vs E=E_0+ΔE obtains $Q^*=Q_0[1+\Delta E/E_0\cos(CuM\hat{}K_1)]_{n=4,\ n'=12}$.

References: [1] W.Y. Liang, *"Research Review, High Temperature Superconductivity"* Cambridge University, editor (1998), [2] JG Chigvinadze et al., *Phys. Letts. A* 300, 524 (2002); [3] DD Gulamova et al., Zh. Tekhn. Fiz.79,98 (2009) [4] JV Acrivos, *Microchemical Journal* 99, 239–245(2011)

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