Guided design of copper oxysulfide superconductors

CHUCK-HOU YEE(a), TURAN BIROL and GABRIEL KOTLIAR

Department of Physics & Astronomy, Rutgers, The State University of New Jersey - Piscataway, NJ 08854, USA

received on 16 June 2015; accepted by S. Savrasov on 30 June 2015
published online 15 July 2015

PACS 74.72.Gh – Hole-doped
PACS 81.05.Zx – New materials: theory, design, and fabrication

Abstract – We describe a framework for designing novel materials, combining modern first-principles electronic-structure tools, materials databases, and evolutionary algorithms capable of exploring large configurational spaces. Guided by the chemical principles introduced by Antipov et al., for the design and synthesis of the Hg-based high-temperature superconductors, we apply our framework to screen 333 proposed compositions to design a new layered copper oxysulfide, Hg(CaS)\textsubscript{2}CuO\textsubscript{2}. We evaluate the prospects of superconductivity in this oxysulfide using theories based on charge-transfer energies, orbital distillation and uniaxial strain.

Copyright © EPLA, 2015

Introduction. – The superconductors with the highest known transition temperatures at ambient pressure are all layered compounds containing planes of copper and oxygen where the superconducting electrons reside, separated by “spacer layers” composed of other elements. For a given compound, varying the doping level to an optimal value near 0.15 holes per copper maximizes the superconducting transition temperature \( T_c \). Since the copper oxide planes are a common ingredient, the large variability in optimal \( T_c \)’s between compounds must then be controlled by the spacer layers, which function to tune the chemical and structural properties of the copper oxide layer. Finding novel compositions for the spacer layers is key to discovering new superconductors with higher transition temperatures.

Theoretical design of new compounds is challenging due to the vast combinatorial space of elements and the large number of constraints: preferred oxidation state, electronegativity, atomic radii, preferred local coordination environment, and overall electrical neutrality. These microscopic properties in turn determine the local structural stability, global configurational minimum, and thermodynamic stability. Finding the global low-energy structure is the computational bottleneck. If a given composition results in a stable compound, we still need to determine whether it tunes the low-energy Hamiltonian so that \( T_c \) is enhanced, which imposes further screening criteria.

Rational design. – The cuprates are a functional stack: the composition of each layer is chosen to play a specific role (fig. 1). The central copper oxide (CuO\textsubscript{2}) plane supports superconductivity and roughly constrains the in-plane lattice constant. The remaining layers must tune the chemical potential of the CuO\textsubscript{2} layer without rumpling the plane or introducing disorder, and isolate each CuO\textsubscript{2} plane to create a 2D system.

In this manuscript, we describe the general framework for guided design of materials, and apply it to a space of 333 candidate compositions based on the single-layer Hg cuprate structure. Our screening criteria identified 20 candidates for in-depth study, of which a single copper oxysulfide Hg(CaS)\textsubscript{2}CuO\textsubscript{2}, which we abbreviate HCSCO, was identified as a promising compound. HCSCO does not exist in the ICSD database [5] and we propose it will be a high-temperature superconductor.

(a)E-mail: chuckyee@physics.rutgers.edu
CuO$_2$ charge dopants structure hamiltonian
HgO$_\delta$ balances -2 charge supplies harbors dopants tunes chemical potential
BaO neutral inert protects CuO$_2$ from disorder tunes in-plane $t$, $t'$, $U$
CuO$_2$ -2 charge/u.c. accepts roughly sets lattice const. superconducts
BaO (same as other CaS layer)

Fig. 1: (Color online) Each layer in the structural stack of HgBa$_2$CuO$_{4+\delta}$ performs a specific chemical, structural and electronic function. We focused on tuning the layers immediately adjacent to the CuO$_2$ plane which function to tune the in-plane Hamiltonian, but must also be charge neutral and not interfere with doping.

separate the superconducting electrons from the detrimental effects of the disordered dopant layer [10,11]. Additionally, the highly ionic nature of the BaO layer means they do not capture dopant electrons intended for the CuO$_2$ plane. The preference of Hg to be dumbbell coordinated bonds the entire structure together without introducing structural distortions [1]. Finally, the highly ionic O-Hg-O dumbbells minimize $c$-axis hopping to maintain 2-dimensionality.

Due to their spatial proximity, the adjacent BaO layers tune the hoppings and interaction strengths of the in-plane Hamiltonian. Designing compounds with novel adjacent layers provides a mechanism for controlling superconductivity by, e.g., reducing the charge-transfer energy. We quickly realized the most stringent constraint is structural stability, so we focused first on isolating stable candidates, then subsequently investigating their electronic properties.

To maximize the likelihood that a proposed composition is stable, we note that the layers adjacent to the CuO$_2$ plane form a rock salt structure. Using materials databases, we selected all naturally occurring rock salt compounds AX, composed of a cation A and an anion X (fig. 2). The phase space is large and the rate limiting step is structural prediction, so we quickly pre-screen candidates by discarding compositions with 1) large lattice mismatches relative to the in-plane Cu-Cu distance, which we took to be $3.82 \pm 3.95$ Å, and 2) anions less electronegative than Cu, as these anions would capture dopants intended for the superconducting plane, producing additional Fermi surfaces.

Given the remaining list of potential compositions, we screened for stable compounds as follows:

1) Local stability — substitute AX for the BaO layer of HBCO structure forming Hg(AX)$_2$CuO$_2$, fully relax the structure, then compute the phonons. Discard if there are many unstable phonons.

2) Configurational minimum — place one formula unit of the elements (1Hg, 2A, 2X, 1Cu 2O) in a box and apply evolutionary algorithms to find most energetically stable crystal structure.

3) Thermodynamic stability — compute the convex hull of Hg-A-X-Cu-O system and determine whether Hg(AX)$_2$CuO$_2$ lies below the hull. Synthesis generally proceeds in oxygen environments so the hull is computed with fixed Hg-A-X stoichiometry and varying oxygen concentration, parameterized by the chemical potential $\mu(O_2)$.

Compositions which pass all these hurdles have a good chance of being synthesized in bulk. However, these criteria are not rigid, as significant systematic uncertainties exist.

We search for compounds which are likely to be stable by eliminating materials which are more than 250 meV/atom above the convex hull. The rationale for this criteria is provided by the fact that in this class of materials there are large uncertainties in the accuracy of LDA total energies in predicting the stability of compounds. For example, we tested our workflow on HgBa$_2$CuO$_4$ (Hg-1201). While we do indeed find that
Guided design of copper oxysulfide superconductors

its phonons are stable, the construction of the convex hull for the Hg-Ba-Cu-O system shows Hg-1201 is unstable by 74 meV/atom. Modeling the doped compound via supercell calculations predicts Hg-1201 to be even more unstable, lying 130 meV/atom above the convex hull. Thus, systematic uncertainties are of at least that magnitude, and likely larger. Additionally, compositions exhibiting only weak phonon instabilities are likely synthesizable as well, especially with the help of epitaxy.

Methods. – The pymatgen implementation of the Materials API [12] was used to access the Materials Project [4] database to select all structures with lattice constants within ~ 5% of 3.9 Å, the nominal Cu-Cu distance.

Structural relaxations within DFT were performed with VASP [2,3] using PAW potentials [13] and the PBEsol functional [14]. We computed phonons at the (0, 0), (π, 0) and (π, π) k-points using 1 × 2 and √2 × √2 supercells constructed with the help of ISOTROPY [15] to check local stability.

We performed a fixed-composition evolutionary search for crystal structure using USPEX [16,17], with VASP as the underlying DFT engine. A unit cell consisting of one formula unit and an initial population of 256 random structures were used, decreasing to 64 in following generations. USPEX successfully found existing cuprate structures (LSCO, YBCO, HBCO) in benchmark tests, demonstrating its efficacy in the few-atom (8 atoms/f.u.) but many-species (5 elements) regime.

The Gibbs phase diagrams for the Hg-A-X-Cu system at varying oxygen potentials μ(O₂) were constructed using the phase diagram implementation in pymatgen [18]. We cross-checked these results with the PBE functional, which is known to give improved atomization energies [14], finding no significant differences in the relative energies between compounds.

The band structure orbital character was analyzed with WIEN2k [19] and structures plotted using VESTA [20]. Electronic parameters were extracted by downfolding to atomic-like orbitals, defined in [21].

Results. – Our materials design framework efficiently isolates compositions with desired crystal structures and properties. From 333 rock salt compounds, pre-screening based on lattice constants and electronegativity selected 20 compositions. Screening for local stability via phonon modes left three compositions: CaS, ZrAs, and YbS. Configurational stability using evolutionary structure prediction showed that a single composition, Hg(CaS)₂CuO₂, adopted the HBCO structure. This compound has sulfur instead of oxygen as the apical atom and has the smaller calcium ion instead barium in the adjacent layer. We also performed structure prediction with two formula units, finding the same HBCO structure. Thermodynamic calculations show HCSCO is marginally unstable, lying 170 meV/atom above the convex hull at fixed oxygen stoichiometry, and 240 meV/atom above the hull at

Fig. 3: (Color online) The Gibbs phase diagram of the Hg-Ca-S-Cu system at an oxygen chemical potential of μ(O₂) = −16.48 eV, chosen because Hg(CaS)₂CuO₂ (red dot) is least unstable at this value. The phase diagram forms a tetrahedron with S, Hg, Cu and CaO at the vertices (elemental Ca is not stable under this oxygen environment). HCSCO lies in the interior of the tetrahedron, on the triangular face formed by Hg, Cu and CaS.

Fig. 4: (Color online) Band structure of HCSCO, with dₓ²−ᵧ² (top) and dₓ₂−ᵧ² (bottom) character highlighted. A single band crosses the Fermi level of mainly dₓ²−ᵧ² character with little admixture of dₓ₂ character.
µ(O₂) = -16.48 eV, with an expected decomposition into Hg, Cu, CaS, and oxygen gas (fig. 3), within the range of systematic uncertainties of our method.

Turning to electronic structure (fig. 4), we observe a single band crossing the Fermi level with strong dₓ²−ᵧ² character, similar to other single-layer cuprates. The Fermi surface is extremely 2-dimension, and comparable to HBCO. Table 1 summarizes a comparison of the salient electronic parameters extracted using down-folding between HCSCO and the single-layer HBCO superconductor.

Discussion. – We evaluate the prospects of superconductivity in HCSCO via three chemically based proposals. Applying in-plane compression induces large increases in transition temperatures, with dTc/d(log a) ~ −600 K in LSCO [7] and −4000 K in HBCO [1], where a is the in-plane lattice constant. We are aware that many variables are involved, especially that compression may induce buckling, which decreases Tc [22]. However, assuming all other factors are held constant, the 1.6% compression of HCSCO relative to HBCO would cause a 60 K increase in Tc.

An alternative proposal argues that tuning the charge-transfer energy Δ pudd, which roughly corresponds to the effective Coulomb interaction, controls superconductivity [8]. As shown in table 1, the negligible difference in Δ pudd between HCSCO and HBCO, combined with similar hopping amplitudes, implies comparable Tc’s (fig. 5). We expected that the increased polarizability of sulfur as compared to oxygen would reduce Δ pudd, an effect which may be captured in methods beyond LDA, like the GW approximation.

Finally, the orbital distillation proposal argues that a large admixture of the apical orbitals, in particular the Cu-dₓ²−ᵧ² orbital, into the dₓ²−ᵧ² band suppresses Tc [9]. The admixture decreases as the splitting between the onsite energies of the two orbitals ΔEz ≡ Eₓ²−ᵧ² − Ez increases. However, HCSCO poses a challenge: although ΔEz is quite small (see table 1), there is little admixture of apical orbital character into the in-plane band, as shown in fig. 4. A small ΔEz implies a low Tc, while a small dₓ²−ᵧ² admixture implies Tc’s comparable to the HBCO superconductors. Synthesis of HCSCO would help clarify the effects of orbital distillation.

Turning to stability against phase separation, our calculations indicate HCSCO lies above the convex hull, but within the systematic errors of the method used to estimate total energies. Furthermore it is known that many interesting functional materials are metastable [25], protected from decay by large energetic barriers. In solid-state synthesis, the Hg cuprates are formed in the presence of gaseous Hg [26] in addition to O₂, providing an additional tuning parameter which may enhance stability. Finally, prior experience with materials design indicates that compounds which are too stable are not easily dopable [27,28]. These considerations suggest avenues for synthesis of HCSCO should be explored, both under pressure in bulk and especially via molecular beam epitaxy.

Conclusions. – We have created a workflow for systematically designing novel compositions based on existing compound families. Guided by chemical intuition and materials databases, our workflow quickly isolates promising compositions for in-depth examination. Combining electronic-structure tools, evolutionary algorithms, and methods for constructing phase diagram, we screen for local, configurational and thermodynamic stability to isolate new compounds with a high probability of synthesis.

We have applied this workflow to design a new layered copper oxysulfide, Hg(CaS)₂CuO₂, which we believe
will be a high-temperature superconductor, with $T_c$’s comparable to those of the mercury cuprates. In the future, we expect the multi-layer family members of HCSCO will be designed, with formulas Hg(CaS)$_2R_{n-1}$(CuO$_2$)$_n$ where R is a 2+ cation placed between the CuO$_2$ planes in the “infinite-layer” stack, as well as systematic extensions to the compositions of other cuprate families.

To date, cuprate superconductors exist with oxygen, chlorine and fluorine in the apical position. The synthesis in the “infinite-layer” stack, as well as systematic extensions to the compositions of other cuprate families.

REFERENCES

[1] Antipov E. V. and Abakumov A. M., Usp. Fiz. Nauk, 178 (2008) 190.
[2] Kresse G. and Furthmüller J., Comput. Mater. Sci., 6 (1996) 15.
[3] Kresse G. and Furthmüller J., Phys. Rev. B, 54 (1996) 11169.
[4] Jain A., Ong S. P., Chen G. W., Richards W. D., Dacek S., Cholia S., Gunter D., Skinner D., Ceder G. and Persson K. A., APL Mater., 1 (2013) 011002.
[5] Belsky A., Hellenbrand M., Karen V. L. and Luksch P., Acta Crystallogr. Sect. B: Struct. Sci., 58 (2002) 364.
[6] Oganov A. R. and Glass C. W., J. Chem. Phys., 124 (2006) 244704.
[7] Loew D., Pernot J., Fompeyrine J. and Mächler E., Nature, 394 (1998) 453.
[8] Weber C., Yee C., Haule K. and Kotliar G., EPL, 100 (2012) 37001.
[9] Sakakibara H., Usui H., Kuroki K., Arita R. and Aoki H., Phys. Rev. Lett., 105 (2010) 057003.
[10] Fujita K., Noda T., Kojima K., Eisaki H. and Uchida S., Phys. Rev. Lett., 95 (2005) 097006.
[11] Hobou H., Ishida S., Fujita K., Ishikado M., Kojima K., Eisaki H. and Uchida S., Phys. Rev. B, 79 (2009) 064507.
[12] Ong S. P., Richards W. D., Jain A., Hautier G., Köcher M., Cholia S., Gunter D., Chevrier V. L., Persson K. A. and Ceder G., Comput. Mater. Sci., 68 (2013) 314.
[13] Blöchil P. E., Phys. Rev. B, 50 (1994) 17953.
[14] Perdew J. P., Burke K. and Ernzerhof M., Phys. Rev. Lett., 77 (1996) 3865.
[15] Stokes H. T. and Hatch D. M., J. Appl. Crystallogr., 38 (2005) 237.
[16] Glass C. W., Oganov A. R. and Hansen N., Comput. Phys. Commun., 175 (2006) 713.
[17] Lyakhov A. O., Oganov A. R., Stokes H. T. and Zhu Q., Comput. Phys. Commun., 184 (2013) 1172.
[18] Ping Ong S., Wang L., Kang B. and Ceder G., Chem. Mater., 20 (2008) 1798.
[19] Blaha P., Schwarz K., Madsen G. K. H., Kvasnicka D. and Luitz J., WIEN2K An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlsruhe Schwarz, Technische Universität Wien, Austria) 2001.
[20] Momma K. and Izumi F., J. Appl. Crystallogr., 41 (2008) 653.
[21] Haule K., Yee C.-H. and Kim K., Phys. Rev. B, 81 (2010) 195107.
[22] Gao W., Liu Q., Yang L., Yu Y., Li F., Jin C. and Uchida S., Phys. Rev. B, 80 (2009) 094523.
[23] Poltavets V. V., Lokshin K. A., Dikmen S., Croft M., Egami T. and Greenblatt M., J. Am. Chem. Soc., 128 (2006) 9050.
[24] Poltavets V. V., Lokshin K. A., Nevidomskyy A. H., Croft M., Tyson T. A., Hadermann J., van Tendeloo G., Egami T., Kotliar G., Aproberts-Warren N., Dioguardi A. P., Curro N. J. and Greenblatt M., Phys. Rev. Lett., 104 (2010) 6.
[25] Zhang X., Yu L., Zakutayev A. and Zunger A., Adv. Funct. Mater., 22 (2012) 1425.
[26] Alyoshin V., Mikhailova D., Rudnyi E. and Antipov E., Physica C: Supercond., 383 (2002) 59.
[27] Yin Z. P. and Kotliar G., EPL, 101 (2013) 27002.
[28] Retuerto M., Yin Z., Egne T. J., Stephens P. W., Li M.-R., Sarkar T., Croft M. C., Ignatov A., Yuan Z., Zhang S. J., Jin C., Paria Sena R., Hadermann J., Kotliar G. and Greenblatt M., Inorg. Chem., 54 (2015) 1066.