Inorganic Chemistry
Editorial
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Editorial for the *ACS Select* Collection on Solid-State Chemistry

"New materials are the lifeblood of solid-state materials research and device technology. Simply put, new materials are discovered by chemists. Thus, the synthetic chemist—especially if s/he develops a proficiency in relating structure, bonding, and other chemical−physical considerations to properties of interest—is in a key position in determining the direction and success of solid-state research, and ultimately, technology." These statements, paraphrased from Dr. Robert Laudise of Bell Laboratories, succinctly summarize the relevance of solid-state materials, which provide the foundation for a variety of commonplace applications. From the batteries in our cellular phones and computers[1] to blue-ray DVD players[2] and sensors and detectors in alarms,[3] as well as medical[4] and oil and gas technologies,[5] solid-state materials are ubiquitous in our daily lives.

This *ACS Select* collection is focused on the accomplishments in solid-state materials chemistry of 13 emerging investigators whose work has been selected from published papers in the American Chemical Society journals *Inorganic Chemistry*, *Journal of the American Chemical Society*, and *Chemistry of Materials* between 2013 and 2014. Many of the articles in this *ACS Select* collection involve, in one manner or another, the synthesis of new solid-state materials in combination with advanced characterization techniques. Progress has occurred not only in the synthesis and functional property characterization of materials but also in theoretical calculations to better understand the complex bonding and interactions observed in many of the reported structure types. Topics covered in this *ACS Select* collection include battery research, magnetic behavior in intermetallics and oxide materials, broad-band white-light emitters, superconductivity, thermoelectricity, and use of density functional theory (DFT) to predict and understand solid-state materials, noncentrosymmetric (NCS) materials, and open-framework compounds. The above list is by no means comprehensive with respect to the current research in solid-state materials chemistry but rather represents the research interests of the authors selected for this *ACS Select* collection.

One of the research themes in this virtual issue involves photoelectrochemical water oxidation. This work, done by Professor Bart Bartlett and co-workers at the University of Michigan (http://www.umich.edu/~bmbgroup/) involves a visible-light-absorbing semiconductor oxynitride $Ti_{1-(5x/4)}Nb_xO_{2-y-d}N_y$,[6] as well as an earth-abundant molecular catalyst, $Fe(tebppmcm)Cl_2$, with a semiconducting photoelectrode, WO_3.[7] The former material was impregnated with RuO_2, which resulted in polycrystalline cocatalyst compounds. The RuO_2 cocatalyst is needed to evolve oxygen, and Bartlett and co-workers demonstrated that the water oxidation activity depends on the cocatalyst weight percent loading. With the iron molecular catalyst, in combination with the semiconducting photoelectrode, WO_3, they noted a dramatic increase in the rate and selectivity of photoelectrochemical water oxidation. In addition, they removed the need for any sacrificial chemical oxidant, e.g., Ce^{4+}.

The synergistic combination of experiment and computation (DFT) for the discovery of new materials with the desired physical properties is the focus of Professor Boniface P. T. Fokwa's research (http://www.ssc.rwth-aachen.de/fokwa/) at RWTH Aachen University. In recent years, Fokwa and co-workers have studied several series of compounds, whose magnetic properties change by chemical tuning through variation of the magnetically *inactive* elements. In a very recent example,[8] they synthesized the complex boride series $Sc_2FeRu_{5-x}Ir_xB_2$ ($x = 0-5$) through arc melting of the elements. By using 4d and 5d elements, they were able to distinguish the respective atomic sites through diffraction techniques and were thus able to investigate the atomic site preference with respect to magnetic properties. Measurements revealed several different types of magnetic ordering, and Fokwa and co-workers were able to correlate this change in magnetism to the valence electron count in the series and specifically to the Ru/Ir site preferences. Finally, they noted that the compositions with $x = 2$ and 3 have the largest measured coercivity to date for the transition-metal borides.

Professor Danny Fredrickson and co-workers at the University of Wisconsin (http://chem.wisc.edu/~danny) combine experiment and theory (DFT) in determining how chemical driving forces underlie the immense structural diversity of intermetallic phases. They report on a new intermetallic phase, $Ca_{10}Cd_{27}Cu_2$, which they encountered in their pursuit of chemical frustration: the idea that structural complexity can emerge from the competition between incompatible bonding types.[9] The geometrical features of this material include the icosahedral clusters occurring in Bergman-type quasicrystals,[10] which here appear as a result of micelle-like segregation between Ca−Cd and Cd−Cu interactions. On the basis of these structural observations and the results of DFT−chemical pressure analysis, they speculate that similarly frustrated systems can be obtained by constructing ternary combinations of the form $A_{1-x}B_xC_y$ ($y \gg 1$), where A−C and B−C phases exhibit positive and negative chemical pressures within the C sublattice, respectively. They employ the μ_3-acidity model—an adaptation of the Lewis acid/base concept to metallic systems—to explain the structural diversity appearing in the Sc-rich phases of the Sc−Ir system.[11] Their research expands on this theme to show how structural incompatibilities can emerge as the stoichiometric ratio of the acidic and basic atoms is changed across a binary phase diagram, resulting in the intergrowth of differing packing types. Finally, they grapple with an incommensurately modulated material, $Co_3Al_4Si_2$. After describing the synthesis and structure determination in 3D + 1D space, they demonstrate how its bonding and stability can be understood through isolobal analogies to metal−metal bonds in molecular transition-metal complexes.[12] This work reaffirms the power of the isolobal analogy to bridge disparate areas of chemistry from organic molecules to inorganic complexes to transition-metal silicides and intermetallics.

Published: October 20, 2014

Prof. Andrew Grosvenor and his group at the University of Saskatchewan (http://www.usask.ca/chemistry/groups/grosvenor/) are concerned with the study of solid-state materials for a variety of applications, with an emphasis placed on those of interest to the nuclear materials community. A unique aspect of his research is the use of X-ray spectroscopy to develop an understanding of solid-state materials. A recent theme of the research conducted by Prof. Grosvenor and co-workers is the investigation of the effect of synthetic methods on the physical properties of materials. In other words, does changing how a material is made change its properties? For example, Walker and Grosvenor investigated the $Al_{1-x}Ga_xFeO_3$ ($0 \leq x \leq 1$) system synthesized through sol−gel, coprecipitation, and ceramic methods.[13] They observed through X-ray absorption near-edge spectroscopy measurements that samples synthesized by the coprecipitation method revealed the largest variability in the metal coordination number depending on the composition and annealing temperature. The coordination number changes were also observed with the sol−gel and ceramic methods but to a much smaller extent. This was rationalized through cation mobility arguments. The polymeric and oxide networks inhibit the cation mobility when sol−gel and ceramic methods are used, whereas there are no such long-range network restrictions for cation mobility for samples produced through the coprecipitation method.

Professor Oliver Janka in the Institute of Inorganic and Analytical Chemistry at the University of Münster (http://www.uni-muenster.de/Chemie.ac/janka/) is also investigating new intermetallic materials. Janka and co-workers report on the synthesis and characterization of the solid solution $CeRu_{1-x}Ni_xAl$ ($0.1 \leq x \leq 0.95$).[14] The materials were synthesized through arc melting of the elements followed by subsequent annealing to yield phase-pure products. A number of these cerium−ruthenium intermetallics exhibit no magnetic ordering down to very low temperatures: "nonmagnetism", as it is often called. The magnetic measurements of Janka and co-workers indicate that the cerium cations do not exhibit a local moment. The mixed-valent nature of the cerium cations was confirmed by X-ray absorption near edge structure (XANES) experiments on $CeRu_{0.5}Ni_{0.5}Al$. Finally, DFT calculations revealed that the stability of the orthorhombic solid solution is critically dependent on the shortest Ce−Ru interactions.

Magnetic oxide materials are also of interest to Professor Houria Kabbour at the University of Lille (http://uccs.univ-lille1.fr/index.php/annuaire/15-fiches-personnels/203-kabbour-houria). Kabbour and co-workers investigate spin dynamics between ferromagnetic chains in a pure inorganic framework.[15] The material that they synthesized and investigated, $BaCo_2(As_3O_6)_2{\cdot}2H_2O$, consists of ferromagnetically canted isolated chains. Interestingly, the material fulfills most of the requirements to be considered a single-chain magnet such as $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$.[16] In a very recent paper, they reinvestigated Bi/M (M = Co and Cu) oxosulfates. This reinvestigation led to the discovery and full characterization of $[Bi_2CoO_3](SO_4)$ and $[Bi_{6.236}Cu_{1.608}](SO_4)_3$, both of which have a doubled-cell parameter with respect to the original reports.[17] The refined structures take into account supercell spots neglected originally. Magnetic measurements reveal that the Co compound exhibits weak ferromagnetism below 17 K, whereas the Cu compound is essentially a paramagnet despite having Cu_2O_6 dimers. Finally, Kabbour and co-workers discovered the first two-dimensional Ising ferromagnetic oxide, $BaFe_2(PO_4)_2$. The material was synthesized hydrothermally and exhibits honeycomb layers consisting of edge-sharing FeO_6 octahedra containing high-spin Fe^{2+} ions. A rare reentrant structural transition is observed at 65.5 K as the material returns to the trigonal $R\overline{3}$ structure in the presence of ferromagnetic domains.[18]

Research in Professor Hemamala Karunadasa's group at Stanford University (http://web.stanford.edu/group/karunadasalab/index.html) includes battery cathode materials and broad-band white-light emitters. Jaffe and Karunadasa showed the first example of Li^+ cycling with high Coulombic and energy efficiencies in a CuCl−polyether hybrid. This hybrid material was synthesized at room temperature and demonstrates that the electrochemical behavior is consistent with a conversion or insertion reaction that is stabilized by the integration of organic and inorganic components.[19] Most interestingly, these hybrid materials permit the independent optimization of the inorganic and organic components. In their work on broad-band white-light emitters, they provide the first reports of layered hybrid perovskites that emit radiation across the entire visible spectrum (similar to sunlight) upon ultraviolet excitation.[20,21] Additionally, they showed that white-light emission from layered hybrid perovskites $(N\text{-MEDA})[PbBr_{4-x}Cl_x]$ (N-MEDA = N_1-methylethane-1,2-diammonium; $x = 0{-}1.2$) can be tuned through halide substitution to generate both "warm" and "cold" white light.[20] They also report the second family of perovskite white-light emitters $(EDBE)[PbX_4]$ [EDBE = 2,2′-(ethylenedioxy)bis(ethylammonium); X = Cl and Br] with improved photoluminescence efficiency.[21] The mechanistic studies indicate that emission arises from the bulk material and is amenable to synthetic design. They have discovered well-defined and tunable structures that provide a flexible platform for investigating intrinsic broad-band white-light emission from bulk materials.

Magnetism, superconductivity, and thermoelectricity in solid-state materials are of interest to Professor Kirill Kovnir's research group at the University of California, Davis (http://chemgroups.ucdavis.edu/~kovnir/index.html). His research group is interested in the synthesis of new materials exhibiting structural features that control specific functional properties. They discovered a new low-dimensional magnetic material, $NH_4FeCl_2(HCOO)$, where infinite zigzag chains of distorted Fe^{2+}-centered octahedra are connected by μ_2-Cl and syn−syn formate bridges.[22] Magnetic measurements and Mössbauer spectroscopy investigation of $NH_4FeCl_2(HCOO)$ revealed complex anisotropic magnetic behavior with a ferromagnetic component in the direction of chain propagation and antiferromagnetic interactions between the chains ($T_N = 6$ K).[22] In their search for new thermoelectric materials, Kovnir and co-workers discovered a new clathrate compound, $Ba_8Au_{16}P_{30}$, with exceptionally low thermal conductivity.[23] This compound crystallizes in an orthorhombic superstructure of clathrate-I and features complete separation of the Au and P atoms over 23 different crystallographic positions. The low thermal conductivity is rationalized through the presence of a large number of heavy atoms (Au) in the structure, and the formation of multiple twinning interfaces and antiphase defects, which act as effective scatterers of heat-carrying phonons.[23] Small variations in stoichiometry led to the discovery of barium−gold phosphide, $BaAu_2P_4$, which has a new structure type.[24] This material features Au−P layers separated by Ba atoms. Magnetic and solid-state ^{31}P NMR measurements, together with analysis of the electronic structure, reveal that $BaAu_2P_4$ is a charge-balanced Zintl phase, $Ba^{2+}(Au^{+})_2(P^{-})_4$.[24]

The synthesis and magnetism of functional materials is the focus of Professor Tyrel McQueen's research group at Johns Hopkins University (https://occamy.chemistry.jhu.edu). They investigated the superconductivity in the Bi−O−S system[25] and determined that $Bi_3O_2S_3$ is a superconductor with T_c = 4.5 K with a superconductivity that rapidly disappears as Bi_2OS-like stacking faults are introduced.[25] A question that McQueen and co-workers are concerned with is, how is the metallic behavior and superconductivity exhibited in $Bi_3O_2S_3$ when a valence-precise Bi^{3+} is observed [assuming an $(S_2)^{2-}$ electron count on the dimers]? They speculate that the physical phenomena are attributable to incomplete charge transfer to the S_2 dimer or due to possible mixtures of disulfide and sulfide in the intermediary layers. McQueen and co-workers build upon their work in the preparation of metastable solid-state materials and synthesize the solid-solution $K_{1-x}Ir_4O_8$ ($0 \leq x \leq 0.7$). In doing so, they are able to tune the formal oxidation state of iridium.[26] While the physical properties between members of the solid solution are similar, all specimens are metallic, and the results yield an understanding of alkali-ion mobility in oxides, driven by the competition between the local charge neutrality and ionic radius. Finally, they investigated the magnetic structure of $LiMBO_3$ (M = Mn, Fe, and Co) using neutron powder diffraction. They observed that for all M upon cooling an incommensurately ordered magnetic phase was followed by a change to a commensurate long-range antiferromagnetic state, an apparently universal feature of magnetically low-dimensional systems.[27] One of the most surprising effects, derived from the trigonal-prismatic coordination of M, is that Fe and Mn show partial unquenched orbital angular momentum, whereas Co does not, opposite to that typically found in transition-metal oxides.

NCS lone-pair materials, specifically selenites, are of interest to Professor Kang Min Ok's research group at Chung-Ang University (http://inmatchem.cau.ac.kr). In order to rationally design novel NCS materials by using asymmetric building units such as polyhedra of lone-pair cations, it is crucial to understand factors controlling the macroscopic symmetry. Therefore, detailed structural analyses along with thorough characterizations have been made on a series of mixed-metal selenites. Ok and co-workers demonstrate how the alkali-metal size impacts the framework geometry.[28,29] Although stoichiometrically equivalent $AGa(SeO_3)_2$ (A = Li, Na, K, and Cs) share a similar bonding network, the channel structures for the materials are quite different.[28] Similar structural variation is also observed from a family of alkali-metal yttrium selenites, $AY(SeO_3)_2$ (A = Na, K, Rb, and Cs). The group concludes that the sizes of the alkali-metal cations within the channels influence the orientation of the lone pairs on the Se^{4+} cation, which subsequently determines the framework architectures of the reported materials.[29] Ok and co-workers also show the macroscopic centricity, i.e., centric versus acentric, is influenced by the interaction between the alkali-metal cation and the oxide ligands on the metal oxygen polyhedra. Interestingly, they discover new lone-pair materials, $YVSe_2O_8$ and $YVTe_2O_8$, for which only the selenite is acentric. They are able to rationalize the different centricities by examining the sizes of the MO_3 (M = Se^{4+} or Te^{4+}) polyhedra.[30] While the larger TeO_3 polyhedra in centrosymmetric $YVTe_2O_8$ are aligned in the opposite direction to avoid unfavorable lone pair−lone pair interactions within a limited space, the smaller rigid SeO_3 groups in NCS $YVSe_2O_8$ could reside in a confined space without any significant repulsion.

Rare-earth intermetallics as thermoelectric materials and applications in condensed matter physics and supramolecular inorganic−organic hybrid materials for optical and catalytic applications are of interest in Professor Sebastian Peter's research group at the Jawaharlal Nehru Centre for Advanced Scientific Research (http://www.jncasr.ac.in/sebastiancp/). They report two new rare-earth intermetallic compounds, $Yb_5Ga_2Sb_6$ and Eu_2AgGe_3.[31,32] $Yb_5Ga_2Sb_6$, a new member in the $RE_5M_2X_5$ thermoelectric family, has an anisotropic structure with infinite anionic double chains $(Ga_2Sb_6)^{10-}$ cross-linked by Yb^{2+} and Yb^{3+} ions.[31] The compound satisfies the Zintl−Klemm concept and is a narrow-band semiconductor. The temperature-dependent power X-ray diffraction and differential thermal analysis data on Eu_2AgGe_3 suggest a structural phase transition from orthorhombic to hexagonal above 477 K and an unusual reversible phase transition to the original structure at 718 K.[32] All phases are ordered superstructures of the AlB_2 type. Magnetic measurements on Eu_2AgGe_3 indicate paramagnetic behavior above 100 K and weak ferromagnetic interactions below 80 K. The new supramolecular compound $[SiMo_{14}O_{44}](H4,4'\text{-bpy})_2{\cdot}xH_2O$, a capped α-Keggin polyoxomolybdate anion with 4,4′-bipyridine, was discovered recently.[33] Absorption measurements indicate possible semiconducting behavior unlike what is typically observed in Keggin ions.

Professor James Rondinelli's group at Northwestern University (http://www.appliedphysics.northwestern.edu/faculty/Rondinelli.html) is interested in harnessing the predictive power of electronic-structure calculations for the design and discovery of new functional inorganic oxides. Young and Rondinelli use first-principles DFT calculations to design polar perovskite oxides that do not contain any second-order Jahn−Teller ions.[34] In doing so, they demonstrate that electrical polarizations arise through a geometric, rotation-induced mechanism and are greater than those induced by spin-driven mechanisms. They generalize these results into a unified set of structural-chemistry guidelines, which may be used to design other cation-ordered polar oxides without the need of performing a simulation. Rondinelli and co-workers expand on this work by formulating predictive guidelines for NCS A_2BO_4 Ruddlesden−Popper (RP) oxides using a combination of Bayesian analysis and DFT.[35] They describe the general methodology, which focuses on identifying suitable structural geometries and finding combinations of cations with the greatest probability toward those structural polymorphs. In doing so, they predict that RP-structured Ca_2IrO_4 could be polar at low temperature and suggest pathways to stabilize it. Finally, they describe a design strategy to realize a deep-UV nonlinear optical material with a large second-harmonic-generation (SHG) response, $Ba_4B_{11}O_{20}F$ (BBOF).[36] They determine that the enhanced SHG intensity in BBOF originates mainly from the F-directed polar displacements and, to a lesser extent, the Ba polarizability by using mode-crystallography analyses to disentangle the atomic structure contributions to the SHG response.

Open-framework materials are of interest to Professor Junliang Sun's research group at Peking University (http://www.chem.pku.edu.cn/issm/Sun%20junliang.html). Sun and co-workers discover an interesting three-dimensional open-framework germanate, GeO-JU90, which was synthesized using a complicated structure-directing agent, 1,5-bis-

(methylpyrrolidinium)pentane dihydroxide.[37] The framework of GeO-JU90 is built up from 7-connected Ge_7 clusters and additional $GeO_3(OH)$ groups that form a three-dimensional open framework with intersecting 12 × 12 × 11 ring tunnels. They demonstrate a powerful use for crystal structure solution by combining powder X-ray diffraction (PXRD) with the charge-flipping algorithm, simulated annealing, and EXAFS characterization. With high-resolution synchrotron PXRD, the framework structure with heavy Ge atoms could first be identified by the charge-flipping algorithm and the location of the light organic structure-directing agent could then be found through simulated annealing. The environments of Ge atoms are consistent with EXAFS analysis. New open-framework vanadoborates, denoted SUT-6-Zn, SUT-6-Mn, and SUT-6-Ni, were recently reported.[38] It is difficult to construct 3D open frameworks through vanadoborate clusters, such as V_6B_{20}, $V_{10}B_{28}$, and $V_{12}B_{18}$. Sun and co-workers succeeded by using TO_X polyhedra (T = Zn, Mn, or Ni) to link the $V_{12}B_{18}$ clusters into 3D frameworks, and the 6-connected $V_{12}B_{18}$ clusters follow a semiregular hxg net topology with 18-ring channels.[38] With V^{4+} and V^{5+} mixed-valence states in the materials, confirmed by X-ray photoelectron spectroscopy analysis, these materials are expected to have redox activities. The experiments show that SUT-6-Zn could be an efficient heterogeneous precatalyst for the oxidation of alkylbenzenes with yields up to 90%. The catalyst can be easily recovered by centrifugation and filtration after oxidation and subsequently used in succesive runs for eight cycles without significant loss in yield.

The articles gathered in this *ACS Select* collection only represent a glimpse of the efforts of these emerging authors and partially reflect the breadth of research in solid-state materials chemistry. The interdisciplinary approaches found in these articles provide a much deeper understanding of the functional materials being investigated. I strongly encourage the submission of breakthrough papers in solid-state materials chemistry to *Inorganic Chemistry*, and I hope you will join me in reading these excellent articles by outstanding scientists in our field.

P. Shiv Halasyamani, Associate Editor

■ AUTHOR INFORMATION

Notes

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