Preface: Overview of the Forum on Functional Inorganic Materials

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Inorganic Chemistry is pleased to present a Forum on Functional Inorganic Materials. A recent workshop sponsored by the National Science Foundation highlighted these materials and their technological impact (Prog. Solid State Chem. 2008, 36, 1–133). As the report makes clear, we are presently at the halfway point of the solid-state century [The Solid State Century. Sci Am. 1997, 8 (1)], in which, to date, functional inorganic materials have played profound societal and technological roles. It is without question that new functional inorganic materials will be indispensable during the second half of the solid-state century. In addition, the Department of Energy recently published their Grand Challenges for Basic Energy Sciences (http://www.science.doe.gov/bes/reports/list.html). Successfully meeting the challenges described in their report will require the synthesis and characterization of new and advanced functional inorganic materials.

Rapidly changing technologies, for example, associated with cell phones, digital video devices, and computers, continue to drive the discovery of new materials. The replacement of SiO₂ as a high dielectric constant (high-κ) material in transistors is crucial if additional microelectronic miniaturization is to be achieved. Currently, hafnium-based oxides and oxynitrides show promise, but it remains an ongoing challenge to discover new high-κ materials. What exactly defines an inorganic material, or for that matter any material, as functional? One broad definition would encompass materials that exhibit properties important to a new or changing technological advance. Functional inorganic materials encompass a vast and growing field, and it is not possible to present all of the ongoing research in one Forum. As part of this important multidisciplinary subject, this Forum on Functional Inorganic Materials deals mainly with oxides and other solid-state materials. Functional inorganic materials are found in batteries and fuel cells, computer memories, sensors, and thermoelectrics. In addition, microporous and open-framework materials including zeolites and metal–organic framework (MOF) compounds increasingly are used in heterogeneous catalysis and gas storage. Materials such as Nd:YAG and GaN are utilized for infrared and blue laser applications. Functional inorganic materials are not limited to nonmolecular compounds and also include numerous molecular compounds. A. F. Wells in his fifth edition of Structural Inorganic Chemistry stated that “the structural [functional] side of inorganic chemistry cannot be put on a sound basis until the knowledge gained from the study of the solid state [molecular and nonmolecular] has been incorporated into chemistry as an integral part of the subject”. A host of other attributes including the oxidation state, ion size, crystallographic order or disorder, coordination number, and symmetry, play a key role in determining the functionality of an inorganic material. The complex associations between these attributes and compound functionality must be fully understood if “rational materials design” is to be achieved.

Interestingly, many of the functionalities described in this Forum have been known for decades, if not centuries. One of the oldest known phenomena is pyroelectricity, the change in polarization as a function of temperature. The effect was first observed over 2400 years ago by the Greek philosopher Theophrastus, although the term was not used until 1824 by Brewster. It was around that same time, in 1822, when Seebeck discovered the thermoelectric effect, the ability of a material to convert heat into electricity. Although thermoelectrics are generally thought to be alloys, Koumoto et al. superbly describe how oxides can exhibit thermoelectric behavior. About a quarter century before the discovery of the thermoelectric effect, in 1800, Volta invented the battery. Other functionalities were discovered about a century later: piezoelectricity in 1880 by the Curies and ferroelectricity in the early 1920s by Valasek.

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Most of the Articles in this Forum deal with, in one way or another, the synthesis of new inorganic compounds as well as advanced characterization techniques. From a practical standpoint, advances in functional inorganic materials will only come about through the synthesis of new compounds in combination with detailed physical property measurements and theoretical calculations. The contributions in this Forum represent Articles authored by leaders in the field. MOFs are the topic of the contribution by Srinivasan Natarajan et al. They discuss how, under hydrothermal conditions, simple variables such as time and temperature influence the dimensionality of the product. Perovskites and their associated functionalities are described by a number of authors. Ordering in perovskites is analyzed by Evgeny Antipov et al., Matthew Rosseinsky et al., and Yuichi Shimikawa et al. Antipov et al. discuss the targeted synthesis of anion-deficient perovskites starting from the Brownmillerite structure, whereas Rossieskky et al. present the synthesis of new cation ordered complex perovskites. These complex perovskites are shown to have interesting dielectric properties that have implications for microwave dielectric behavior. Shimikawa et al. discuss the use of high pressure to synthesize perovskite materials with ordered “A” cations. In doing so, various magnetic interactions including ferromagnetism, antiferromagnetism, and ferrimagnetism are observed. Miguel Alario-Franco et al. describe the use of high pressure and high temperature to stabilize a variety of Cr$^{4+}$ materials ranging from “simple” cubic perovskites to misfit layer compounds. Structural complexity is often manifested through their electronic and magnetic properties. Magnetism in perovskites and other materials is presented by Antione Maignan et al. In their article, they examine multifunctional properties, specifically focusing on triangular lattices, as well as layered cobaltites. Mixed-anion systems are the focus of the contributions by Kenneth R. Poeppelmeier et al. and Simon Clarke et al. Poeppelmeier et al. describe a new oxyfluoride compound Ag$_4$V$_2$O$_6$F$_2$ (SVOF). This new mixed-anion compound represents a new battery cathode material that has potential uses in implantable cardioverter defibrillators. Mixed-anion systems are also discussed by Clarke et al. They analyze oxychalcogenides that exhibit a variety of interesting physical properties including semiconducting behavior, magnetism, and redox properties. Clarke et al. also describe recent research in the area of oxypnictides, which has seen an upsurge of interest attributable to the discovery of high-temperature superconductivity (>40 K) in derivatives of LaOFeAs. High-temperature superconductivity is also the subject of the contribution by Michel Pouchard et al. They discuss the existence of copper(III) in addition to charge-transfer excitons in superconducting cuprates. Important functionalities of inorganic materials also involve optoelectronics. Ram Seshadri et al. analyze band-gap engineering in Zn$_{1-x}$M$_x$O (M = Mg, Be, and Cd) solid solutions. This band-gap tuning has profound implications for desired device functionalities. Functional properties with respect to noncentrosymmetric (NCS) materials are the focus of the contributions by P. Shiv Halasyamani et al., Alex Norquist et al., and Jiang-Gao Mao et al. Halasyamani et al. have synthesized a series of polar hexagonal tungsten bronze-type oxides that exhibit a variety of phenomena including ferroelectricity and piezoelectricity. The polarity in the reported materials can be attributed to the octahedrally coordinated d$^0$ transition metals, e.g., Nb$^{5+}$ and W$^{6+}$, which undergo second-order Jahn–Teller (SOJT) distortions. Norquist et al. focus on materials that contain the SOJT-distorted Mo$^{6+}$ cation in combination with chiral organic amines. In doing so, they have synthesized a variety of polyoxomolybdates whose crystal structures range from zero- to three-dimensional. Mao et al. also discuss SOJT cations but with lone-pair metals, specifically Se$^{4+}$ and Te$^{4+}$. These cations exhibit a stereoactive lone pair that results in a locally asymmetric coordination environment often associated with NCS structures.

The Forum Articles represent fundamental research on the synthesis, characterization, and structure—property relationships in functional inorganic materials authored by leaders in the field. We thank all of the authors from the United States, United Kingdom, France, Spain, Russia, India, China, and Japan for writing articles that demonstrate the interdisciplinary nature and excitement of solid-state inorganic chemistry.

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