Advanced Inorganic Materials: An Open Horizon

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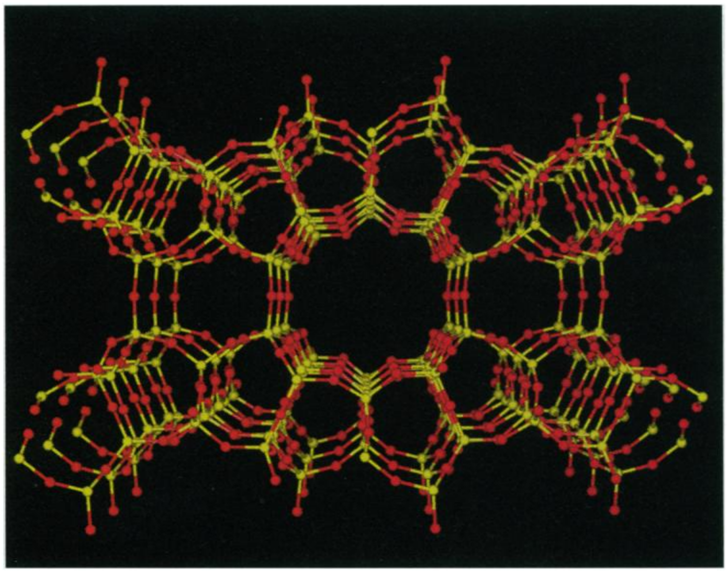
Materials science has traditionally been dominated by the study of structural materials, electronic materials, and polymers, but a new discipline has begun to emerge at the interface between materials science and inorganic chemistry. The emergence has been gradual, and many important inorganic materials, particularly those with simple stoichiometries, have a long history of use. Important examples include the binary oxides of iron, such as γ-Fe_2O_3, which are widely used for magnetic recording and data storage; ZnS, which is found in x-ray scintillation detectors and cathode ray tubes; TiO_2, which finds widespread use as a pigment in paints; and MoS_2, a widely used lubricant.

The field received an enormous boost from the discovery of the superconducting cuprates in 1987, and it has become strikingly apparent that the most interesting of these materials exhibit complex stoichiometries—even nonstoichiometries—and include several components. A good example is $HgBa_2Ca_2Cu_3O_8$, with a critical temperature, T_c, of up to 155 K under pressure (*1*). More recently, the explosion of interest in fullerenes and related materials has given the field a further boost (leaving aside the semantic question as to whether the fullerenes are inorganic materials). The trend toward greater complexity is to be found in other areas, too (Table 1).



Channel viewing. A [001] view of siliceous ferrierite down the 10-ring channel. The 8-ring channel, which is not visible, runs along the [010] direction, across the figure, forming a substantial cavity at the intersection.

Why do such complex stoichiometries lead to materials with such remarkable properties? Variations in the elemental components allow us to fine tune a range of properties, mainly as a consequence of our ability to alter the interatomic distances (by using cations with carefully selected ionic radii), the degree of covalency (by judicious choice of elements), and electronic properties (by varying the oxidation states of key components in a controlled manner). These variations permit us to select the region of phase space that is of particular interest, to adjust important parameters such as the temperatures at which phase transitions occur, and to ensure that the material adopts the preferred crystal structure.

The antiferroelectric perovskite PLSnZT [(Pb,La)(Sn,Zr,Ti)O_3], which is of interest for high-displacement piezoelectric mechanical actuators (*2*), represents an interesting example in which the composition was selected by rational design. The PZT system, $PbZr_{1-x}Ti_xO_3$, has been extensively studied because of its interesting ferroelectric properties, and it is well established that the Curie temperature and dielectric properties can be adjusted by changing the Zr/Ti ratio. Partial replacement of titanium by tin, which as a nontransition metal has less of a propensity to exhibit ferroelectric displacements, causes the high-temperature antiferroelectric phase to be stabilized at room temperature, opening up the possibility of making a switching device. Replacement of some of the Pb^{2+} by La^{3+}, on the other hand, suppresses the formation of lead defects and facilitates the fabrication of materials that are transparent across the entire visible spectral range.

Complex inorganics are playing an increasingly important role in the optical materials area, where relatively simple compounds such as Nd-doped yttrium-aluminum-garnet (for infrared YAG lasers), $LiNbO_3$ (for nonlinear devices) and Cr-doped Al_2O_3 (ruby) have been in use for some time. KTP, $KTiOPO_4$, has attracted a great deal of attention on account of its efficient doubling of the frequency of infrared lasers, such as the 1064-nm line of Nd-YAG, into the visible region (*3*). This property depends on the particular crystal symmetry of KTP, but other remarkable features include its ability to accommodate a wide range of substitutions (for example, Na, Rb, or Tl for K; Sn or Zr for Ti; and As for P), which enables important properties such as the refractive indices to be varied systematically. Another feature is its highly anisotropic ion-exchange behavior, which facilitates the fabrication of high-performance optical wave guides (*4*).

Taking into account the wide range of criteria that have to be met for a compound to perform well in either laser or frequency-doubling applications, it is remarkable that chemistry has yielded a material, Nd-doped $YAl_3(BO_3)_4$, that can successfully perform both of these functions to furnish a self-doubling laser (*5*).

In a rather different area of optical inorganic materials, recent work has shown that red, green, blue, and even ultraviolet light can be generated from an infrared input by a mechanism known as up-conversion. In crystals of Tm-doped $BaY_{2-x}Yb_xF_8$, which has a fluorite-related structure, infrared radiation can be absorbed by the ytterbium ions and transferred by a cross-relaxation mechanism to populate a wide range of the energy levels of thulium; higher energy levels can be accessed by successive excitations (*6*). By working with fluorides rather than oxides, researchers can minimize depopulation of the thulium levels by lattice vibrations and achieve population inversions that enable laser action to take place at a number of different frequencies.

Subtle control over material properties can be achieved by variation of the crystalline architecture as well as the chemical composition, a strategy that is used with remarkable success in microporous materials such as zeolites. This is elegantly illustrated by the extensive range of silica and $AlPO_4$ polymorphs (Table 2), most of which comprise simple corner-sharing SiO_4 (or AlO_4 and PO_4) tetrahedra that can be assembled in an apparently infinite number of ways. The figure shows a typical ex-

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Optical and electronic applications	
Nd-doped $YAl_3(BO_3)_4$	Self-doubling laser
$KTiOPO_4$(KTP)	Frequency doubling and optical wave guides
$YBa_2Cu_3O_{7-x}$	High-T_c superconductor
Rare-earth palladium borocarbides	Superconductor
Tm-doped $BaY_{2-x}Yb_xF_8$	Up-conversion laser
Catalytic and molecular sieving applications	
γ-$(VO)_2P_2O_7$	Butane $\rightarrow$ maleic anhydride
$Cu_2Al_6B_4O_{17}$	Oxidative dehydrogenation
Zeolites and AlPOs	See Table 2
Ceramic applications	
ZrO_2-based systems	Sensors, solid-state electrolytes
Cordierite	Microelectronic packaging
$PbZr_{1-x}Ti_xO_3$	Ferroelectrics and others
$NaAl_{11}O_{17}$	β-alumina solid electrolyte
Others	
Apatites	Synthetic biomaterials (also lasers)
Metal hydrides ($LaNi_5H_x$)	Energy storage
Fullerenes	Molecular electronics
Fe-Nd-B	Permanent magnets

Table 1. Some examples of advanced inorganic materials and their applications.

ample, that of siliceous ferrierite (*7*), in which two types of channels—one defined at its narrowest point by a ring of 10 tetrahedral atoms, and the other, by 8 tetrahedral atoms—intersect to form a larger cavity. Properties such as molecular sieving can be finely honed by the selection of the appropriate pore structure, and shape-selective catalytic functionality can be imparted by the introduction of Brønsted acid sites or redox centers; these properties are exhibited, for example, by the recently reported DAF-1 (*8*), which displays both chemical and structural complexity. Furthermore, the cavities can play host to a range of other species, including small clusters of II-VI semiconductors, coordination complexes for oxygen adsorption or light conversion, and metal clusters for electronic or catalytic applications.

It is not a coincidence that most of the important microporous materials are based on systems containing silicon, aluminum, and phosphorus, because microporous materials are metastable with respect to their condensed polymorphic analogs (although the differences in energy between, say, the various silica polymorphs are only a few kilojoules per mole). They owe their existence to the collapse of the kinetic barriers, which stem from the strengths of the Si–O, Al–O, and P–O bonds, and in this respect, there is an analogy with the kinetic stability of organic materials with respect to combustion. This perspective yields some insight into other systems that might be stabilized in microporous form. Borates are potential candidates, as are systems containing octahedrally coordinated transition metal ions that are stabilized by ligand field effects, such as Cr^{3+} and Rh^{3+}. One of the recently discovered titano-silicate sieves contains octahedrally coordinated Ti^{4+} as a discrete structural element, rather than as a substituent for tetrahedrally coordinated silicon (*9*). Other classes of periodic microporous materials are certain to emerge as the synthetic effort in this area intensifies.

In many systems that have been studied to date, it must be admitted that discoveries have arisen not from rational design but serendipity or shear perseverance, as is apparent from much of the work in the high-T_c area. But greater emphasis is now being placed on more rational synthetic strategies along the lines that have long been commonplace in organic and organometallic chemistry. For example, the strategy known as "chimie douce," or "soft chemistry," has had a major impact on our ability to prepare metastable insertion compounds of the early transition metal oxides (*10*), some of which show promise for applications in batteries and electrochromic devices. Zeolites are being used not only as microporous solids but also as versatile precursors for the synthesis of high-performance ceramics (*11*). And in another recent example, the self-assembling surfactant templates have been used in the synthesis of a new class of mesoporous solids (*12*). Future developments will also include greater emphasis on combined inorganic-organic materials, including composites, a trend that was clearly apparent in the sessions on sol-gel synthesis at a recent meeting of the Materials Research Society (*13*). Attention must focus not only on chemical composition, structure, and reactivity, but also, for materials that must be functional as well as interesting, on issues such as microstructure, processibility, and durability.

Silica polymorph	Pore system	Applications	$AlPO_4$ analog
Faujasite (zeolite X,Y)	Three-dimensional 12-ring windows	Catalytic cracking	$SAPO_4$-37*
ZSM-5 (silicalite)	Two-dimensional 10-ring windows	Xylene isomerization, methanol to gasoline	Unknown
SSZ-24	One-dimensional	Hydrocracking	$AlPO_4$-5
Ferrierite	Two-dimensional 10- and 8-ring windows	C_4 isomerization	Unknown
Chabazite†	One-dimensional 8-ring windows	Cation exchange	$SAPO_4$-34

*$SAPO_4$ materials are $AlPO_4$ structures that also contain framework silicon atoms. †Forms only as an aluminosilicate; pure silica polymorph unknown.

Table 2. Some examples of microporous silica and $AlPO_4$ polymorphs.

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