Robert E. McCarley

Solid-State and Metal Cluster Chemistry

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Synthesis in solid state chemistry represents the overall theme of research in this group. For many years, we have excelled in the synthesis of new compounds whose structures are dominated by strong metal-metal bonding. Among the objectives here are the preparation of materials containing either discrete molecular cluster units or extended chains, sheets and networks. Examples include the first preparation of molecular analogs of the famous superconducting Chevrel phases, viz. the molecular cluster complexes Mo$_6$S$_8$L$_6$, with L = PR$_3$, CsH$_5$N, etc., and halide substituted members Mo$_6$S$_8$-xCl$_x$L$_6$. A number of unprecedented structures having strong M-M bonding has resulted from our work on the reduced oxide systems of molybdenum: Ba$_{1+}$M$\text{Mo}_6$$\text{O}_{16}$ and Nd$\text{Mo}_6$$\text{O}_{14}$ with discrete cluster units; Na$_3$Mo$_6$O$_{14}$, Na$_2$$\text{Mo}_5$$\text{O}_{11}$, Gd$_4$Mo$_{11}$O$_{22}$, Ce$_7$Zn$_{25}$Mo$_4$O$_{7}$, and Ca$_{18}$Mo$_{18}$O$_{32}$ with infinite chains in one dimension; Li$_2$Mo$_6$O$_{10}$ and Zn$\text{Mo}_6$$\text{O}_{10}$ with infinite chains in two dimensions; and Li$\text{Mo}_6$O$_2$ with infinite sheets. Besides synthesis this work includes characterization by structure determination and elucidation of important physical properties and chemical reactivity. We have found that several of these compounds are essentially one- or two-dimensional metals because electrical conductivity is limited to the chain directions of the structures.

A new area of research for us concerns the synthesis of novel materials by low temperature approaches utilizing reactive molecular precursors. Many of the target materials will be thermodynamically unstable and thus special approaches are needed in their preparation. Examples here include oxides, nitrides and sulfides such as Nb$_2$N$_5$, WN$_2$, Mo$_2$O$_5$, and W$_6$S$_8$ which should have interesting structures and properties, but are presently unknown. To prepare these materials we must obtain conversion at lower temperatures than usual in order to prevent their decomposition. Special emphasis is placed on design and synthesis of reactive precursors which can be converted to the desired compounds by suitable reactions at lower than usual temperatures. In general the methods used here will lead to amorphous or polycrystalline powders and methods such as X-ray and neutron powder diffraction Rietveld analysis, EXAFS, FT-IR, and solid state nmr must be used to obtain structural information.

Selected Publications


