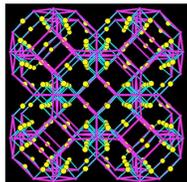


Designing Intermediate Range Order in Amorphous Materials

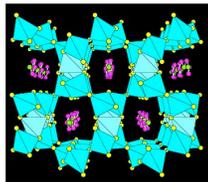
J. D. Martin, S. J. Goettler, N. Fossé (North Carolina State University) and L. E. Iton (ANL-MSD)

The intermediate-range order (IRO) in zinc chloride-based network glasses has been identified with the arrangement of voids in the network. The signature of IRO is the low-Q peak in the total structure factor, which can be measured with neutrons in an amorphous diffraction experiment. We have used organic templating cations and applied the principles of crystal engineering to show how the IRO in the zinc chloride-based glasses can be systematically manipulated. The structures of the resulting glasses can be analyzed on the basis of the structures of the corresponding crystalline nanoporous materials.

HALOZEOTYPE MATERIALS



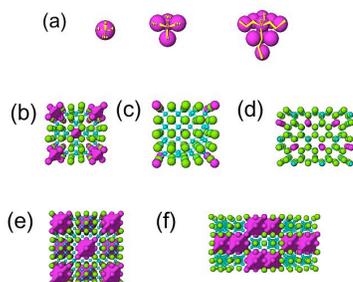
CZX-1 "Sodalite"
[HNMe₃][CuZn₅Cl₁₂]



CZX-2&3
[H₂NR₂][CuZn₅Cl₁₂]
(R = Me or Et)

A family of crystalline, nanoporous copper/zinc chloride materials formed with the incorporation of non-framework organic templating cations as network modifiers. The alkylammonium templating cations occupy regular voids in the framework. The charge on the templating cation is compensated by substitution of monovalent copper ions for divalent zinc ions in the network in analogy with the zeolitic aluminosilicates. This prevents depolymerization of the ZnCl₂ network. The compounds melt at moderate temperatures (150 - 250 K) and can be quenched into glassy forms.

AMORPHOUS MATERIAL DESIGN

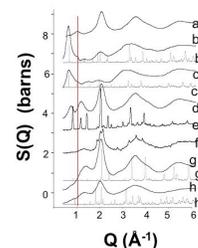


Alkylammonium templating ions were chosen with sizes to match an integral number of chloride anions being displaced in creating a void (1, 4, and 10 chlorides for methylammonium (MA), trimethylammonium (HTMA), and tetrapropylammonium (TPA) ions, respectively.) Equimolar amounts of CuCl and the alkylammonium chloride are incorporated into ZnCl₂.

Structural models of templates and networks show: (a) Comparison of alkylammonium templates to the close-packed assembly of one, four, and ten chlorides. (b)-(f) Network structures for: (b) CZX-1, [HTMA]₂Cu₂Zn₁₀Cl₂₄; (c) CZX-5, [MA]₂M_{24-x}Cl₃₀; (d) β-CZX-4, [MA]Cu₂Zn₂Cl₇; (e) CZX-7, [TPA]₄M_{40-x}Cl₆₈; and (f) CZX-6, [TPA]CuZn₃Cl₈. The cation-filled network voids are represented by the purple-shaded polyhedra with purple spheres in sites where chloride ions have been displaced from the close-packed anion sublattice. Blue spheres correspond to metal sites, and green spheres represent the chloride ions.

TUNING INTERMEDIATE-RANGE ORDER

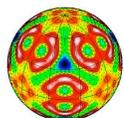
Neutron diffraction measurements made on GLAD at IPNS for glass compositions corresponding to known or postulated crystalline structures. Total structure factors are shown for: vitreous (a) ZnCl₂; (b) [d²⁸-TPA]-1:1:5; (c) [d²⁸-TPA]-1:1:3; (d) [d¹⁰-HTMA]-1:1:5; and (g) [d⁶-MA]-1:1:5; for (e) recrystallized [d¹⁰-HTMA]-1:1:5; and (f) recrystallizing vitreous [d⁶-MA]-1:1:5. Calculated powder diffraction patterns are shown for the model lattices CZX-7 (b'), CZX-6 (c'), CZX-5 (g'), and β-CZX-4 (h'). The low Q structures exhibit a pronounced dependence on the composition. The templates systematically modify the IRO. The low Q structure can be indexed in each case to Bragg reflections from planes in the corresponding crystalline model. The IRO is associated with the pseudo-ordering of voids on the nanometer length scale.



IMPACT AND IMPLICATIONS

The association between IRO and void arrays has been established. The principles of amorphous network engineering employed in this work can be extended to other classes of materials, such as halides, chalcogenides, oxides, fluorides, and perhaps even alloys. Similar variations in amorphous structure have been observed in scattering from unheated zeolite synthesis gels. Furthermore, the IRO can be interpreted using crystalline lattice models. Therefore, complex IRO can be designed by suitable choice of templating ions and adhering to zeolite-type network charge compensation guidelines. Specific optical, electronic and mechanical properties might thereby be engineered. The concept of designed IRO could also be extended to structuring of fluids for control of thermal and other properties.

J. D. Martin, S. J. Goettler, N. Fossé, and L. E. Iton, *Nature* 419, 381 (2002)



BES - DOE

This work was supported by the NSF and by the U.S. Department of Energy, Basic Energy Sciences, under contract W-31-109-ENG-38.

MSD - ANL

