

Designing Structure in Molten Metal-Halide Networks over Angstrom to Nanometer Length Scales.

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The liquid state of matter remains one of the least understood states of matter from an atomic and molecular perspective. Nevertheless, as a condensed state of matter, atom-atom contacts in liquids are virtually identical to atom-atom contacts in crystalline solids. Therefore, chemical bonding in the liquid state must be strongly related to the nature of chemical bonding in the crystalline condensed state of matter. Our exploration of the relationship between chemical bonding in crystalline and molten systems is uncovering unprecedented possibilities for amorphous materials engineering that are analogous to recent advances in crystal engineering.^{1,2}

Liquid crystals represent the most highly ordered form of liquid matter, with regular molecular organizations over length scales of hundreds of nanometers such that optical interference with polarized visible light can be observed as complex textures. Such molecular organization, in the liquid state, is typically achieved through the synthesis of highly anisotropic molecular shapes. Although liquid crystallinity was recognized in inorganic sols of V_2O_5 in 1925,³ synthetic control over molecular structure afforded by well known organic syntheses has resulted in the vast majority of liquid crystals being organic molecules, or molecules with anisotropic organic ligands affixed to metals to form metallomesogens.

Anisotropic structure is observed in numerous inorganic systems including anisotropic networks, 1-D chains, and 2-D layers. These have largely been studied in the crystalline solid-state. Very little is understood about the structure of these in the molten state. Nevertheless, liquid crystalline behavior in inorganic fluids should be possible if anisotropic structure can be retained, or designed into the liquid phase.

Many glass forming inorganics, such as SiO_2 , GeS_2 , and $ZnCl_2$, are known to retain significant network structure into their melts.^{4,5} Exploiting the relatively low melting temperature of late transition-metal and main-group chlorides, as well as the significant covalency of their bonding, we have investigated the nature of, and design of structure in their melts.

The melts of materials across the periodic series $CuCl$, $ZnCl_2$, $GaCl_3$ and $GeCl_4$ provide an understanding of the development of network structure in binary melts. The structure of each of these melts is impacted by the symmetry with which the respective metal cations are bonded throughout an approximately close packed anion sublattice.

These network structures can readily be templated, even in the molten state, using alkylammonium or alkali metal cations to yield anisotropic or network structures. 1-D chains $[Cu_2Cl_3^-]_n$ are formed in the crystalline state with a variety of templating cations.

The nature of the templating cation/anionic chain interactions has a dramatic effect on the melting point of these materials. And significant structure is preserved into the molten state.

Using a zeolite-type templating strategy, combining equal amounts of a templating salt, AlCl_3 , and CuCl with ZnCl_2 , halozeotypes, $\text{A}_n[\text{Cu}_n\text{Zn}_{m-n}\text{Cl}_{2m}]$, have been prepared.⁶ Much of the zeolites-type network structure is retained in the low temperature melts of these materials.¹ These patterns of organization are demonstrated to persist over tens to hundreds of angstroms with small alkylammonium cations as templates. However, when alkylammonium surfactants are employed as the templating agents classic metallotropic liquid crystalline behavior, related to smectic-type organization, is observed for materials with up to 80 mole percent of the inorganic halide.

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³ Zocher, H., Über freiwillige Strukturbildung in Solen. *Z. Anorg. Allg. Chem.*, **147**, 91-111 (1925).

⁴ M. P. Tosi, D. L. Price and M.-L. Saboungi, *Ann. Rev. Phys. Chem.*, **1993**, *44*, 173-211

⁵ W. A. Crichton, M. Mezouar, T. Grander, S. Stølen, and A. Grzechnik, *Nature*, **2001**, *414*, 622-625.

⁶ J. D. Martin and K. B. Greenwood. *Angew. Chem.*, **1997**, *36*, 2072-75.