DESIGN AND STRUCTURES OF POROUS MOF CRYSTALS LARGELY COMPOSED OF NOTHING

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A strategy based on reticulating metal ions and organic carboxylate links into extended networks has been advanced to a point that allowed the design of porous structures in which pore size and functionality could be varied systematically. The pore size can be varied from 3.5 to 28.8 Å and crystal density from 1 to 0.2 g/cm^3.

Keywords: MICROPOROUS DESIGN METAL ORGANIC

UNUSUAL STRUCTURAL BEHAVIOR IN PURE SILICA ZEOLITES

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We have recently studied in detail two unusual structural phenomena, giving rise to interesting materials properties, in some pure silica (SiO_2) polymorphs having zeolitic structures. The first is an extension of our earlier work on the observation of strong negative thermal expansivity (thermal contraction) in a wide variety of zeolitic materials (1). These studies have now been extended to single crystal diffraction analysis, using synchrotron radiation, on microcrystals of around 4000 cubic micron size. We shall present results on two pure silica zeolites, ITQ-4 (IFR) and ferrierite (FER), which show an overall volume contraction over a wide temperature range. In the case of IFR this is shown to be related to distortions of particular secondary building units, rather than changes in individual bond lengths and angles (2). The second phenomenon is the remarkable imposition of polar guest (template) ordering in IFR, mediated by ordering of fluoride ions within small cages of the IFR framework. This represents a novel way of designing non-linear optical materials using chemical control at the synthesis stage (3).

References
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Keywords: ZEOLITES, THERMAL CONTRACTION, OPTICAL ACTIVITY

THE DEVELOPMENT OF DIRECT-SPACE TECHNIQUES FOR SOLVING CRYSTAL STRUCTURES FROM POWDER DIFFRACTION DATA

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Many solids can be prepared only as microcrystalline powders and are therefore not suitable for structural characterization by conventional single-crystal diffraction methods. For such materials, it is necessary to tackle structure determination using powder diffraction data. Although there are many examples in which traditional techniques for structure solution from powder diffraction data have been applied successfully in this field, organic molecular crystals represent a particularly challenging case. The direct-space approach [1] for structure solution has led to new opportunities in this field, and is now used widely in structure determination of molecular crystals from powder diffraction data. In the direct-space strategy, a hypersurface defined by an appropriate R-factor (in our case the powder profile R-factor R_{wp}) is searched using an appropriate global optimization technique. Currently, we are focusing [2-4] on the implementation and application of Genetic Algorithm techniques in this field. The lecture will describe new developments in our understanding of fundamentals of the Genetic Algorithm technique and the optimum strategies for its implementation in powder structure solution. Recent results obtained from the application of this method will be presented.

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TOWARDS A GLOBAL METHODOLOGY FOR DIRECT METHODS: FEASIBLE SETS

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Classically, direct methods have developed by exploiting either atomistic or statistical equalities, inequalities or probabilities to generate relationships between the phases of diffracted beams. These have then been combined with a method such as the tangent formula to generate improved phase estimates from some initial methods. We have recently pointed out that the contemporary mathematical approach called "feasible sets" can be exploited to provide a general framework for direct methods within which new strategies can be developed. The feasible set approach considers constraints as equivalent to sets, and the true solution as the intersection of these sets. Remarkable, a simple strategy called projections is known to rapidly produce solutions, functionally equivalent to gradient-based methods without the computational cost associated with specifically calculating them. It is also relatively simple to include unconventional (for crystallography) constraints such as those associated with dynamical diffraction. This presentation will provide an overview of the feasible set approach, ranging from simple examples such as describing difference maps as a projection onto a known structure to more complicated cases such as maximum entropy as a banach projection and the inclusion of finite supports to solve three-dimensional surface structure problems.

Keywords: DIRECT METHODS SURFACES ELECTRON DIFFRACTION