

Barcelona (UB-IEEC), Barcelona (Spain). <sup>c</sup> Department of Chemistry, Yale University, (USA). E-mail: sabino@icmm.csic.es

The classical nucleation theory is applied to the modelling of the cluster size distribution in supersaturated boiling sodium chlorate solutions. It was recently reported by the authors that under these conditions a strong bias of enantiomorphic crystals of the same chiral sign is obtained [1]. Given the catastrophic nature of the crystal nucleation process in boiling highly concentrated solutions, it was reasonable to hypothesize that the chiral selection was a result of molecular recognition among the clusters by collisions in the metastable period. Experimental support of this assumption was obtained recently by us in a series of experiments where the supersaturated solution carefully extracted, before the appearance of the first crystals, was also able to develop nearly homochiral samples [2]. Nevertheless, this mechanism only could be operative if the subcritical clusters have enough size to have a definite chiral sign.

In this contribution we evaluated the cluster size distribution in equilibrium with isolated molecules of sodium chlorate using the classical approach applied to cubic clusters using the formalism of K. Sangwal [3] and the value of 0.012 J/m<sup>2</sup> for the solid-solution surface energy for the sodium chlorate [4]. The critical cluster obtained by the degree of supersaturation attained at the onset of the nucleation contained 61 chlorate units, a cluster of such size clearly has a definite chirality as supposed, i.e. it cannot racemize. The metastability of the system was evaluated assuming that the nucleation appears when the first critical nucleus is formed giving a result comparable with the experimental. Finally the wall effect, (high temperature gradients are always presents in boiling systems near the heating wall), was also simulated showing a shift towards smaller cluster sizes in hotter zones. This phenomenon is important because it drives the partial dissolution of the clusters (recycling), an effect of importance in all the theoretical symmetry breaking scenarios. What is more, the calculations showed that this recycling increases with the supersaturation. As a result the degree of the homochirality of the population of crystals obtained should increase with the supersaturation and this is what effectively was observed.

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### The effect of solvents on the dissociation and association of decavanadates

Tatsuhio Kojima,<sup>a</sup> Mark R. Antonio<sup>b</sup> and Tomoji Ozeki,<sup>a</sup> <sup>a</sup>Department of Department of Chemistry and Materials Science, Tokyo Institute of Technology. <sup>b</sup>Chemical Sciences and Engineering Division, Argonne National Laboratory. E-mail: tkojima@chem.titech.ac.jp

Tetra-*n*-amylammonium decavanadates show both the dimeric and monomeric hydrogen-bonded molecular complexes in the crystalline state, depending upon the protophobic or protophilic nature of the solvent. On the one hand, protonated decavanadate anions self-assemble into self-complementarily hydrogen-bonded dimers,  $\{[H_3V_{10}O_{28}]_2\}^{6-}$ , when crystallized with acetone. On the other hand, they form hydrogen bonds with solvent molecules and remained monomers,  $[H_4V_{10}O_{28}]^{2-}$ , when crystallized with 1,4-

dioxane.<sup>[1]</sup> By using SAXS and <sup>1</sup>H- and <sup>51</sup>V-NMR, we revealed that the behavior of the protonated decavanadate anions between the dimers and monomers depends on the protophobic and protophilic nature of acetone and 1,4-dioxane, respectively, also in the solution state.<sup>[2]</sup>

Herein, in order to compare the effect of other solvents on the dissociation or association between the dimers and monomers, we measured SAXS, <sup>1</sup>H-NMR and <sup>51</sup>V-NMR spectra of  $[(n-C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$  in acetone, acetonitrile, tetrahydrofuran, 1,4-dioxane and the mixtures of these solvents. Radius of gyration,  $R_g$ , estimated from the observed SAXS data was employed as a measure of the dimer formation. In order to determine the average  $R_g$ , we used three fitting methods (Guinier, form factor, and pair-distribution analyses) on the SAXS data that were collected at 12ID-B and 12ID-C beamlines in APS.  $R_g$  for the solution in 100% acetone and 100% acetonitrile were 5.9(1) Å and 5.8(1) Å, respectively. These values agree with those calculated from the crystal structure 5.1 Å for the dimer,  $\{[H_3V_{10}O_{28}]_2\}^{6-}$ , indicating that the decavanadate anions associate to the dimer. On the other hand,  $R_g$  for the solution in the tetrahydrofuran was 4.3(3) Å. This value is between those for the dimer (5.1-6.6 Å) and monomer (3.5 Å), indicating that a certain amount of decavanadate anions dissociate into the monomers. In case of the system of acetone and 1,4-dioxane, the dissociation into the monomers was completed in the mixed solvent consisting of 20% acetone and 80% 1,4-dioxane. Therefore, tetrahydrofuran has a weaker effect on the dissociation of the dimer into the monomers than 1,4-dioxane. These results are also confirmed by <sup>1</sup>H-NMR and <sup>51</sup>V-NMR spectra.

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### Spontaneous mirror symmetry breaking in the crystallization of NaClO<sub>3</sub>

Josep M. Ribó,<sup>a</sup> Zoubir El-Hachemi,<sup>a</sup> Joaquim Crusats,<sup>a</sup> J. Michael McBride,<sup>b</sup> Sabino Veintemillas-Verdaguer,<sup>c</sup> <sup>a</sup>Department of Organic Chemistry and Institute of Cosmos Science, University of Barcelona (IEEC-UB) Barcelona (Spain). <sup>b</sup>Department of Chemistry, Yale University, New Haven CT (USA). <sup>c</sup>Centro de Astrobiología, CSIC-INTA, Madrid (Spain) and Departament of Biomaterials and Bioinspired Materials, Instituto de Ciencia de Materiales de Madrid CSIC, Madrid (Spain). E-mail: jmribo@ub.edu

A transition towards chirality in the crystallization of NaClO<sub>3</sub> in supersaturated boiling solutions is reported [1]. The results agree with previous one obtained by wet grinding and point to a different mechanism than those of previous reports originated by secondary nucleation growth of a single chiral Adam crystal.

The phenomenon is discussed here on the basis of a thermodynamic scenario of non-uniform temperature distribution in the metastable supersaturated state. During this period, the evolution of the population of sub-critical nuclei takes place without any other noticeable crystal growth process. The fast evolution of supercritical nuclei and the experimental procedure of immediate separation of the crystals formed reasonable excludes secondary nucleation and Ostwald ripening as the cause of the transition towards chirality in these experimental conditions. Therefore, the evolution towards homochirality should be attributed to the primary nucleation process when maintained in a stationary state. The bifurcation towards a stationary homochiral state is a consequence of the instability of the system due to the chiral

recognition of enantiomorphic solid phases as thermodynamically distinguishable entities and the absence of degrees of freedom when P and T are fixed in the 2-component system (compound and solvent).

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### Multiquot algorithm for the automation of structure determination from powder

Smirnova Olga, Institute of Chemical Research, Kyoto University (Japan). E-mail: smirnova@msk.kuicr.kyoto-u.ac.jp

Recently mentioned [1] inconsistency of figures of merit [2], [3] when indexing high symmetry lattices turned to a conclusion the smaller cells of lower symmetry can be applied as building units when solving a structure by direct space methods. The approach is expected to decrease time necessary for simulated annealing of one structure solution and may appear particularly useful for large organic structures. The poster illustrates the approach based of example compounds with a small pyrochlore structure. The indexing program suggest several possible solutions and the correct solution of highest symmetry among them. The repetition of the same lattice described by different cells should be considered as an indication of the correct indexing solution. From the other hand, that might be random and unfruitful indexing solution if the lattice is non-primitive but is not observed among proposed cells with its primitive representation. The extension to indexing algorithms, eliminating lower symmetry cells for the same lattice described by high-symmetry cell, and the corrected figures of merit taking into account the number of equal proposal cells might be drawn as follows:

$$M'(20) = M(20) \cdot N_{ep}$$

$$F'(20) = F(20) \cdot N_{ep}$$

where  $M(20)_h$  and  $F(20)_h$  are  $M(20)$  and  $F(20)$  for the highest symmetry cell

$N_{ep}$  is the number of equal proposal cells

Then, one may start to search for the structural model applying a cell of lower/volume symmetry providing it may represent a building unit for the larger cell of higher symmetry or may assist to find a sublattice.

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### Optimizing the input parameters for powder charge flipping

Dubravka Šišak, Christian Baerlocher, Lynne B. McCusker, Laboratory of Crystallography, ETH Zurich, (Switzerland). E-mail: dsisak@mat.ethz.ch

The charge-flipping structure-solution algorithm [1,2] implemented in the program *Superflip* [3] and adapted to accommodate powder diffraction data [4] is proving to be a powerful one for solving the structures of polycrystalline materials. A variety of structures have been solved, but as the program is relatively new, the selection of the values for the input parameters has been rather arbitrary. Consequently, a systematic study of the effect of the different parameters on the structure solution was undertaken. Several aspects were investigated: (1) the effect of the input parameters themselves, (2) the effect of data resolution, and (3) the effect of including information from other sources. In parallel, criteria for identifying the better solutions were sought.

As it was not considered to be sensible to test all combinations of all parameters, a more pragmatic approach was followed. Combinations of input parameters chosen to fall into what were thought to be sensible ranges were tested. The parameters were: (1) the reflection overlap factor ( $\kappa$ ), (2) the isotropic atomic displacement factor ( $B_{iso}$ ), (3) the cycle for starting the repartitioning of overlapping reflections and the repeat interval, and (4) the threshold value for charge flipping ( $\delta$ ). To investigate possible differences between inorganic and organic materials, the tests were performed on the zirconium phosphate (ZrPOF-Q1) [5] and on D-ribose data [6].

The structure of ZrPOF-Q1 was originally solved using *Superflip*, but the solutions lacked locations of a few of the Zr, P and O atoms in the zirconium phosphate layers and of the quinolinium ions between the layers. Furthermore, the presence of a center of symmetry only became apparent during the refinement. With optimized input parameters, the centro-symmetric space group was recognized by *Superflip* and complete zirconium phosphate layers could be found in the electron density map. Diffuse clouds of electron density between the layers (quinolinium ions) were apparent.

The structure of D-ribose was solved using a combination of simulated annealing and difference Fourier analysis. None of the initial tests of the *Superflip* input parameters yielded a structure solution. Reasoning that starting with more realistic set of phases might help, possible models were generated using the direct-space program FOX [7]. None of these were correct, but by using the phases calculated from a flexible model to generate starting phase sets, and varying the input parameters once again, a set of optimal parameters could be found, and easily interpretable electron density maps with the correct symmetry generated.

In both cases, the optimization procedure was repeated for lower resolution data. For ZrPOF-Q1, the structure could still be solved with 1.8 Å data, and for D-ribose, with 1.18 Å data. Recognizing the best solutions from *Superflip* remains a challenge, but a cluster analysis of the solutions looks promising and is currently being investigated more carefully.

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### More reliable intensity extraction from powders using texture

Jürgen Grässlin,<sup>a</sup> Lynne B. McCusker,<sup>a</sup> Christian Baerlocher,<sup>a</sup> Fabia Gozzo,<sup>b</sup> Bernd Schmitt,<sup>b</sup> Luca Lutterotti,<sup>c</sup> <sup>a</sup>Laboratory of Crystallography, ETH Zurich, (Switzerland). <sup>b</sup>Swiss Light Source,