

## Hydrogen-bonding Patterns and Ice Nucleation

INVESTIGATIONS of hydrogen-bonding patterns of organic crystal surfaces in these laboratories have shown that the ability to nucleate ice can be predicted reliably if the complete crystallographic structure is known. Both 'parametric' fit and the density of hydrogen-bonding groups are essential factors conferring nucleative ability, and it is on these principles (which will form the subject of a more detailed presentation in the near future) that a new organic highly effective nucleating material has been forecast for the first time.

A consideration of the crystal structure<sup>1</sup> of the  $\alpha$ -isomer of 1:3:5-cyclohexanetriol dihydrate ( $\alpha$ -phloroglucitol dihydrate) led us to expect high nucleative power, which was confirmed by cloud chamber tests. Counts of up to  $10^{11}$  nuclei/g were obtained at a temperature of  $-12^\circ\text{C}$ , although owing to the high solubility of the compound tests could not be run above  $-8^\circ\text{C}$ . In comparison, the most active organic nucleators known at the present time (phloroglucitol dihydrate and  $\alpha$ -phenazine) produce  $10^{11}$ – $10^{12}$  nuclei/g under identical conditions, whereas silver iodide is slightly more active still.

Each oxygen atom in the 111 plane of the rhombohedral  $\alpha$ -phloroglucitol dihydrate corresponds to an ice oxygen, the discrepancy being 4.8 per cent. The density of oxygen groups is very close to that of ice and about 50 per cent greater than on the 100 plane of phloroglucitol dihydrate.  $\alpha$ -Phloroglucitol, being a polyalcohol, shows a much higher solubility in water and it is also more difficult to sublime without decomposition. It does not, however, possess a sweet taste like phloroglucitol as stated in Beilstein.

The compound was prepared by the method of Wislicenus<sup>2</sup> in which phloroglucitol is hydrogenated with sodium amalgam. After removing all traces of phloroglucitol as well as the  $\beta$ -isomer of phloroglucitol, the correct m.p. of  $184^\circ\text{C}$  was obtained.

Because of its alicyclic nature and polyalcoholic character,  $\alpha$ -phloroglucitol is probably non-toxic.

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<sup>1</sup> Anderson, P., and Hassel, O., *Acta Chem. Scand.*, 2, 5, 537 (1948).

<sup>2</sup> Wislicenus, W., *Ber.*, 27, 357 (1894).

## High-pressure Polymorph of Zirconium Pyrophosphate

ZIRCONIUM pyrophosphate is one of a group of isostructural compounds of the Type  $X^{+4}P_2O_7$ , where X may be zirconium, hafnium, titanium, silicon, tin or uranium<sup>1,2</sup>. It is cubic (Type  $K6_1$ ) with zirconium octahedrally, and phosphorus tetrahedrally, co-ordinated with oxygen. The structure may be compared with that of NaCl (Type B1) by considering the zirconium ions and  $P_2O_7$  groups to be at sodium and chlorine sites, respectively.

Reagent grade  $ZrP_2O_7$  containing ~12 per cent of water, which corresponds to  $ZrP_2O_7 \cdot 2H_2O$ , was obtained from Bios Laboratories, Inc., New York. This material was heated in air at  $700^\circ\text{C}$  for 4 h, and its identity as anhydrous cubic  $ZrP_2O_7$  was confirmed by X-ray powder diffraction ( $a_0 = 8.26 \text{ \AA}$  in agreement with the observation by Harrison *et al.*<sup>3</sup>). The anhydrous  $ZrP_2O_7$  was subjected to pressures between 25 and 100 kbars and temperatures of  $750^\circ$  and  $1,000^\circ\text{C}$  in a 'belt'<sup>4,5</sup> and a 'girdle' apparatus<sup>6</sup>. The samples were quenched under pressure and then examined optically and by X-ray powder methods. The conditions and results of these experiments are given in Table 1.

One hundred per cent conversion to a new quenchable high-pressure polymorph of  $ZrP_2O_7$  was effected at 55 and 100 kbars. The new phase is colourless under the microscope and white in powder form. It is uniaxial positive

Table 1. HIGH-PRESSURE HIGH-TEMPERATURE EXPERIMENTS ON  $ZrP_2O_7$ .

Pressure (kbars)	Temperature ( $^\circ\text{C}$ )	Time (h)	Product
25	1,000	18	Cubic $ZrP_2O_7$
35	750	19	Cubic $ZrP_2O_7$
55	750	20	High-pressure polymorph
100	1,000	3	High-pressure polymorph

The 100-kbar run was made in a 'girdle' apparatus; the others were made in a 'belt' apparatus

Table 2. X-RAY POWDER DIFFRACTION DATA FOR HIGH-PRESSURE POLYMORPH OF ZIRCONIUM PYROPHOSPHATE (Mn-filtered  $FeK\alpha_1$  radiation,  $\lambda = 1.93597 \text{ \AA}$ , 57.3 mm camera)

$d(\text{\AA})$	I	$d(\text{\AA})$	I
4.76	10	1.302	2
3.72	50	1.281	5
3.465	2	1.272	1
3.316	15	1.253	15
3.207	2	1.227	25
3.155	60	1.214	10
2.948	40	1.167	4
2.597	3	1.156	20
2.445	3	1.135	2
2.411	4	1.115	20
2.319	6	1.099	2
2.160	3	1.087	20
2.041	100	1.074 <sub>B</sub>	2
1.873	10	1.061	30
1.806	1	1.055	1
1.748	30	1.054	1
1.632	1	1.052	10
1.615	50	1.034	5
1.586	5	1.029	20
1.521	1	1.022	70
1.485	5	1.005	1
1.462	50	0.9954	2
1.449	1	0.9928	7
1.420	30	0.9862	30
1.392	1	0.9817	3
1.382	15	0.9796	2
1.353	1	0.9730	10
1.328	3		

Table 3. MOLAR REFRACTION AND SPECIFIC REFRACTIVITY OF THE CUBIC AND HIGH-PRESSURE POLYMORPHS OF  $ZrP_2O_7$ .

Polymorph	Mean refractive index ( $n$ )	Density ( $d$ ) g/c.c.	Molar refraction $(\frac{n^2-1}{n^2+2} \cdot \frac{M}{d})$	Specific refractivity $(\frac{n-1}{d})$
Cubic	1.661	3.13	31.31	0.211
High-pressure	1.761*	3.62	30.17	0.210

\*  $\sqrt[3]{\omega^2}$   
 $M$  = molecular weight

with  $\epsilon = 1.773$ ,  $\omega = 1.755$ , both  $\pm 0.003$ , and  $\epsilon - \omega = 0.018$ . The crystallites have an average size of about  $20\mu$ , but a few crystals as large as  $40\mu$  were observed. The crystallites are anhedral so there is no direct indication whether this phase is tetragonal or hexagonal. X-ray powder diffraction data are given in Table 2. The density of the new phase is  $3.62 \pm 0.02$  as determined by float-sink methods using Clerici's solution. The high-pressure phase, therefore, is 15.7 per cent denser than the cubic form, which has a density of 3.13, calculated from its lattice parameter.

The high-pressure phase inverts to the cubic form within 3 h when heated at ambient pressure in air at  $1,000^\circ\text{C}$ .

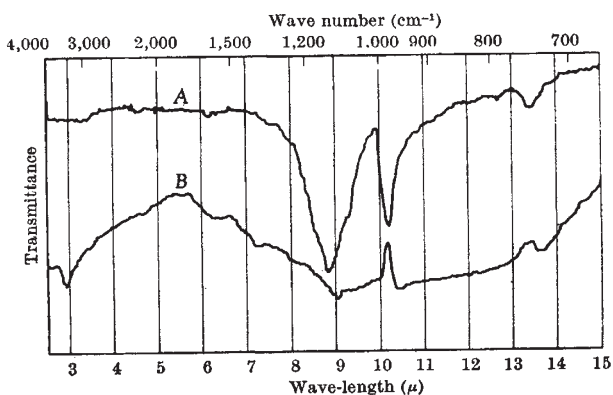


Fig. 1. Infra-red absorption spectra of the cubic and high-pressure polymorphs of  $ZrP_2O_7$ . Spectra obtained with Perkin-Elmer Infracord recording spectrophotometer using the KBr disk technique. A, cubic form preheated at  $700^\circ\text{C}$ ; B, high-pressure form prepared from (A) at 55 kbars and  $750^\circ\text{C}$