

X-ray diffraction studies of some sols and gels

The development of highly concentrated sols and gels has promoted keen interest in the ceramics industry by virtue of the improved fabrication routes available [1-4], but to our knowledge no serious X-ray diffraction study of sols, gels, or the gelation process, has previously been attempted. Cogliati *et al.* [5] used X-ray line broadening to characterize colloidal dispersions of thorium produced at different temperatures. They found that the average size of the ordered regions (crystallites) is greater in solutions prepared at higher temperatures, material produced at 80°C having an average crystallite size between 50 and 100 Å. The angular shift of the diffraction maxima with respect to standard thorium oxide was attributed to a lattice expansion. Similar techniques have been used by these and other workers [6] to measure the crystallite size of uranium (IV) and boehmite colloidal dispersions, but the interpretation of the results was usually superficial.

In the present work crystalline changes occurring on gelation were studied using X-ray methods. Both sols and gels* were examined on a Philips P.W. 1050/25 diffractometer using a standard 20 mm × 10 mm aluminium sample holder backed by a glass plate. Continuous and intermittent scans were obtained and the numerical data processed by computer [7]. Where possible, two diffraction peaks were used to calculate the crystallite size and three measures of line breadth were employed, namely the slope (K) and intercept (W_0) of the variance-range characteristic and the profile integral breadth. To preserve the smooth sample surface and prevent gelation during the examination of sols, the top of the sample holder was covered with a very thin film of celloidin and the specimen cavity was filled from the rear.

A high nitrate dispersible alumina gel gave a diffraction pattern which could not be ascribed to any known hydrate or oxide of alumina, although the structure may be related to the basic carbonate or the acetate hydroxide (Table I). This extremely well defined pattern was destroyed by dispersing the gel in water, the resultant sol giving two broad diffraction bands centred at 13.3° 2θ and 28.0° 2θ corresponding to a poorly crystalline pseudo boehmite. Although the structure of this compound

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TABLE I The X-ray diffraction pattern of dispersible alumina

d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
8.04	75	3.572	40	2.691	4
7.80	45	3.507	20	2.554	4
7.21	55	3.473	20	2.396	15
6.82	10	3.413	35	2.295	20
6.38	10	3.389	15	2.227	15
4.748	45	3.281	20	2.204	10
4.353	35	3.187	40	2.180	10
4.244	100	2.987	4	2.033	6
4.075	35	2.908	5	1.959	8
3.914	10	2.799	9	1.940	10
3.644	30	2.730	10	1.817	8

resembles that of boehmite, previous workers [8] suggest that the short range order results from a micellar structure in which the elementary micelles have a leaf-like character and that the diffuse reflection at 13.3° 2θ is associated with the stacking of these layers; variations in the peak position are attributed to changes in the layer spacing caused by differing amounts of water or foreign ions entrained within the micelles. On drying at 80°C, the alumina sol became amorphous and the sharp diffraction maxima of the original pattern did not re-appear.

The diffraction pattern from a calcium-stabilized zirconia had no distinct peaks, although several broad bands were evident. These bands corresponded to the X-ray pattern of monoclinic zirconia, but owing to the extreme line broadening (> 4.0° 2θ for the (111) reflection) and the low symmetry of the unit cell the precise determination of crystallite size was impossible. However, from experience with MgO powders [7], the broadened reflections suggested a crystallite size of < 30 Å. Two gel compositions were formed by mixing the high nitrate alumina and zirconia sols in the ratio 1:3 and 3:1, the gelation process taking only a few minutes in each case. After drying at 80°C, these Al₂O₃/ZrO₂ mixtures yielded X-ray diffraction patterns which were indistinguishable from the diffuse ZrO₂ traces. There was no evidence of crystallite growth or of compound formation.

A sample of titania sol proved to have the anatase (tetragonal) structure and the crystallite sizes were calculated from the (101) and (200) reflections (Table II). Consideration of the shape factors and the apparent crystallite sizes in-

TABLE II The crystallite size of TiO_2 sol calculated from different reflections by assuming various crystalline shapes

Crystallite shape	Crystallite size (Å)					
	(101) reflection			(200) reflection		
	k	W_0	β	k	W_0	β
Cube	28	31	31	21	0	44
Octahedron	23	0	31	35	45	48
Tetrahedron	29	38	39	44	57	61
Sphere	24	0	32	26	0	47

TABLE III The crystallite size of TiO_2 gel calculated from different reflections by assuming various crystallite shapes

Crystallite shape	Crystallite size (Å)					
	(101) reflection			(200) reflection		
	k	W_0	β	k	W_0	β
Cube	28	32	35	20	0	38
Octahedron	23	0	34	34	44	42
Tetrahedron	29	39	32	42	55	52
Sphere	24	0	35	25	0	41

icates that the form of the "average" crystallite is best approximated by a shape intermediate between an octahedron and a cube. Because of the low ratio of peak/background radiation the most reliable size value was provided by the slope of the variance function, the best estimate of crystallite size being 26 Å. The comparative crystallite sizes from titania gel are given in Table III. There is no detectable difference between the two sets of data; this fact is further evidence that crystallite growth does not occur on gelation. However, measurement of the peak positions showed that the lattice of both the sol and the gel were dilated.

Calculations with the (020) reflection from a pseudo boehmite gel gave a crystallite size of 50 Å. Moreover, no significant change in size was found in gels prepared by flocculation with nitric acid before drying. In fact, variation of the pH value from 3.5 to 0.7 had no detectable effect on crystallite size, although the particle size obviously exhibited a large change. These observations were confirmed when the pH of a titania sol was varied between 1.25 and 0.25.

In this limited study, we have shown that it is possible to characterize both sols and gels using X-ray methods and to obtain a measure of crystallite size of a variety of compositions.

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