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Application of Integrated X-ray Powder Diffraction Software: PDXL

Crystallite-size and size-distribution studies using a direct convolution technique

Crystallite size and its distribution are important information to investigate physical properties of materials. Precise determination of these values requires that the effect from instrument and strain should be separated. For this reason, it is suitable to use the whole powder pattern data which can evaluate the 2θ dependence of the peak shape.

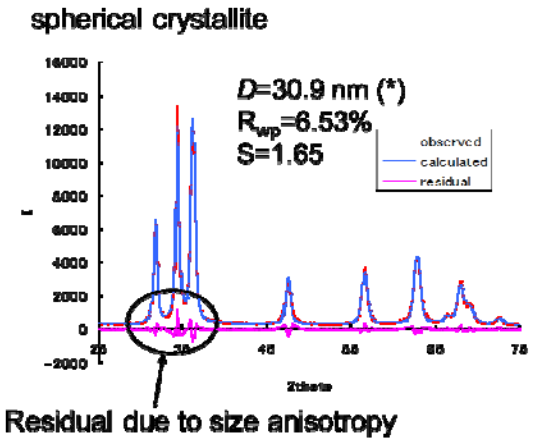
To eliminate the instrumental aberrations, we apply a convolution method between instrumental and physical profiles.

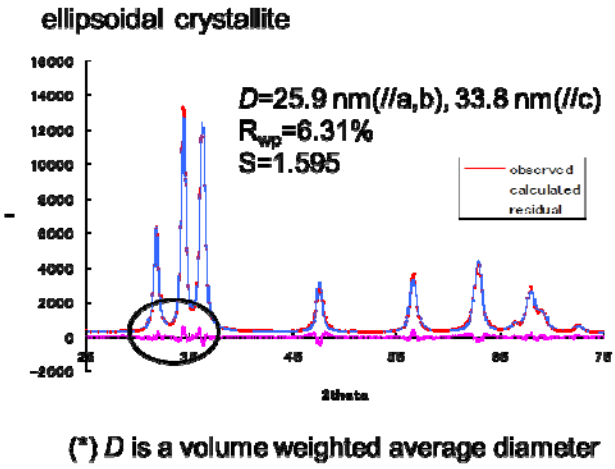
$$f = \underbrace{G(\text{instruments})}_{\text{Known profile shape}} \otimes \underbrace{H(\text{size, distribution, strain})}_{\text{Unknown profile to be determined}}$$

ZnO nanocrystals have attracted attention because of its photocatalytic property which is considered to be related with the crystallite size. This article describes the size-distribution analysis results obtained from ZnO nanoparticle samples.

Size anisotropy

Observed powder diffraction patterns were fitted with both spherical and ellipsoidal crystallite models which have the lognormal size distribution. The ellipsoidal model gave better results than the spherical model did.





(*) *D* is a volume weighted average diameter

Correlation between size distribution and strain

Optimal values obtained with whole pattern refinement were

$$e(\text{strain}) = 0.0044,\ D_{//a,b} = 25.9\ \text{nm},\ D_{//c} = 33.8\ \text{nm},\ C = 1.09$$

Separation of strain broadening is important to obtain reasonable values of size and distribution. Next table shows the optimal values when the strain value was fixed as 0, 0.001, 0.002,...

e(strain)	R_{wp}[%]	$D_{//a,b}$[nm]	$D_{//c}$[nm]	C	
0	8.42	14.8485	17.9147	0.498	
0.001	8.17	15.1438	18.306	0.518	
0.002	7.55	16.1363	19.6262	0.579	
0.003	6.84	18.115	22.3798	0.693	
0.004	6.37	22.4579	28.6562	0.927	
0.0044	6.31	25.9	33.8	1.09	optimal
0.005	6.4	33.9312	46.68	1.45	

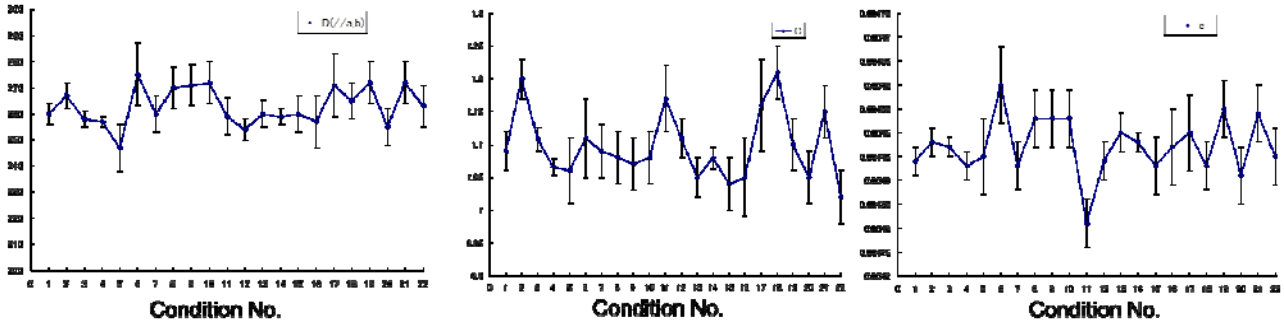
If we assumed the strain was zero, the diameter and distribution were completely different from their optimal values. The strain value should be known or be refined simultaneously with size and distribution.

Reproducibility

An advantage of the direct convolution with theoretical profiles of instrumental functions is that you don't need to measure a standard reference sample. We examined to what extent the refined values were reproducible for various experimental conditions. 22 types of experimental conditions are summarized in the next table.

Condition No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Soller slit[deg]	5	5	5	5	5	5	5	5	5	5	5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
scan mode	cont.	step	cont.	cont.	cont.	step	cont.	cont.	cont.	cont.	cont.	cont.	step	cont.	cont.	cont.	step	cont.	cont.	cont.	cont.	cont.
step[deg]	0.02	0.02	0.01	0.05	0.1	0.1	0.05	0.05	0.05	0.05	0.05	0.02	0.02	0.01	0.05	0.1	0.1	0.05	0.05	0.05	0.05	0.05
DS,SS[deg]	2/3	2/3	2/3	2/3	2/3	2/3	2/3	2/3	2/3	1/3	1	2/3	2/3	2/3	2/3	2/3	2/3	2/3	2/3	2/3	1/3	1
RS[mm]	0.1	0.1	0.1	0.1	0.1	0.1	0.05	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.05	0.2	0.3	0.1	0.1

Next three plots are the condition dependences of volume averaged diameter *D*, normalized standard deviation *C* and strain *e*. The deviations from their mean values are comparable to the estimated errors of the least square refinement.



Conclusion

We studied the crystallite size and size distribution using convolution method with the theoretical instrument model for Bragg-Brentano geometry. As an example, the powder diffraction data of ZnO nano-particles were refined. We found that the slight size anisotropy and strong correlation between size/distribution and strain which could not be obtained with single line profile analysis. Reproducibility of the values were examined with changing the experimental conditions and found that the deviations from their mean values were comparable to their estimated errors of the least-square refinement.

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