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Preferred Orientation of Particles in Reflection-type Powder Diffractometry. Preferred Orientations in Benzamide and α-2-Pyrazinecarboxamide Powders

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An improved method for the determination of the orientation distribution function of a powder consisting of preferentially oriented plate-like and needle-like particles was reported. Using this method, the coarse and fine powders of benzamide and α-2-pyrazinecarboxamide were investigated. It was found that the domains (a domain is defined as a collection of particles having the same preferred orientation plane or axis) of preferentially oriented particles exhibit two distinct changes when undergoing grinding of the powder. One change involves a decrease and the other an increase in volume, indicating that the particles in the domain showing the former change transform into those in the domain showing the latter change following grinding. The increase in volume of the domain can be well explained in relation to the existence of molecular layers connected to each other by weak van der Waals force in the crystal.

Takaki and Yamaguchi[1] reported a process for the determination of an orientation distribution function for preferentially oriented plate-like particles by the usual reflection-type powder diffractometry. The orientation distribution function, $N(\alpha)$, is defined in such a way that the fractional number of plate-like particles whose normals are contained in a solid angle $d\Omega$ at an angle α to the direction normal to the sample-holder is given by $N(\alpha)d\Omega$. They showed that $N(\alpha)$ can be obtained from the distribution function $\rho(\alpha)$

$$\rho(\alpha) = K\cdot N(\alpha) = I_{\mathrm{pre}}(\alpha)/I_{\mathrm{ran}}(\alpha), \quad (1)$$

where K is a constant, $I_{\mathrm{pre}}(\alpha)$ is the intensity for an hkl reflection from preferentially oriented particles, $I_{\mathrm{ran}}(\alpha)$ is that from randomly oriented particles and α is an angle between an hkl plane and the plane of preferred orientation.

As for the analytical approximation to the mean distribution function $N(\alpha)$, Uda and Sasa[2–5] and Toraya and Marumo[6] have shown in their studies on preferred orientation in inorganic powder samples that a Gaussian-type function

$$N(\alpha) = C_0 + C_1 \exp(-P\alpha^2) \text{ and } C_0 + C_1 = 1 \quad (2)$$

gives an excellent approximation to the distribution of oriented plate-like particles. The first term is a constant which is responsible for the random orientation of particles in a powder, the second term is a mean distribution function for preferentially oriented particles and P represents the degree of preferred orientation. On the other hand, Yamaguchi *et al.*[7] have shown that a Cauchy-type function

$$N(\alpha) = C_0 + C_1\{1/[1+P\alpha^2] + 1/[1+P(\pi-\alpha)^2]\} \quad (3)$$

gives a good approximation to the distribution function in γ_{II}-Li_2ZnSiO_4 and *p*-iodobenzamide powder samples.

We have found that the above function is unsuitable to express the distribution for very poorly oriented plate-like particles since, for a very small value of P, the value of $N(\alpha)$ at $\alpha=0$ is smaller than that at $\alpha=\pi/2$. Therefore, we will use the following revised distribution function

$$N(\alpha) = C_0 + C_1/[1+P\alpha^2], \quad (4)$$

where the first and the second terms express contributions from randomly oriented and preferentially oriented particles, respectively.

Then, using distribution functions of the above Gaussian (2) and Cauchy (4) types, we reexamined the preferred orientations in several inorganic and organic substances of which X-ray powder-diffraction data or observed orientation-distribution curves have been given.[3–12] The results indicate that, as has already been reported,[6] the Gaussian-type function is superior to the Cauchy-type function in representing the distribution of plate-like particles for exceedingly oriented powders,[3,4,6] while the Cauchy-type function gives a good approximation for all the other poorly oriented powder samples.

Similar to the case of plate-like particles, the distribution of preferentially oriented needle-like particles may be obtained from the distribution function

$$\rho(\beta) = K\cdot N(\beta) = I_{\mathrm{pre}}(\beta)/I_{\mathrm{ran}}(\beta), \quad (5)$$

where β is the acute angle between the axis normal to an hkl plane and that of preferred orientation. Function $N(\beta)$ can then be obtained[6] in the form

$$N(\beta) = C_0 + C_1'/[1+P'(\pi/2-\beta)^2]. \quad (6)$$

The preferred orientation of needle-like particles in an *m*-iodobenzoic acid powder sample has been well explained using expression (6).

Recently, Yamaguchi *et al.*[8] and Kurisu *et al.*[9] have extended the above treatment to include domains with different preferred orientations, where a domain is defined as a collection of particles having the same preferred orientation plane or axis. The orientation distribution functions given by them are:

$$N(\alpha) = C_0 + \sum C_n/[1+P_n\alpha_n^2], \tag{7a}$$

for plate-like particles and

$$N(\beta) = C_0 + \sum C_n'/[1+P_n'(\pi/2-\beta_n)^2], \tag{7b}$$

for needle-like particles. Here $N(\alpha)\equiv N(\alpha_1, \alpha_2, \cdots, \alpha_n, \cdots, \alpha_m)$ and $N(\beta)\equiv N(\beta_1, \beta_2, \cdots, \beta_n, \cdots, \beta_m)$, where m is the number of preferred orientation planes (or axes), α_n is the acute angle between an hkl reflection plane and the nth plane of preferred orientation and β_n is the acute angle between the axis normal to an hkl reflection plane and the nth axis of preferred orientation.

Here, we have extended the above treatment to include the case where domains with plate-like and needle-like particles coexist in a powder. The distribution function is then given by

$$\begin{aligned} N(\alpha, \beta) = C_0 &+ \sum C_n/[1+P_n\alpha_n^2] \\ &+ \sum C_m'/[1+P_m'(\pi/2-\beta_m)^2], \end{aligned} \tag{8}$$

where the second and the third terms give contributions from plate-like and needle-like particles, respectively.

The relative volumes of domains in a powder sample are obtained from the following expressions:[9]

$$V_0 = 4\pi C_0\int_0^{\pi/2} \sin\alpha d\alpha = 4\pi C_0, \tag{9}$$

$$V_n = 4\pi C_n\int_0^{\pi/2} \{1/[1+P_n\alpha_n^2]\} \sin\alpha d\alpha, \tag{10a}$$

for plate-like particles and

$$V_m = 4\pi C_m'\int_0^{\pi/2} \{1/[1+P_m'(\pi/2-\beta_m)^2]\} \sin\beta d\beta, \tag{10b}$$

for needle-like particles, where V_0, V_n, and V_m are normalized in such a way that

$$V_0 + \sum V_n + \sum V_m = 1.$$

In this paper we apply the above treatment to coarse and fine powders of benzamide[13] and α-2-pyrazinecarboxamide[14] and examine the change in the preferred orientation of particles following a grinding of the powder.

Experimental

Powder samples were prepared by grinding an aggregate of each crystal in an agate mortar. X-Ray powder diffraction patterns were taken with an X-ray powder diffractometer (Rigaku-Denki, D-2F) with Cu$K\alpha$ radiation using a divergence slit of 1° and a scanning speed of 1° (2θ/min). Each powder sample was packed in a standard specimen holder without any special treatment and was pressed gently to make a flat surface at constant pressure. Diffraction-intensity measurements were made by cutting out the background-subtracted peak areas from each trace and weighing.

Intensities, I_{ran}, were calculated from the following expression:

$$I_{\text{ran}} = m\cdot Lp\cdot F_o^2, \tag{11}$$

where F_o's are observed or calculated structure factors, m is multiplicity and Lp is Lorentz-polarization factor. Low-angle reflections ($2\theta<13°$) were not used for least-squares calculations since the intensities of these reflections were

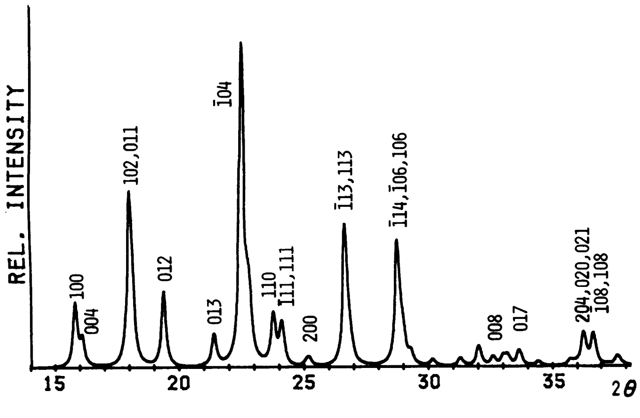

Fig. 1. Calculated powder intensity pattern for randomly oriented particles of benzamide.

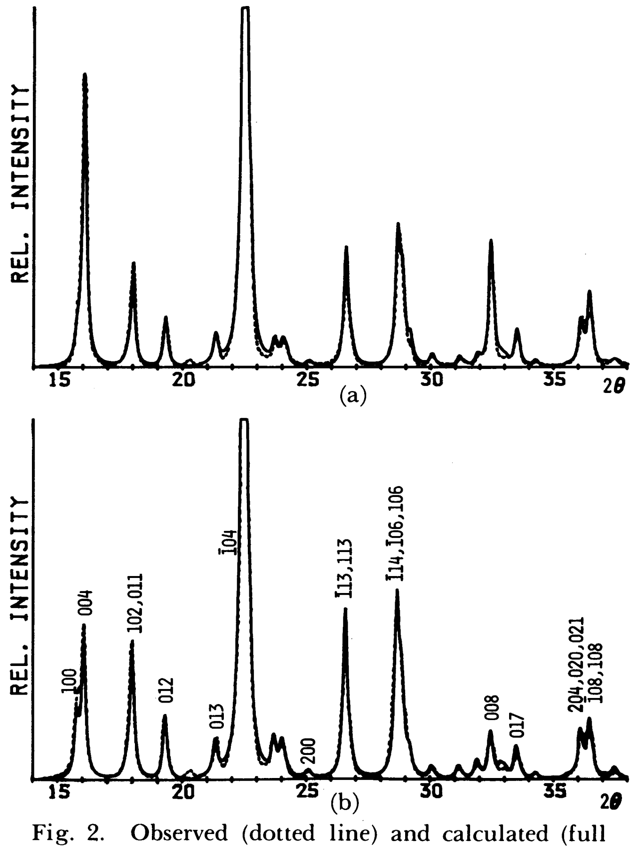

Fig. 2. Observed (dotted line) and calculated (full line) powder intensity patterns for benzamide. (a) Coarse powder. (b) Fine powder.

TABLE 1. PREFERRED ORIENTATION PARAMETERS FOR BENZAMIDE POWDER SAMPLES. E.S.D.'S ARE GIVEN IN PARENTHESES.

	C_0[a)]	C_1[a)]	P_1	C_2[a)]	P_2	V_0[b)]	V_1[b)]	V_2[b)]	R[c)]	R_0[d)]
Orientation plane		(001)		$(\bar{1}04)$						
Coarse powder	0.00(1)	0.92(3)	18(1)	0.08(1)	12(5)	0.02	0.88	0.10	0.06	0.60
Fine powder	0.02(1)	0.70(5)	6.4(5)	0.28(2)	4.7(4)	0.09	0.61	0.30	0.05	0.44

a) Parameters C_j's are so normalized that $C_0+C_1+C_2=1$. b) V_0, V_1, and V_2 are relative volumes of domains. c) $R=\sum|I_{\mathrm{pre}}-I_{\mathrm{ran}}\cdot N(\alpha)|/\sum I_{\mathrm{pre}}$. d) R_0 is the initial value of R.

seriously affected by the size of the divergence-slit.

Powder-intensity profiles were calculated from the following expression:

$$y_i = \sum\left[\frac{2}{3}I_nL(2\theta_i, 2\theta_{n1}) + \frac{1}{3}I_nL(2\theta_i, 2\theta_{n2})\right] \qquad (12)$$

where y_i is the intensity at a given point $2\theta_i$ in a profile.

The summation is taken over all possible contributing reflections at $2\theta=2\theta_i$; I_n is the intensity for the nth reflection from preferentially oriented particles; $L(2\theta_i, 2\theta_{n1})$ and $L(2\theta_i, 2\theta_{n2})$ are line shape functions for Cu $K\alpha_1$ and Cu $K\alpha_2$, respectively, and are represented by a Cauchy function with the half width of the diffraction peak, H_n. The angular dependence of H_n is represented by

$$H_n^2 = U\cdot\tan^2\theta_n + V\cdot\tan\theta_n + W \qquad (13)$$

where U, V, W are constants.

Results and Discussion

Benzamide. Figure 1 shows the intensity pattern for randomly oriented particles calculated from observed F_o's for 42 reflections.[13] X-Ray intensity patterns taken at two different stages of grinding are shown in Fig. 2. Comparing Figs. 1 with 2(a), one can see that the intensities of both the 004 and 008 reflections are prominently enhanced in Fig. 2(a), indicating that the 001 plane is a plane of preferred orientation.

To obtain the distribution function $\rho(\alpha)$, we selected 23 reflections from diffraction peaks in each of the two powder patterns; seven reflections, 012, 013, $\bar{1}04$, 110, 200, 008, 017, with single peaks, five pairs of reflections (100, 004), (102, 011), ($\bar{1}11$, 111), ($\bar{1}13$, 113), ($\bar{1}08$, 108), and two triad reflections ($\bar{1}14$, $\bar{1}06$, 106), (204, 020, 021) with overlapped peaks.

Preferred orientation parameters of $N(\alpha)$ for the 001 preferred orientation plane for the two powder samples were determined by a least-squares technique using a modified program based on one written by Kurisu *et al.*[9] At this stage, we calculated the intensity pattern using the above preferred-orientation parameters and found that the observed intensity for the $\bar{1}04$ reflection was still remarkably strong (especially in the fine powder) as compared with the corresponding intensity in Fig. 1, suggesting that the $\bar{1}04$ plane is another plane of preferred orientation. The final preferred orientation parameters obtained from the above two preferred orientation planes are listed in Table 1. Calculated intensity patterns are shown in Fig. 2.

In Fig. 2, one finds that the calculated intensity patterns are in good agreement with the observed patterns for both the coarse and fine powders. As seen in Table 1, the value of P_1 for the 001 preferred orientation plane decreases from 18 (coarse powder) to 6.4 (fine powder). Similarly, the value of P_2 for the $\bar{1}04$. plane decreases from 12 to 4.7.

The relative volume of V_1 decreases from 0.88 to 0.61, while that of V_2 increases significantly from 0.10 to 0.30. This suggests that a considerable part of the particles in the domain of V_1 change with grinding into those having the $\bar{1}04$ preferred-orientation plane. The existence of this preferred-orientation plane can well be explained from the fact that molecular layers parallel to ($\bar{1}04$) in the crystal are connected with each other by weak van der Waals force.[13]

A microscopic examination revealed that the majority of particles in the coarse powder were thin plates. Comparing the above result, one may say that these plates would probably be those with (001) well developed.

α-2-Pyrazinecarboxamide. Takaki *et al.*[14] have reported that crystals obtained from crystal growth are colorless needles elongated along the c axis and sometimes laths with (010) well developed. A microscopic observation of a coarse powder showed many typical needles. Therefore, it is very interesting to examine the change in the preferred-orientation parameters for needle-like particles following the grinding of the powder.

A total of 16 reflections were used for obtaining preferred-orientation parameters. There included four reflections, 310, 410, $\bar{4}01$, 320, with single peaks, three pairs of reflections, (210, 400), (600, 510), ($\bar{2}10$, 001), and a hexad of reflections (201, 610, $\bar{1}11$, $\bar{2}11$, 220, 011) with overlapped peaks.

Preferred-orientation parameters for coarse and fine powders were obtained by introducing two kinds of domains with preferentially oriented particles; one was the domain with the c preferred orientation axis and the other was that with the 100 preferred orientation plane. Final parameters are listed in Table 2. Figure 3(a) shows the intensity pattern for randomly oriented particles calculated from observed F_o's for 53 reflections.[14] The observed and calculated intensity patterns for the fine powder are shown in Fig. 3(b).

As seen in Table 2, all P values decreased upon grinding. The relative volume of the domain with the c preferred orientation axis decreased from 0.58 (coarse powder) to 0.42 (fine powder), indicating that many of

TABLE 2. PREFERRED ORIENTATION PARAMETERS FOR α-2-PYRAZINECARBOXAMIDE POWDER SAMPLES

	C_0	C_1'	P_1'	C_2	P_2	V_0	V_1	V_2	R	R_0
Orientation axis or plane	c-axis			(100)						
Coarse powder	0.05(1)	0.30(1)	7(1)	0.65(3)	22(2)	0.19	0.58	0.23	0.06	0.69
Fine powder	0.06(1)	0.28(1)	2.5(7)	0.66(8)	4.1(7)	0.16	0.42	0.42	0.08	0.47

TABLE 3. PREFERRED ORIENTATION PARAMETERS OBTAINED BY USE OF THE GAUSSIAN- TYPE FUNCTION FOR FINE POWDER SAMPLES OF BENZAMIDE AND α-2-PYRAZINECARBOXAMIDE

	C_0	C_1 C_1'	P_1 P_1'	C_2	P_2	V_0	V_1	V_2	R	R_0
Benzamide	0.12(1)	0.61(5)	3.0(2)	0.27(1)	3.1(3)	0.46	0.38	0.16	0.06	0.44
α-2-pyrazine-carboxamide	0.20(1)	0.22(1)	2.4(11)	0.58(9)	1.9(2)	0.43	0.26	0.31	0.10	0.47

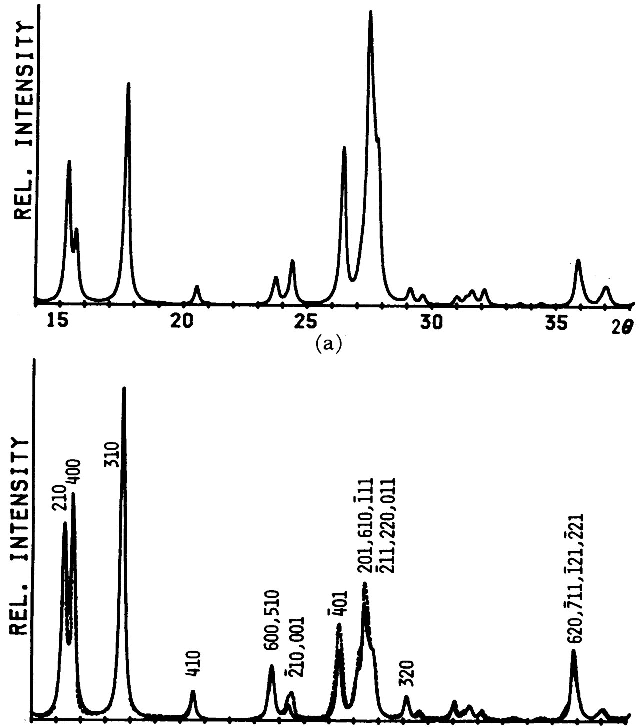

Fig. 3. Powder intensity patterns for α-2-pyrazine-carboxamide.
(a) Calculated intensity pattern for randomly oriented particles. (b) Observed (dotted line) and calculated (full line) intensity patterns for the fine powder.

the needle-like particles obtained from crystal growth retained their shape unchanged, although they diminished in size upon grinding. On the other hand, the domain with the 100 preferred orientation plane increased noticeably in volume from 0.23 to 0.42. The above results may suggest that particles in domains V_0 and V_1 change into those having the 100 preferred orientation plane upon grinding. The existence of the 100 preferred orientation plane can be well explained in terms of the layer structure of the crystal.[14]

Concluding Remarks

In Table 3, we give preferred orientation parameters obtained by use of the Gaussian-type function for the above fine-powder samples. Comparing the parameters in Tables 1 and 2 with those in Table 3, one may find that the R values for both benzamide and α-2-pyrazinecarboxamide fine powders are smaller than the corresponding values in Table 3, showing that in this case also a Cauchy-type function gives a good approximation for representing distribution function of preferentially oriented particles. It is to be noted that significant discrepancies can be found in the values of C_0 for two types of distribution functions, owing to the characteristic features of the Cauchy and Gaussian functions.

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