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The Prediction of Preferred Orientation Planes in X-Ray Powder Diffractometry

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A method for predicting possible preferred orientation planes in organic and inorganic powders of known crystal structures is presented. The usefulness of this method is demonstrated by applying it to the powders of benzamide, the α-form of 2-pyrazinecarboxamide, benzoic acid, olivine, and the high-temperature form of Li_3PO_4. It should be noted that the existence of preferred orientation axes found in the powders of benzoic acid and Li_3PO_4 can be well explained in terms of zone axes, each formed by two sets of cleavage planes.

A treatment of preferred orientations in X-ray powder diffractometry using an orientation-distribution function for preferentially oriented particles has previously been developed by Uda and Sasa.[1–3] Recently, we extended the above method to include oriented plate-like and needle-like particles in the powder.[4–6]

By using this method, Nakata *et al.*[6] have closely examined the preferred orientations in coarse and fine powders of benzamide and the α-form of 2-pyrazinecarboxamide and have found that the occurrence of preferred orientation planes can be well explained in terms of the layer structure, the layers being linked with each other by weak van der Waals forces. In the above study, the preferred orientation planes for the two substances were found by comparing the observed X-ray powder intensities with those from randomly oriented particles (calculated intensities).

The preferred orientation planes can be easily predicted if one takes into account the well-known fact that cleavages causing preferred orientation effects on X-ray intensities are inherently dependent upon the anisotropic character of the crystal structure and on the strength of bonds between atoms or molecules. From this point of view, we wish here to present a method for predicting possible preferred orientation planes for organic and inorganic powders, the crystal structures of which are known.

Procedure

Prediction of Preferred Orientation Planes for Organic Powders. Organic (molecular) crystals are characterized by the presence of van der Waals bonding as a fundamental type of bonding. Further, strong hydrogen bonds play an important role in the formation of characteristic types of structure in chain structures and in layer structures. Cleavages may then occur along the planes parallel to the chain or to the layer if they are linked by weak van der Waals forces only. Therefore, preferred orientation planes can be predicted by the following procedure:

1) Since cleavages are usually parallel to the planes with simple Miller indices, in our computer calculation (the program is written in N_{88}-BASIC), they are examined for planes (hkl) having interplaner spacings (d-values) larger than 3.0 Å.

2) In a crystal, a plane parallel to (hkl) is represented by:

$$hx + ky + lz = p, \tag{1}$$

where x, y, and z are the fractional coordinates referred to the crystal axes, and where p is a constant.

By varying the value of p, we obtain possible cleavage planes (hkl) from a requirement that the cleavage does not break covalent bonds (molecules) and hydrogen bonds.

3) For each of the possible cleavage planes obtained above, a lattice spacing[7] at right angles to the cleavage plane (D-value, see Fig. 1) is calculated. In this calculation, non-hydrogen-bonded H atoms are omitted since the strength of bonds from an H atom to other atoms is considered to be weak; thus, these bonds do not exert any serious effect on the cleavage. The D-value is used as an indication of the weakness of bonds linking layers of molecules across the cleavage plane.

4) By examining the D values, possible preferred orientation planes are selected.

Prediction of Preferred Orientation Planes for Inorganic Powders. In inorganic crystals, the ionic bond is a fundamental type of bonding linking atoms across a cleavage plane. Therefore, like the lattice spacing, the number of ionic bonds per unit area[8] can also be used as an indication of the weakness of the bonds. In this paper, however, the large D-values are mainly used for selecting preferred orientation planes, since a weak bond is usually accompanied by a large lattice spacing.[7] The following is a procedure for predicting possible preferred orientation planes in inorganic powders:

1) Cleavages are examined for the planes (hkl) with d-values larger than 3.3 Å.

2) Possible cleavage planes are obtained from a requirement that the cleavage does not break covalent bonds.

3) For these cleavage planes, lattice spacings (D-

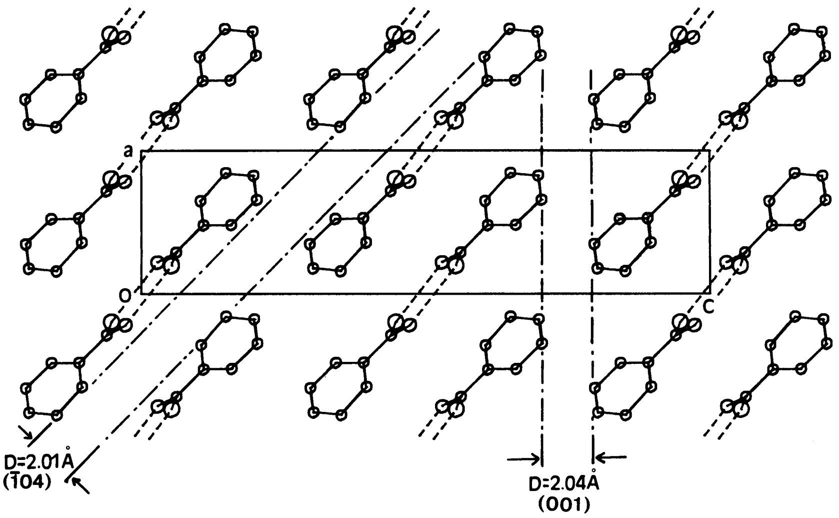

Fig. 1. The crystal structure of benzamide[9)] projected along the b axis, showing the cleavages parallel to (001) and ($\bar{1}04$) and their lattice spacings (*D*-values).

values) are calculated (H atoms are omitted from the calculation).

4) The number of bonds (*N*) across each cleavage plane in a unit cell is calculated. Within a unit cell, the area of the cleavage plane (*S*) parallel to (*hkl*) is also calculated.

5) By examining the values of *D* (and *N*/*S*) and confirming the presence or absence of the sheet of water molecules if the crystal is a hydrate, possible preferred orientation planes are selected.

Prediction of Preferred Orientation Axes. If the crystals obtained from crystal growth are shaped like needles, we must examine the needle axis as a possible preferred orientation axis.[5,6)]

In some cases, a zone axis formed by two good cleavage planes coincides with a preferred orientation axis, especially when the zone axis is the needle axis of the crystal, as in the benzoic acid powder. The preferred orientation axis should be examined when the preferred orientations in the powder sample cannot be explained from the cleavage planes predicted by the above procedure.

Application

Benzamide. Crystals[9)] are monoclinic, with a=5.607, b=5.046, c=22.053 Å, β=90.66°, and space group $P2_1/c$. Four molecules are contained in a unit cell.

Two possible preferred orientation planes and their *D*-values, as obtained by the above method, are listed in Table 1. Nakata *et al.*[6)] found preferred orientation planes of (001) and ($\bar{1}04$) and explained the occurrence of these planes in terms of the layer structure (Fig. 1). One can see that these two preferred orientation planes are the same as the planes listed in Table 1, and that the two *D*-values are both larger than 2 Å, indicating that the forces linking layers are very weak.

Table 1. Possible preferred orientation planes for benzamide, the α-form of 2-pyrazinecarboxamide and benzoic acid

	hkl	*d*/Å	*D*/Å
Benzamide	001	22.05	2.04
	$\bar{1}04$	3.95	2.01
α-Form of 2-pyrazine-carboxamide	100	22.65	1.76
Benzoic acid	$\bar{1}02$	5.16	2.44
	001	21.79	2.33
	100*	5.46	0.44

* The next most possible preferred orientation plane.

α-Form of 2-Pyrazinecarboxamide. The crystals[10)] are monoclinic, with a=23.07, b=6.73, c=3.73 Å, and β=101.0° and with the space group $P2_1/a$. Four molecules are contained in a unit cell.

One possible preferred orientation plane (100) was predicted by the present method (Table 1). It is identical with that found by Nakata *et al.*[6)] They found also the c preferred orientation axis, which had been predicted from the needle axis.

Benzoic Acid. The crystals[11)] are monoclinic, with a=5.510, b=5.157, c=21.973 Å, and β=97.41° and with space group $P2_1/c$. Four molecules are contained in a unit cell.

The three possible preferred orientation planes obtained are listed in Table 1. After the *D*-values had been examined, the $\bar{1}02$ and 001 planes were selected as the most probable preferred orientation planes. Nakata[12)] examined preferred orientations in fine powders and found a great many preferentially oriented needle-like particles with the b axis as the preferred orientation axis and a very small number of plate-like particles with (001) as the preferred orientation plane. The b preferred orientation axis could thus be pre-

TABLE 2. POSSIBLE PREFERRED ORIENTATION PLANES FOR OLIVINE AND THE HIGH-TEMPERATURE FORM OF Li_3PO_4

	hkl	d/Å	D/Å	S/Å^2	N	N/S
Olivine	010	10.19	0.56	28.4	6	0.211
High-temperature form of Li_3PO_4	010	10.49	1.85	30.2	4	0.133
	120	3.98	0.75	79.6	12	0.151
	101*	3.84	0.42	82.7	10	0.121
	011*	4.46	0.30	71.2	16	0.225
	021*	3.59	0.14	88.3	20	0.226
	100*	6.13	0.06	51.9	12	0.231

* The next most possible preferred orientation planes.

dicted as the zone axis formed by the $\bar{1}02$ and 001 cleavage planes.

Olivine. The crystals of forsterite[13] are orthorhombic, with a=4.756, b=10.195, and c=5.981 Å and with space group Pbnm. Four formula units are contained in a unit cell.

One possible preferred orientation plane, along with the values of D, N, S, and N/S, is listed in Table 2. Yamaguchi *et al.*[14] found that the preferred orientations in powders of olivine from Kaimon-dake can be explained mostly from the 010 preferred orientation plane, in agreement with the prediction of Table 2. Note that the small value of D, 0.56 Å, for the plane (010) may support the fact that the cleavage parallel to (010) is imperfect.[13]

High-temperature form of Li_3PO_4. The crystals[15] are orthorhombic, with a=6.12, b=10.53, and c=4.93 Å and with space group Pmnb. Four formula units are contained in a unit cell.

Six possible preferred orientation planes were obtained (Table 2). By examining the D-values, the (010) and (120) planes were selected as the most highly probable preferred orientation planes. From a close examination of fine powder samples, Yamaguchi[16] found that the preferred orientations can be explained mainly in terms of the 010 preferred orientation plane and, to some extent, the c preferred orinetation axis. The c preferred orientation axis could also be predicted as a zone axis formed by the 010 and 120 cleavage planes.

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