JOURNAL OF MATERIALS SCIENCE 8 (1973) 312-316

Integrated intensity changes of X-ray diffraction lines for crystalline powders by grinding and compression. Relations between effective Debye parameter and lattice strain

MICHIO INAGAKI, HIROSHI FURUHASHI, TOMOMASA OZEKI, SHIGEHARU NAKA
Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

The relations between the effective Debye parameter and lattice strain are investigated on some non-metallic crystalline powders, CoO, $Co_{0.5}Mg_{0.5}O$, $CoAl_2O_4$, TiO_2, CaF_2, $BaTiO_3$ and graphite. The effective Debye parameter B_{eff} was determined from the integrated intensities of X-ray diffraction lines with different $\sin\theta/\lambda$-values and the lattice strain, ϵ, was determined from the half-widths of the diffraction lines. Both B_{eff} and ϵ increased with increase in grinding time and pressure. B_{eff} showed a relatively sharp increase, but tended to saturation. However, ϵ increased slowly even after prolonged grinding, and B_{eff} increased with increase in ϵ. When $\epsilon > 0.2 \times 10^{-2}$, however, B_{eff} tended to a limit. The limiting values of B_{eff} were varied from sample to sample. An attempt was made to explain the changes of B_{eff} and ϵ with grinding and compression to large shear by the introduction of various defects into the structure. B_{eff} was found to give some information on the deformed structure of crystalline powders.

1. Introduction

Previously [1], we reported that the effective Debye parameter in the temperature factor for X-ray integrated intensity, increased with grinding and compression of crystalline powders. The value of the effective Debye parameter, B_{eff}, depends not only on dynamic displacement (thermal vibration) but also on static displacement of constituent atoms from the normal position [2-4]. The effect of grinding and compression has often been followed by measuring the lattice strain, which is evaluated from the half-widths of X-ray diffraction line profiles [5].

In the present work, the relationship between B_{eff} determined from integrated intensities, and lattice strain, ϵ, from half-widths of diffraction lines, is investigated for some non-metallic crystalline powders, in order to accumulate data on many samples and to evaluate usefulness of B_{eff}.

2. Experimental

The samples used are listed in Table I together with the structure type and a brief description of the mode of preparation. Grinding was performed in air at room temperature, by using an agate mortar. A small amount of each sample was taken for X-ray analysis after grinding. Compression was carried out at room temperature for 1 h by using a girdle-type high-pressure apparatus [6]. Shear seemed to be mainly worked on the sample powder during compression because of the large stress gradient in the pressure cell [6].

The integrated intensity of diffraction lines for the sample was measured by scanning the scintillation counter over an appropriate range of 2θ and by subtracting the background intensity. B_{eff} was determined from the observed intensities I_{obs} according to Equation 1,

$$\ln (I_{obs}/I_{calc}) = \ln k - 2 B_{eff} (\sin^2\theta/\lambda^2), \quad (1)$$

TABLE I The samples used

Sample	Type of crystal structure	Preparation
CoO	Rocksalt	Heat-treatment of Co_3O_4 at 1000° C for 1 h in the flow of N_2
$Co_{0.5}$ $Mg_{0.5}O$	Rocksalt	Solid-state reaction between CoO and MgO at 1300° C for 28 h
$CoAl_2O_4$	Spinel	Solid-state reaction between CoO and Al_2O_3 at 1400° C for 2 h
TiO_2	Rutile	Hydrolysis of Ti-isopropoxide and heat-treatment at 1300° C for 2 h
CaF_2	Fluorite	Reagent grade
$BaTiO_3$	Perovskite	Co-precipitation from $Ba(OH)_2$ and Ti-isopropoxide and heat-treatment at 1300° C
Graphite	Graphite	Annealing and purification of Ceylon natural graphite at 2700° C in the flow of halogen gas

where I_{calc} is the theoretical intensity calculated from the Lorentz-polarization factor, multiplicity and structure amplitude, and k is a constant. The line profile of the diffraction lines were recorded at the same time as the intensity measurement. From the half-width, β, of the profile, the lattice strain, ϵ, was determined by using Equation 2,

$$\beta \cos\theta/\lambda = K/L + 2\epsilon\,(\sin\theta/\lambda), \qquad (2)$$

where K is the shape factor and L is the crystallite size. For all samples except graphite, the absorption effects on intensity and half-width were neglected because of the high absorption coefficient of the samples. For graphite, the absorption factor was incorporated into the theoretical intensity I_{calc} and the observed half-widths were corrected for the instrumental broadening [7], evaluated from an internal standard of silicon. For the samples with rocksalt-type structure, CoO and $Co_{0.5}$ $Mg_{0.5}O$, the diffraction lines of which all the indices were even, were used. For graphite, only $00l$ diffraction lines were used and so the obtained values of B_{eff} and ϵ were those corresponding to the c-axis.

3. Results

The relations between ln (I_{obs}/I_{calc}) and $\sin^2\theta/\lambda^2$ obtained for ground specimens of $Co_{0.5}$ $Mg_{0.5}O$ are shown in Fig. 1a. The relations between $\beta\cos\theta/\lambda$ and $\sin\theta/\lambda$ for the same specimens are shown in Fig. 1b. For TiO_2 and $CoAl_2O_4$, the changes of the relationship with compression are shown in Figs. 2 and 3, respectively. With the increase in grinding time and compressing pressure, both slopes of the relationships, i.e., effective Debye parameter, B_{eff} and lattice strain, ϵ, increase.

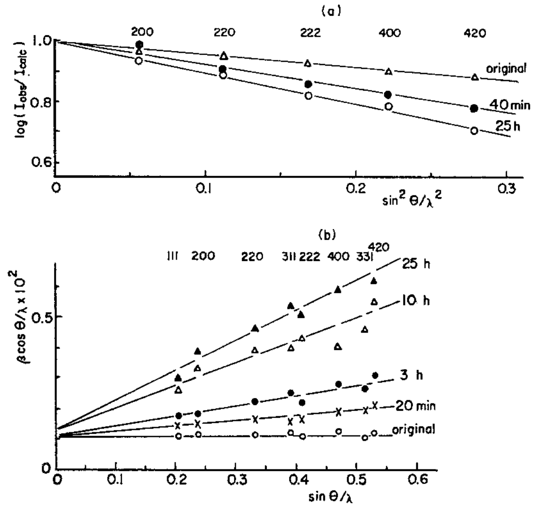

Figure 1 Changes of the relations (a) between ln (I_{obs}/I_{calc}) and $(\sin^2\theta/\lambda^2)$, and (b) between $\beta\cos\theta/\lambda$ and $\sin\theta/\lambda$, for $Co_{0.5}$ $Mg_{0.5}O$ with grinding.

The changes of both B_{eff} and ϵ with grinding time are shown in Fig. 4 for all the samples examined. In CaF_2, for example, the value of B_{eff} becomes about four times larger than the original, by 20 h of grinding, while it does not increase appreciably by further grinding up to 167 h. On the other hand, the value of ϵ increases relatively slowly with grinding and continues to increase after prolonged grinding, even though the increasing rate becomes small. For $Co_{0.5}$ $Mg_{0.5}O$, changes of B_{eff} and ϵ similar to those of CaF_2 are observed. In graphite, however, the changes are different, both B_{eff} and ϵ increasing after 30 h of grinding.

In Fig. 5, the changes of B_{eff} and ϵ with compressing pressure are shown. Similarly in the case of grinding, the values of B_{eff} and ϵ

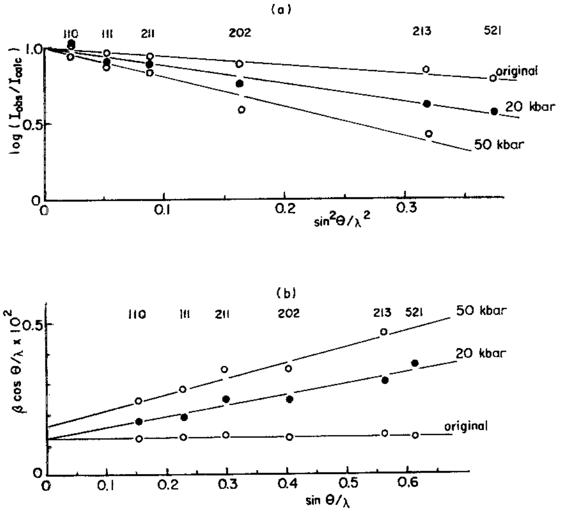

Figure 2 Changes of the relations (a) between ln (I_{obs}/I_{calc}) and ($\sin^2\theta/\lambda^2$), and (b) between $\beta\cos\theta/\lambda$ and $\sin\theta/\lambda$, for TiO_2 with compression.

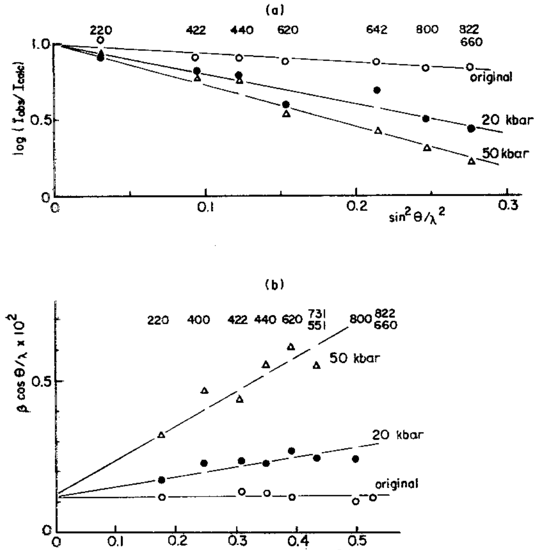

Figure 3 Changes of the relations (a) between ln (I_{obs}/I_{calc}) and ($\sin^2\theta/\lambda^2$), and (b) $\beta\cos\theta/\lambda$ and $\sin\theta/\lambda$ for $CoAl_2O_4$ with compression.

show a rapid initial increase which then slows down with the increase in pressure. The increase of ϵ becomes gradual in the high-pressure region for CoO and $BaTiO_3$, which both have small values of B_{eff}. However, TiO_2 and $CoAl_2O_4$ have large values of B_{eff} and show a continuous increase in ϵ. This correlation between B_{eff} and ϵ agrees with the grinding results.

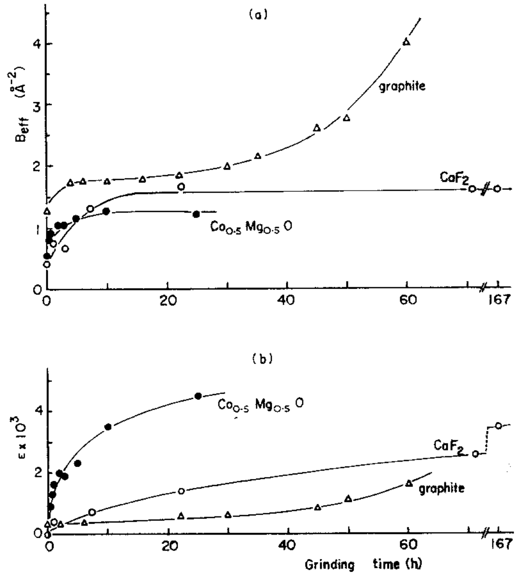

Figure 4 Changes of effective Debye parameter B_{eff} (a) and lattice strain ϵ (b) with grinding time.

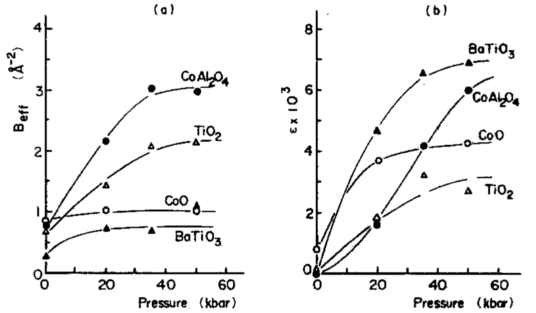

Figure 5 Changes of effective Debye parameter B_{eff} (a) and lattice strain ϵ (b) with compression.

The relationship between B_{eff} and ϵ for all samples are shown in Fig. 6. B_{eff} increases with increase in ϵ. Above $\epsilon = 0.2 \times 10^{-2}$, however, B_{eff} tends to be saturated. The saturated value of B_{eff} varies from sample to sample. For graphite, the B_{eff}-value increases very rapidly, but ϵ did not exceed 0.2×10^{-2} in the present work. Therefore, the saturated value of B_{eff} for graphite is not known.

4. Discussion

The changes of effective Debye parameter, B_{eff} and lattice strain, ϵ, with grinding and compression to large shear, and the relationship between these two parameters, can be explained

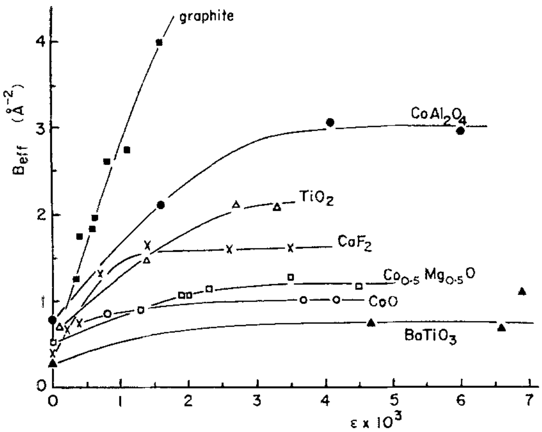

Figure 6 Relationship between effective Debye parameter B_{eff} and lattice strain ϵ.

by the introduction of various defects into the structure. The Debye parameter B is related to the mean square displacement $\overline{u^2}$ of atoms from the normal position as follows [2, 3],

$$B = (8\pi^2/3)\,\overline{u^2}.$$

The mean square displacement $\overline{u^2}$ consists of not only thermal vibration (dynamic displacement) but also the static displacement of atoms. This displacement arises from the presence of defects, and therefore, the introduction of various defects by either grinding or compression to large shear, causes the increase in the component of static displacement in $\overline{u^2}$, and therefore the increase in B_{eff}. The lattice strain, ϵ, determined from half-widths, is the mean fluctuation of interlayer spacing from the mean value. The fluctuation of interlayer spacing, i.e., the lattice strain ϵ, increases owing to the introduction of defects.

The introduction of defects by grinding and compression to large shear must occur heterogeneously, some parts having a large defect concentration and the others a small one. If the part has a large defect concentration, i.e., too deformed, it does not contribute to the intensities of the X-ray crystalline diffraction lines. B_{eff} obtained from intensities of the crystalline diffraction lines is therefore related only to the mean square displacement of the less deformed regions. This might be the reason for the existence of a limiting value of B_{eff}, and there might be a critical lower value of deformation capable of being detected by B_{eff}. On the other hand, the substantially deformed regions affect the interlayer spacing in that neighbourhood enlarging it, and causing the fluctuation of interlayer spacing to increase with increase of the greatly deformed parts. Therefore, ϵ shows an increase even by prolonged grinding and by compression under high pressure.

The limiting value of B_{eff} depends strongly on the nature of the sample. It is at least twice as large as the B_{eff} value of the starting material. Qualitatively, therefore, the large saturated value of B_{eff} corresponds to the fact that the crystal can accept large average static displacement of atoms. Graphite seems to have a very high saturated value of B_{eff} along the c-axis, although its value could not be established in the present work. This fact can be understood in terms of the weak van der Waal's binding force between layer planes of graphite. For graphite, the behaviour of B_{eff} and ϵ with grinding is different from other crystals, as shown in Fig. 4; this will be discussed from the view point of structural change elsewhere [8]. The other crystals examined have relatively small, but different limiting values of B_{eff}. The limiting value may be determined from the co-operative combination of many elemental properties, such as bond nature, structure, density, rigidity, etc. In the present work, it is not possible to draw any conclusion on this problem because of scarcity of data and of the inability to separate the static displacement component from the thermal vibration component in B_{eff}.

From the present results, it can be concluded that the effective Debye parameter, B_{eff}, gives some information on the deformed structure of the crystal. At least with respect to the process of grinding and compression, B_{eff} is more sensitive to a small deformation of structure than is ϵ. Moreover, B_{eff} can be determined more accurately than ϵ, because the value of ϵ is influenced strongly by the conditions of the measurement, e.g., density and thickness of the specimen. The scatter of the measured points is smaller in the determination of B_{eff} than in that of ϵ. The pure component of the static displacement of atoms in B_{eff} is more useful than the value of B_{eff} itself. The simple subtraction of the theoretical B-value (if the Debye temperature of the sample is known) or of the value for the well-annealed sample from B_{eff}, seems to be one approach [3]. However, it is more fundamental and desirable to know the component of thermal vibration of atoms by measuring the dependence of diffraction intensities on temperature.

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Received 1 May and accepted 29 September 1972.