Letter

Integrated Intensity Changes for Crystalline Powders by Grinding and Compression—Changes in Effective Temperature Factor

The so-called temperature factor

$$\exp(-2B \cdot \sin^2\theta/\lambda^2)$$

for X-ray diffraction intensity [1] was measured on some crystalline powders and it was found to depend strongly on the crystalline state of the powders.

The Debye parameter B in the temperature factor is obtained from the slope of the relation between the observed diffraction intensity of the (hkl) line, I_{obs} (hkl), and $\sin^2\theta/\lambda^2$ [2]. The relation is written as follows:

$$\log (I_{obs}/I_{calc}) = \log k - 2B \cdot \log e \cdot (\sin^2\theta/\lambda^2),$$

where k is the sale factor, θ diffraction angle, λ wavelength of X-ray and I_{calc} the theoretical intensity for (hkl) line. I_{calc} corresponds to the intensity where all atoms are fixed on the ideal lattice sites and can be calculated from structure factor, Lorentz-polarisation factor, multiplicity, absorption factor for the diffraction line. The parameter B thus obtained was called the effective Debye parameter B_{eff} in the present work, because it is related not only to thermal vibration but to static displacement of atoms from the normal position [1, 2].

The integrated intensity of each diffraction was determined by scanning the scintillation counter over a suitable range of diffraction angle 2θ and by subtracting from the registered intensity, the background intensity corresponding to the scanned angle range. Care was taken in the

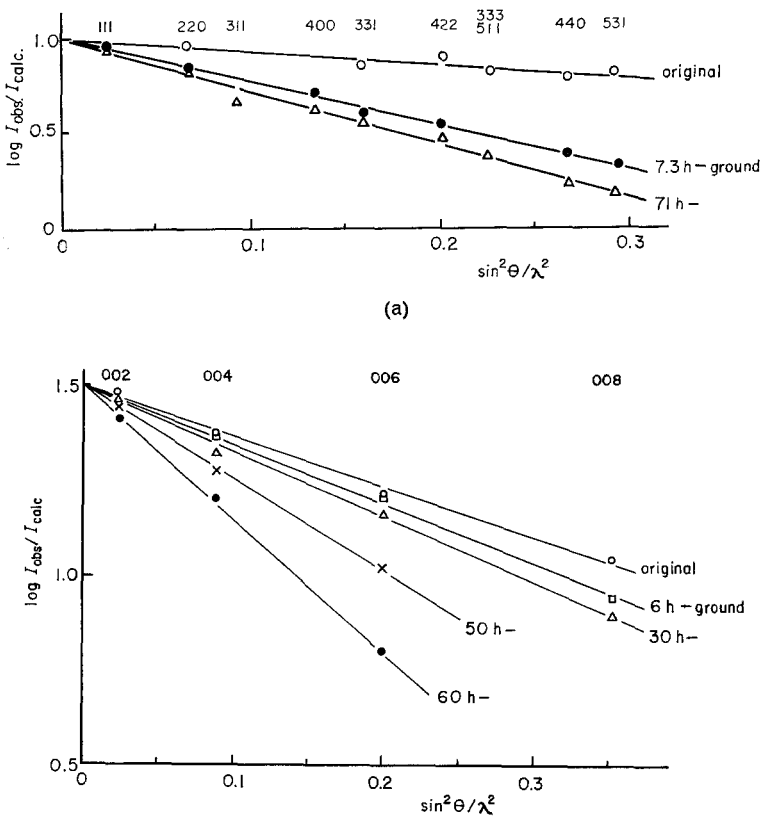

Figure 1 Effect of grinding on the relation between log (I_{obs}/I_{calc}) and $\sin^2\theta/\lambda^2$. (a) CaF_2. (b) graphite.

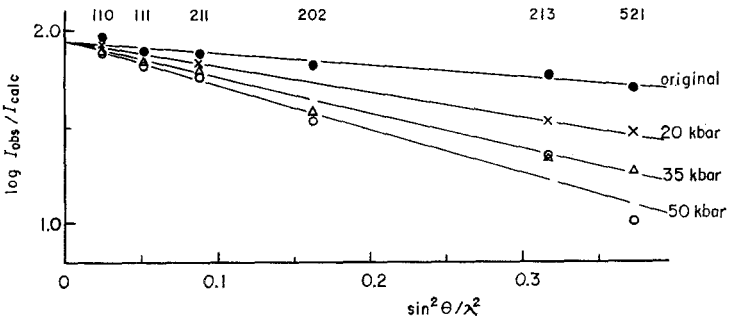

Figure 2 Effect of compression on the relation between log (I_{obs}/I_{calc}) and $\sin^2\theta/\lambda^2$ of TiO_2.

measurement of the background, to ensure that no overlapping with the broadened peaks or their "tails" occurred. Therefore, the number of diffractions usable was limited. Simultaneously with the intensity registration, the line profile of each diffraction was recorded. The monochromatisation of the X-rays was carried out by using a suitable filter and pulse-height analyser.

Fluorite, CaF_2 (reagent grade), and purified Ceylon natural graphite were ground in an agate mortar. The relations between $\log(I_{obs}/I_{calc})$ and $\sin^2\theta/\lambda^2$ are shown for different grinding times in figs. 1a and b. The effective Debye parameter B_{eff} increases notably with the increase in grinding time. The present results agree with the well-known fact that the diffraction intensity, particularly of high-angle diffraction, decreased with grinding time. By using the parameter B_{eff}, the change of diffraction intensity (i.e. the change of structure), with grinding is represented quantitatively. The change of B_{eff} with grinding time seems to be different for fluorite and graphite.

Rutile TiO_2, which was prepared by the hydrolysis of tetra iso-propyl titanate [3] and heating to 1300°C, was compressed under high pressures at room temperature. A girdle-type high pressure apparatus was used for compression [4]. With the increase in pressure, B_{eff} increases remarkably, as shown in fig. 2.

A spinel-type compound $NiAl_2O_4$, which was prepared by solid-state reaction from the component oxides [5] was quenched from different temperatures to 0°C. With the increase in heating temperature, B_{eff} increases as shown in fig. 3. In this case, the cation distribution in the spinel-type structure was assumed to be $(Ni_{0.82}Al_{0.18})_{tetra}\,(Ni_{0.18}Al_{1.82})_{octa}O_4$ [5].

As can be seen from the above four examples, the effective Debye parameter, i.e. the effective temperature factor, depends strongly on the state of the sample. On the binary alloy and a few mixed crystals of alkaline halides, the observed Debye parameter has been found to be much larger than expected and has been discussed in relation to disorder in the lattice [2]. Therefore, the effective temperature factor can be used as one of the parameters for characterisation of crystalline powders, which appears to have many kinds and large amounts of defects. In the present work, certain qualitative correspondence of broadening of diffraction and B_{eff} for ground and compressed samples was observed. The quantitative relation between B_{eff}

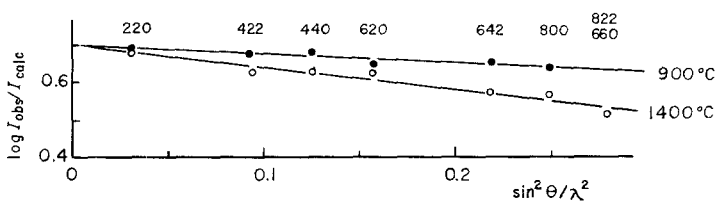

Figure 3 Effect of heating temperature on the relation between log (I_{obs}/I_{calc}) and $\sin^2\theta/\lambda^2$ of $NiAl_2O_4$.

and so-called strain determined from half-width of diffractions must be investigated.

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