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# A Method for Digitizing the X-ray Diffraction Pattern on X-ray Film by Gandolfi Camera

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**Abstract**

Gandolfi camera is a classical X-ray camera used to obtain a powder-like X-ray diffraction pattern from a small single crystal. After Gandolfi (1964) had proposed the convenient method, some attachments and techniques have been developed to improve the Gandolfi camera. Especially recent IP techniques improve the classical method as a digitized analytical instrument. However, a Gandolfi camera equipped with IP is expensive for normal use. In this paper, we establish a method to convert an X-ray diffraction pattern on X-ray film to digital data by visual basic on Excel and imaging scanner for personal use. The most probable pixel of $2\theta = 0$ and numerical data of $2\theta$-Intensity can be calculated speedily and precisely by this programming method.

**Key-words** : Gandolfi camera, X-ray diffraction pattern, X-ray film, visual basic on Excel.

## Introduction

Gandolfi (1964, 1967) proposed a method to obtain an X-ray diffraction pattern from a small single crystal by attaching a simple accessory apparatus to a standard Debye-Scherrer camera. It was called Gandolfi camera, and the diffraction pattern obtained by the Gandolfi camera looks like a diffraction pattern from powdered sample. Thus, all diffractions can be measured from a single crystal with the Gandolfi camera and the method a very useful in identifying very small minerals, because X-ray powder diffraction patterns can be obtained from a small amount of samples (Nakamuta, 1993). Since classical methods using X-ray film in a Gandolfi camera generally need long experimental and analytical time, an X-ray diffractometer can be widely used because of its convenience. Recently, X-ray camera methods have been improved by the use of an imaging plate (IP). Nakamuta (1999) made precise analysis of a very small mineral by a Gandolfi camera with IP. He established a system to convert X-ray intensities recorded on IP to $2\theta$-Intensity data of high signal to noise ratio by summing data of a wide area. While the Gandolfi camera with IP gives an excellent method, IP is expensive, and is not easy to be purchased for general use. Recently, an image-scanner of personal use has been well developed where the blacking-density on X-ray film measured with a Gandolfi camera can be converted to digital data with high precision. In this study, we established techniques to digitize the X-ray diffraction pattern of X-ray film obtained by the Gandolfi camera into precise powder-like X-ray diffraction pattern on X-ray film with image scanner of personal use.

## Gandolfi method

Fig. 1 illustrates the principle used to obtain a powder-like X-ray diffraction pattern from a single crystal by a Gandolfi camera (Gandofi, 1967), where $\theta_B$ is a Bragg angle, O is the origin of the reciprocal lattice, $\mathbf{r}_{hkl}$ is a reciprocal vector to a *hkl* point, C is the center of Ewald sphere, $\lambda$ is a wavelength of an incident X-ray. In the case of powdered samples, $\mathbf{r}_{hkl}$ forms sphere $S_{hkl}$ with $|\mathbf{r}_{hkl}|$ radius because of randomly oriented

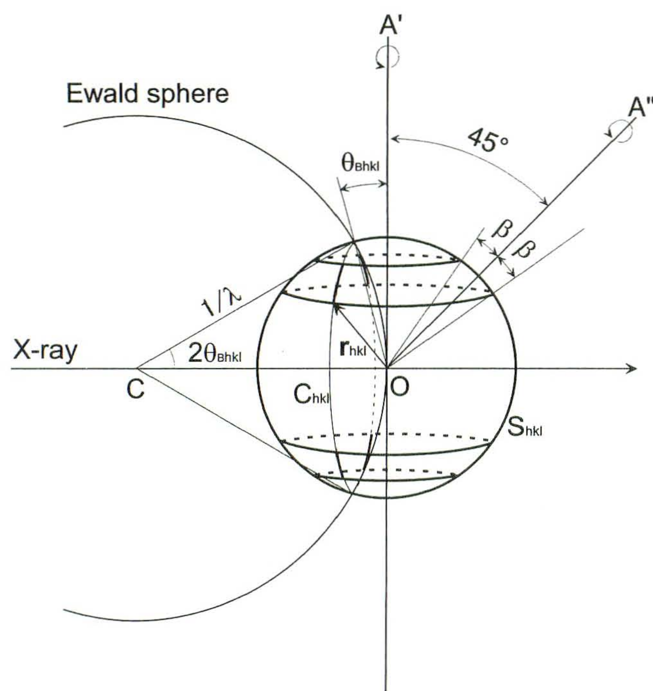
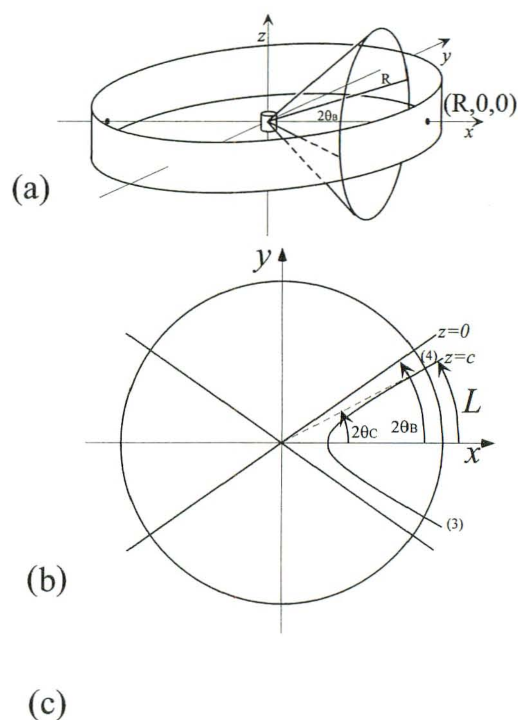



Fig. 1 X-ray diffraction condition arranged by the Gandolfi camera. By rotation of two axes (A' and A"), a reciprocal vector $\mathbf{r}_{hkl}$ generally intersects with Ewald sphere at arcs on circle $C_{hkl}$. Resultantly, X-ray powder-like pattern can be obtained from a single crystal by the Gandolfi camera.




(c)

(R,0,0) c L

$$2\theta_B = \tan^{-1}\left[\pm\sqrt{\left(\frac{R^2+c^2}{R^2}\right)\left\{1+\tan^2\left(\frac{180L}{\pi R}\right)\right\}-1}\right]$$

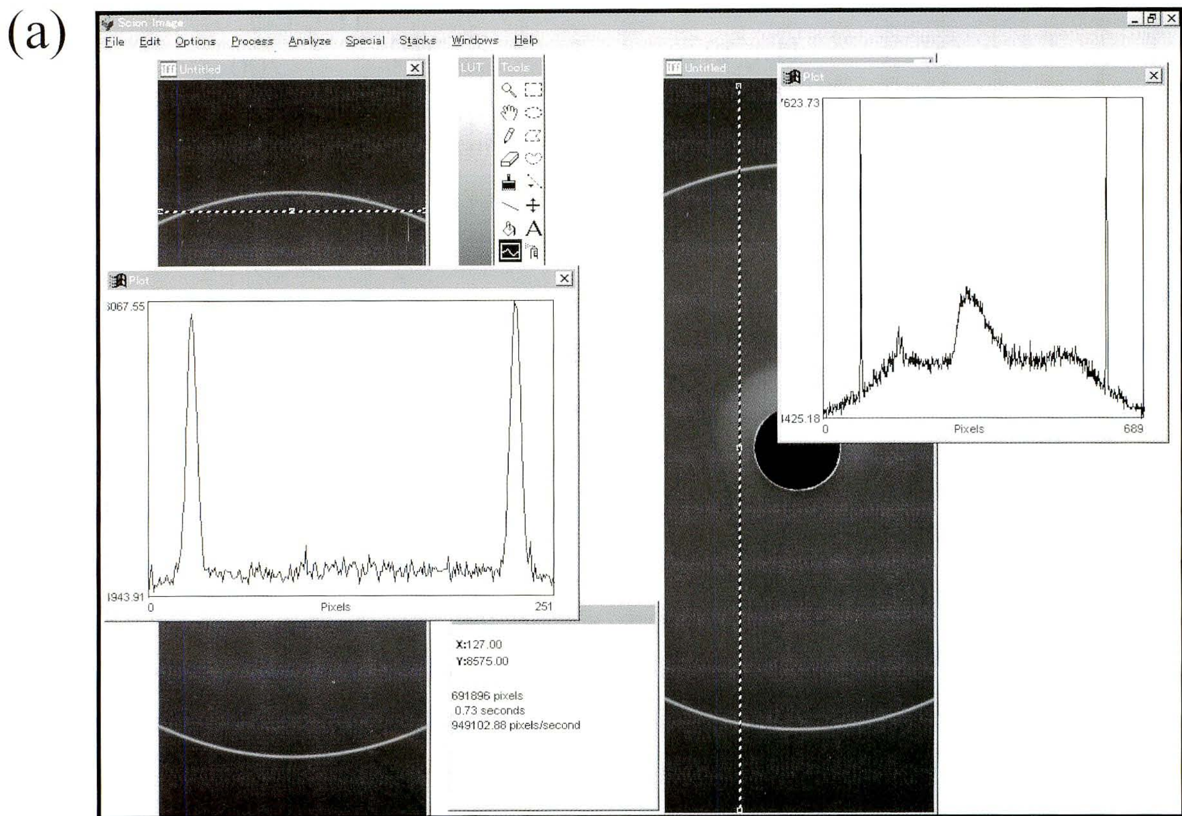
Fig. 2 (a) Schematic geometry of a circular cone as a diffracted X-ray and a circular column as X-ray film. (b) From the coordinate of the intersection of the cone and the column at $z = c$, (c) a pixel addressed at L and c on X-ray film is expressed with $2\theta_B$.

innumerable small crystals, hence a circular intersection of $S_{hkl}$ and Ewald sphere gives a diffraction cone, $C_{hkl}$. Gandolfi camera works with two rotation-axes. One is A', being perpendicular to the X-ray beam. The other is A" which intersects with A' at an angle of 45°. A reciprocal vector $\mathbf{r}_{hkl}$ rotates around A" axis and forms a circle on $S_{hkl}$ at the conical angle $\beta$. The circle of $\beta$ rotates around A' axis, and crosses on the Ewald sphere as two arcs on $C_{hkl}$ circle. Resultantly, $\mathbf{r}_{hkl}$ partially crosses the Ewald sphere and crossed intersections form arcs on $C_{hkl}$ circle by rotations of two axis A' and A". The length of arc resulting from intersection of $\mathbf{r}_{hkl}$ and Ewald sphere depends on the angle $\beta$. When the angle $\beta$ is 45° or 90°, $\mathbf{r}_{hkl}$ moves on all $C_{hkl}$ circle. In the case of $\beta \neq 45°$ and $\neq 90°$, crystals except for the triclinic system yield two or more reciprocal lattice points equivalent to $\mathbf{r}_{hkl}$ by crystallographic symmetry. As a result of overlaps of these equivalent $\mathbf{r}_{hkl}$, an unbroken diffraction cone is recorded on X-ray film.

## Measurement

We used sealed off X-ray tube (Cu target) at 30kV and 10mA. The inside of the circular cylinder of a Gandolfi camera is evacuated by rotary pump to avoid scattering of X-ray beam by air. The sample is prepared as 10 to 100$\mu$m size, in order to minimize the displacement of peak position by the absorption effects of X-rays (Nakamuta, 1993). The exposure time to X-ray is 5 to 48 hours. The X-ray film used "Industrial X-RAY FILM IX 100 (35.6×43.2cm)" FUJI PHOTO FILM CO., LTD., which was cut into a rectangle of size with 3.5×35cm by a desk cutter. The time to develop the X-ray film with developer RENDOL is 4 minutes at 20℃, the stop bath time to use acetic acid 10 seconds, and the fixing time to use RENFIX 10 minutes. By scanning the developed X-ray film with an image scanner, the blacking-density of X-ray film is saved as image data of TIFF format. In this study, X-ray film is scanned under the conditions of 800dpi, 12 bits and positive transmission mode. The image data of TIFF format can be converted to numerical data and saved in text-file format by using a public domain software

(a)




(b)

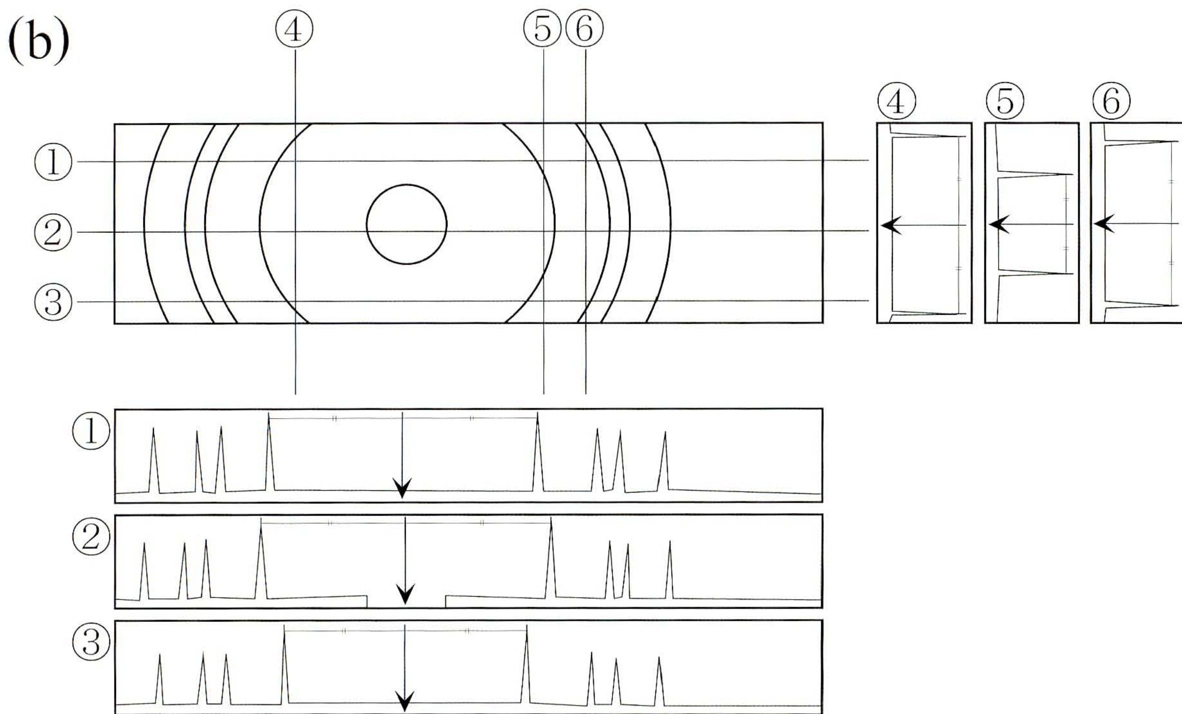



Fig. 3 (a) A screen shot of line profile analysis with NIH Image for Macintosh or Scion Image for Windows ("Plot profile" function) representing the scanned image of the X-ray film showing diffracted pattern and the window showing blacking-density versus pixel along an analytical line (dotted line). (b) Schematic figure of diffraction pattern on X-ray film and six analytical lines. Six line profiles of blacking-density versus pixel correspond to each line along L(1-3) and c(4-6). A temporary coordinate of a center position indicated by arrows is calculated from a pair of diffracted arc by the same lattice plane. However, coordinates of center calculated from line profiles involve accidental error.

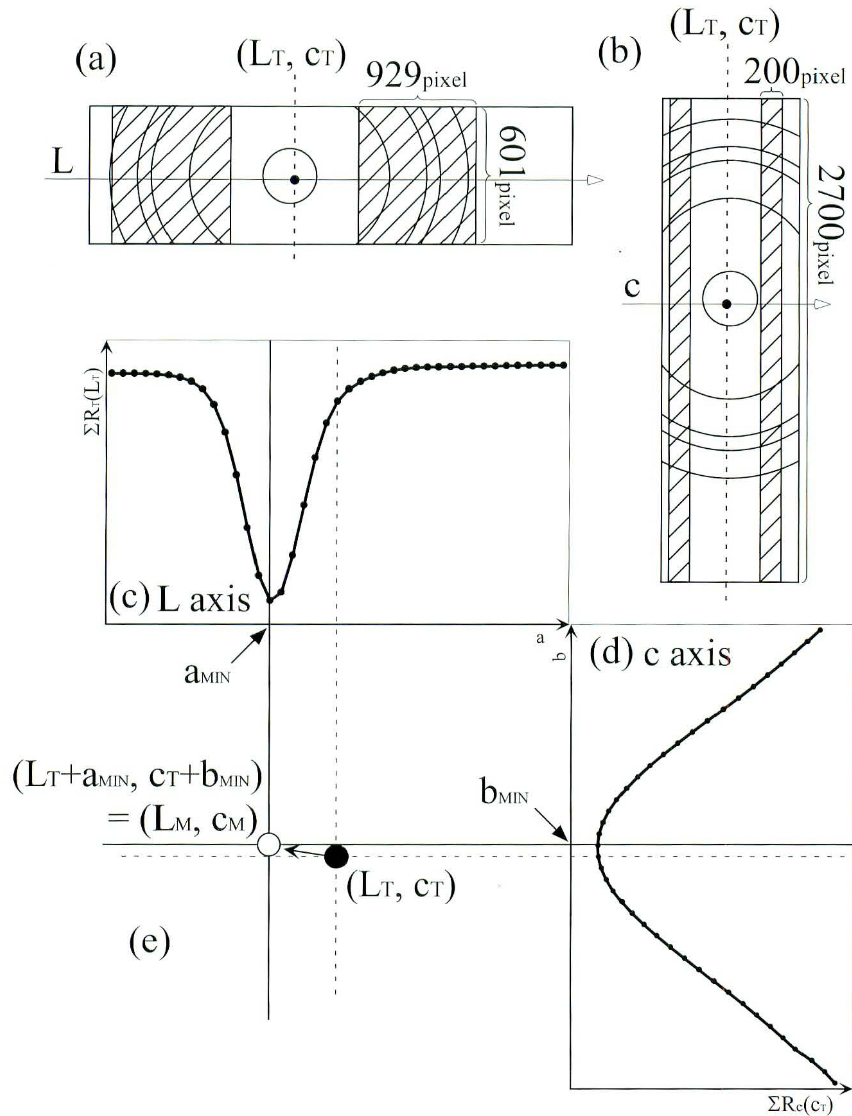


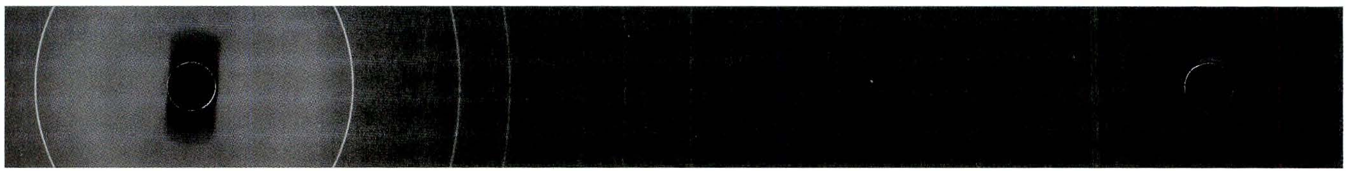

Fig. 4 A principle to determine the coordinates of $2\theta_B = 0$, $(L_M, c_M)$. (a) and (b) show directions of L and c axis, respectively. $(L_T, c_T)$ is the temporary position of $2\theta_B = 0$ which is obtained by line profile analysis (shown in Fig. 3). Shaded areas show all analytical pixels over which sums of square of residuals of blacking-density ($\Sigma R_L(L_T)$ and $\Sigma R_c(c_T)$) are calculated. (c) and (d) Plotting $\Sigma R_L(L_T)$ against a and $\Sigma R_c(c_T)$ against b, $a_{MIN}$ and $b_{MIN}$ are the values to minimize $\Sigma R_L(L_T)$ and $\Sigma R_c(c_T)$ are determined. (e) Finally, $(L_M, c_M)$ is determined as $(L_T+a_{MIN}, c_T+b_{MIN})$.

NIH-image on Macintosh (or Scion-image on Windows).

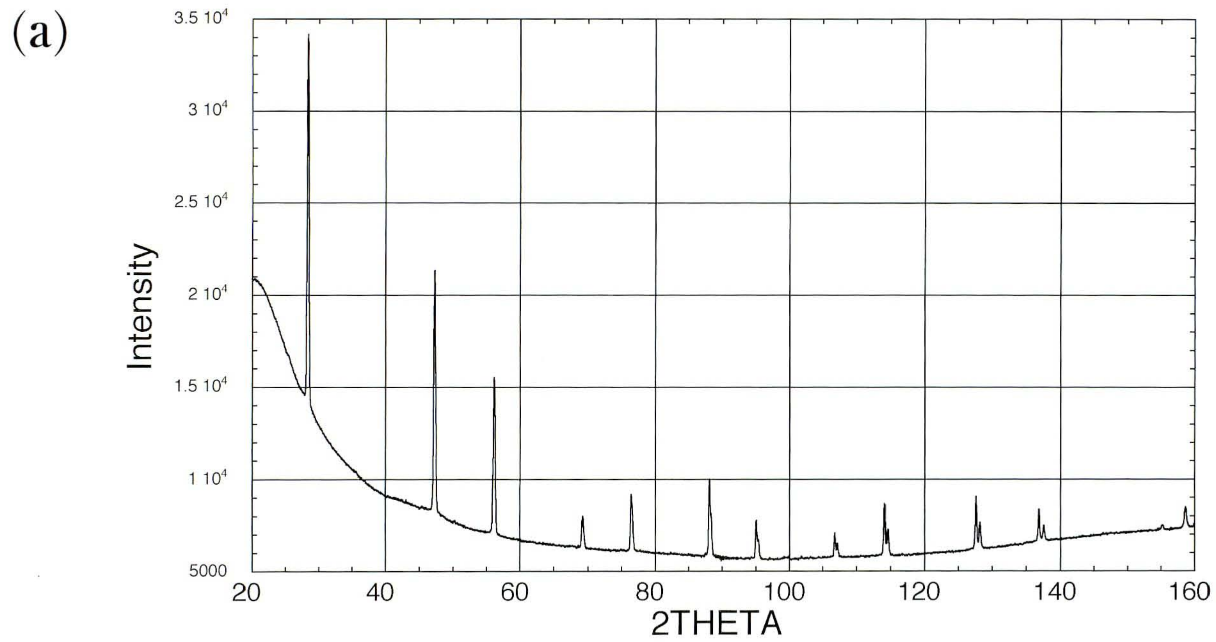
## Discussion

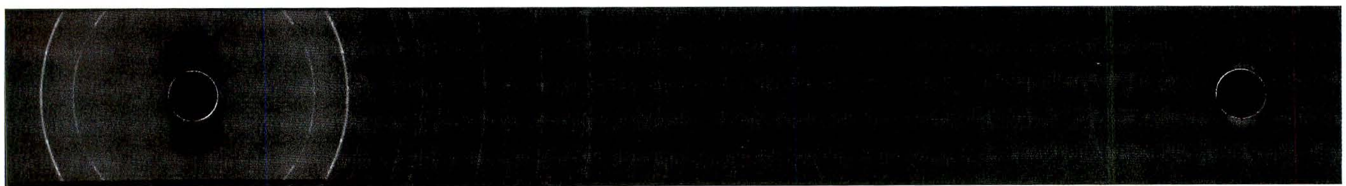
### Conversion of image data into $2\theta$-Intensity data

In order to convert digitized gradation of X-ray film with a scanner to data of $2\theta$-Intensity of high S/N ratio, the data processing system is arranged from geometry of X-ray film and diffracted X-ray from a sample in Gandolfi camera (Fig.2). Supposing that the radius of Gandolfi camera is $R$, the direction of the incident X-ray is x-axis, the perpendicular of the incident X-ray in the horizontal is y-axis and the vertical is z-axis, the position of the sample is (0, 0, 0), the position with $2\theta_B = 0$ Bragg angle on X-ray film is (R, 0, 0). A diffracted X-ray forms a circular cone and X-ray film is located as a circular cylinder.



(a)



(b)

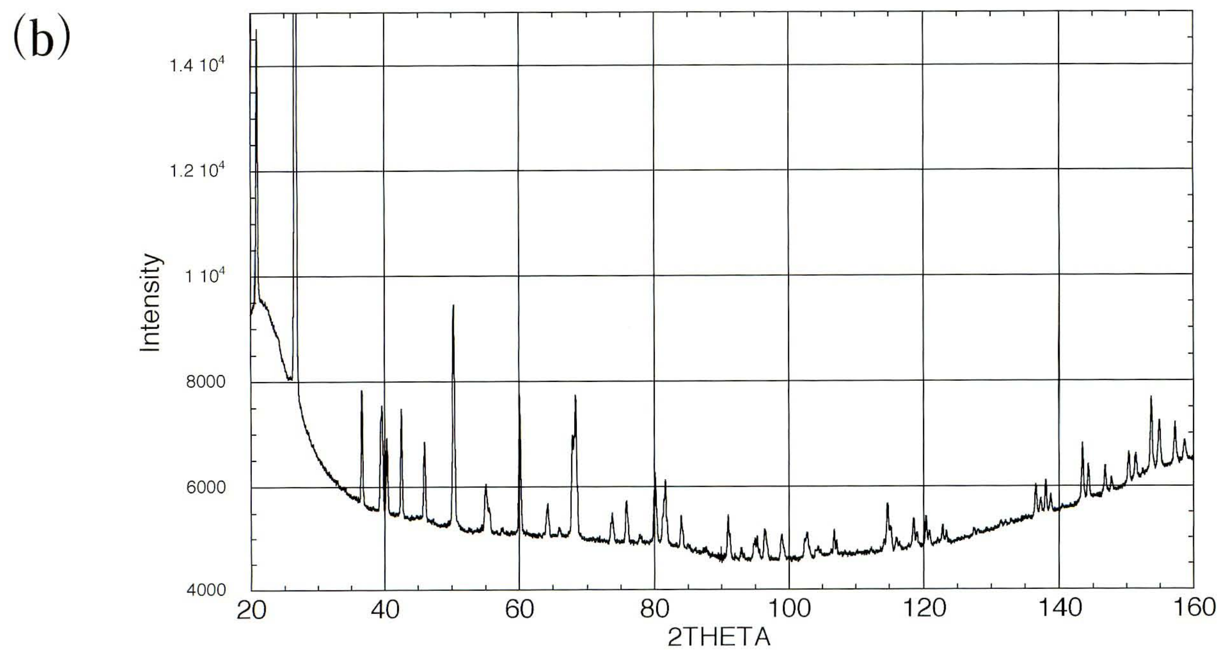



Fig. 5 X-ray diffraction film of powdered silicon (a) and quartz single crystal (b), and X-ray diffraction chart converted from the X-ray film by the method of this study.

Table 1 Comparing tables have converted data and ASTM cards.

| Silicon | | | | | | |
|---|---|---|---|---|---|---|
| (hkl) | 2θ obs (°) | dobs (Å) | dASTM (Å) | Δd (Å) | Iobs | IASTM |
| 111 | 28.36 | 3.144 | 3.136 | -0.009 | 100 | 100 |
| 220 | 47.29 | 1.920 | 1.920 | 0.000 | 66 | 55 |
| 311 | 56.16 | 1.636 | 1.638 | 0.001 | 42 | 30 |
| 400 | 69.20 | 1.356 | 1.358 | 0.001 | 9 | 6 |
| 331 | 76.41 | 1.245 | 1.246 | 0.001 | 15 | 11 |
| 422 | 88.11 | 1.108 | 1.109 | 0.001 | 21 | 12 |
| 511 | 95.03 | 1.044 | 1.045 | 0.001 | 10 | 6 |
| 440 | 106.79 | 0.959 | 0.960 | 0.001 | 6 | 3 |
| 531 | 114.18 | 0.917 | 0.918 | 0.001 | 14 | 7 |
| 620 | 127.62 | 0.858 | 0.859 | 0.000 | 15 | 8 |
| 533 | 136.90 | 0.828 | 0.828 | 0.000 | 8 | 3 |
| 444 | 158.64 | 0.784 | 0.784 | 0.000 | 6 | -- |
| Quartz | | | | | | |
| (hkl) | 2θ obs (°) | dobs (Å) | dASTM (Å) | Δd (Å) | Iobs | IASTM |
| 100 | 20.87 | 4.253 | 4.257 | -0.004 | 31 | 22 |
| 101 | 26.64 | 3.343 | 3.342 | 0.001 | 100 | 100 |
| 110 | 36.59 | 2.454 | 2.457 | -0.003 | 13 | 8 |
| 102 | 39.43 | 2.283 | 2.282 | 0.001 | 11 | 8 |
| 111 | 40.33 | 2.234 | 2.237 | -0.003 | 8 | 4 |
| 200 | 42.50 | 2.125 | 2.127 | -0.002 | 12 | 6 |
| 201 | 45.86 | 1.977 | 1.979 | -0.002 | 9 | 4 |
| 112 | 50.26 | 1.814 | 1.818 | -0.004 | 25 | 14 |
| 202 | 55.04 | 1.667 | 1.672 | -0.005 | 5 | 4 |
| 103 | 55.54 | 1.653 | 1.659 | -0.006 | 3 | 2 |
| 211 | 60.08 | 1.539 | 1.542 | -0.003 | 16 | 9 |
| 113 | 64.07 | 1.452 | 1.454 | -0.001 | 4 | 1 |
| 212 | 67.93 | 1.379 | 1.382 | -0.003 | 11 | 6 |
| 203 | 68.34 | 1.371 | 1.375 | -0.004 | 16 | 7 |
| 104 | 73.69 | 1.284 | 1.288 | -0.004 | 3 | 2 |
| 302 | 75.82 | 1.254 | 1.256 | -0.002 | 5 | 2 |
| 213 | 80.07 | 1.197 | 1.200 | -0.002 | 8 | 2 |
| 114 | 81.62 | 1.179 | 1.184 | -0.006 | 7 | 3 |
| 311 | 83.95 | 1.152 | 1.153 | -0.002 | 4 | 1 |
| 312 | 91.03 | 1.080 | 1.081 | -0.002 | 5 | 2 |

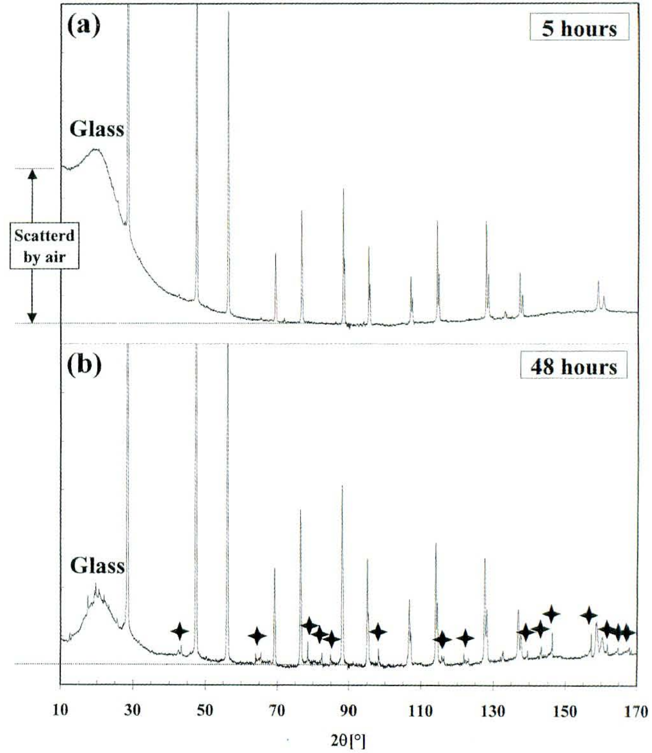



Fig. 6 Some noises in converted data result from difference of evacuating time. A broad shoulder in the lower angle in (a) is due to scatter by air (both arrows). Many tiny peaks in (b) are due to cracks on X-ray film (star marks). The broad peak at low angle (near $2\theta = 15°$) is due to a glass bar used to fix the sample.

The equations of the circular cone and the circular cylinder are expressed as

$$y^2 + z^2 - (x \tan 2\theta_B)^2 = 0 \quad (1),$$

$$x^2 + y^2 = R^2 \quad (2),$$

where $2\theta_B$ is Bragg angle and $z$ is arbitrary in equation (2). Diffraction patterns recorded on X-ray film are expressed as intersections of (1) and (2). When $z = c$ ($c \neq 0$), (1) represents two hyperbolas and the equation of which is

$$y^2 = (x \tan 2\theta_B)^2 - c^2 \quad (3).$$

The intersections of (2) and (3) are given as coordinates of

$$\left( \pm\sqrt{\frac{R^2+c^2}{1+\tan^2 2\theta_B}},\ \pm\sqrt{R^2 - \frac{R^2+c^2}{1+\tan^2 2\theta_B}},\ c \right) \quad (4).$$

Therefore,

$$2\theta_c = \tan^{-1}\left[ \frac{\pm\sqrt{R^2-(R^2+c^2)/(1+\tan^2 2\theta_B)}}{\pm\sqrt{(R^2+c^2)/(1+\tan^2 2\theta_B)}} \right] \quad (5).$$

The length of the arc L, which is the horizontal distance from (R, 0, c) to a diffracted X-ray on the X-ray film, is

$$L = \frac{2\theta_c \pi R}{180} \quad (6).$$

From (5) and (6), the $2\theta_B$ angle at the position on X-ray film, being $x = R \cdot \cos 2\theta c$, $y = R \cdot \sin 2\theta_c$, $z = c$, can be written as

$$2\theta_B = \tan^{-1}\left[ \pm\sqrt{\left(\frac{R^2+c^2}{R^2}\right)\left\{1+\tan^2\left(\frac{180L}{\pi R}\right)\right\} - 1} \right] \quad (7).$$

To calculate $2\theta_B$ from (7), 5657 pixels are allocated for $2\theta_B = 180°$ range in reference to the diffraction of silicon. The summed area of X-ray film is 800×5657 pixels (25×180mm$^2$).

According to (7), a point at (L, c) on the X-ray film can be converted to $2\theta_B$. The $2\theta_B$ values calculated from (7) are rounded to every 0.025°. After rounded $2\theta_B$ sheets of 800×5657 cells were formed on an Excel sheet, every observed numerical intensity of 800×5657

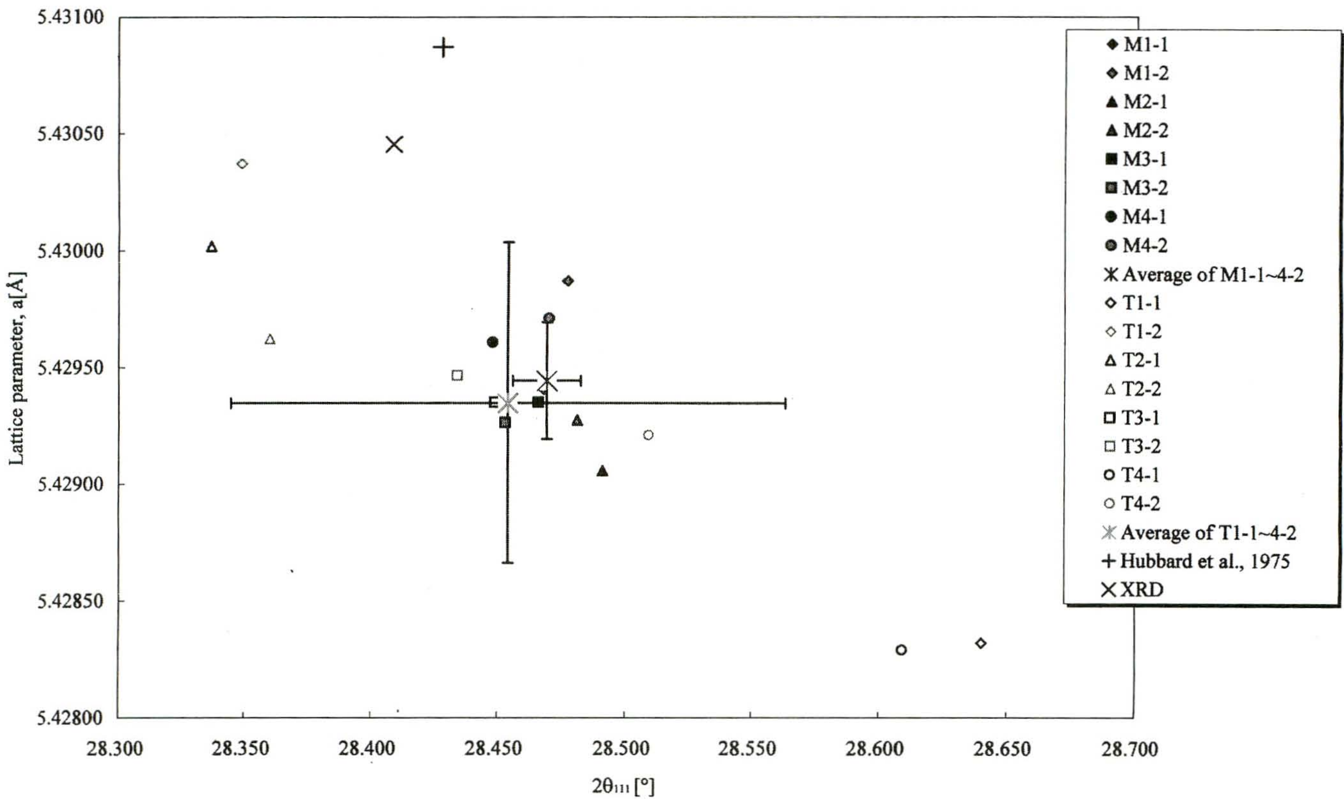



Fig. 7 $2\theta_{111}$ of the intense peak of silicon versus lattice parameter, a, of silicon. The lattice parameters are calculated with extrapolation based on $\lambda(\mathrm{CuK}\alpha_1) = 1.5405$Å. Error bars are standard deviations, $\sigma$, of average. Filled marks (M) are the values determined from the most probable $2\theta = 0$, open marks (T) are from ($L_T$, $c_T$), and poly-cross-shaped marks are their average. Cross-shaped mark is a reference value (Hubbard *et al.*, 1975). An X mark is obtained from the powder X-ray diffractometer.

pixels on X-ray film are correlated with the corresponding rounded $2\theta_B$. All observed intensities, which are assigned to the same rounded $2\theta_B$, were summed with "sumif" function ($\Sigma I(2\theta_B)$). The number of the cell of the same $2\theta_B$ was counted with "countif" function ($\Sigma N(2\theta_B)$). Averaged intensities of each 0.025 are calculated from $\Sigma I(2\theta_B)/\Sigma N(2\theta_B)$. Finally, $2\theta_B$-$I_{obs}$ data are saved as text format. The summing and counting processes were programmed with visual basic on Excel. An important process during the above calculation is the determination of the most probable pixel of $2\theta_B = 0$.

**Determination of the pixel of $2\theta_B = 0$ on X-ray film**

A temporary coordinate ($L_T$, $c_T$) of $2\theta_B = 0$ is determined as the first approximate pixel of $2\theta_B = 0$ with line profile of NIH-image ("Plot profile" function). Fig. 3 schematically shows the way to determine a temporary pixel of $2\theta_B = 0$. Line profiles of two directions along L and c are measured across a pair of diffraction arc, two center pixels of $L_T$ and $c_T$ direction are calculated from two intense peaks of line profile, and the ($L_T$, $c_T$) pixel is assigned to the temporary pixel of $2\theta_B = 0$. Although the temporary coordinate of $2\theta_B = 0$ can be easily determined using line profile, an accidental error is unavoidable.

Therefore, accidental errors are compensated for calculating squares of residuals of blacking-densities of two points at the same distance away from the temporary center ($L_T$, $c_T$) in the symmetrical areas of $601 \times 929$ and $200 \times 2700$ pixels along L and c axes (Fig. 4(a) and (b)). Fixing ($L_T$, $c_T$) as a center of pixels squares of residuals of blacking-densities against every symmetrical pixel in the $601 \times 929$ area is summed up ($\Sigma R_L(L_T)$). In the same way, squares of residuals of $200 \times 2700$ pixels are summed up ($\Sigma R_c(c_T)$). Varying ($L_T$, $c_T$) by one pixel step between $\pm$a along L, and $\pm$ b along c, $\Sigma R_L(L_T)$ and $\Sigma R_c(c_T)$ are calculated against a and b (Fig. 4(c) and (d)). Finally position ($L_M$, $c_M$) of minimizing squares of residuals of blacking-densities are the most probable pixels of $2\theta_B = 0$ (Fig. 4(e)). The way to determine the position of $2\theta_B = 0$ is programmed with visual basic on Excel.

Fig. 5 shows X-ray patterns of powdered silicon

and a quartz single crystal measured with a Gandolfi camera and $2\theta$-Intensity graphs drawn from the data converted by this method. Table 1 shows comparative tables of converted data by this method and ASTM cards. The d-values and the relative intensities show good agreement. The inside of a Gandolfi camera is evacuated by a rotary pump to avoid scattering of X-ray by air. Insufficient evacuation of the inside of a Gandolfi camera results in a broad shoulder at a low angle (both arrows in Fig.6(a)). On the other hand, evacuation over 5 hours causes many cracks on the X-ray film and appeared as many false peaks in the converted data. In this study, the inside of a Gandolfi camera was evacuated for no more than 5 hours. In Fig.6, a broad peak near $2\theta = 15°$ is due to a glass fiber used to support a sample.

**Lattice parameter of silicon by this method**

Based on the resultant ($L_M$, $c_M$), accuracy of lattice parameter obtained from Gandolfi camera is examined. Fig.7 shows $2\theta_{111}$ of silicon and lattice parameters by extrapolation calculated from X-ray film of Gandolfi camera with ($L_M$, $c_M$) (filled marks, M), ($L_T$, $c_T$) (open marks, T), from powder X-ray diffractometer, and reference value (Hubbard *et al.*, 1975). M1~4 and T1~4 result from different samples and M and T#-1 and -2 are the same sample but from a different image scan.

While averaged $2\theta_{111}$ and lattice parameters fall within approximately the same value, standard deviations of lattice parameter and $2\theta$ estimated from ($L_M$, $c_M$) ($2.5 \times 10^{-4}$Å and $1.3 \times 10^{-2}$Å) are smaller than values from ($L_T$, $c_T$) ($6.9 \times 10^{-4}$Å and $1.1 \times 10^{-1}$Å). The precision of lattice parameter calculated from ($L_M$, $c_M$) is much better than that of ($L_T$, $c_T$). Thus, the process of determining most probable $2\theta_B = 0$ is necessary for calculation of reliable data from X-ray film.

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