Principles and applications of multilayer mirror optics for X-ray diffraction measurements —CBO series for SmartLab—

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1. Introduction —What is CBO?—

A parabolic multilayer mirror as an X-ray optical device has been applied to general-purpose X-ray diffractometers since the 1990s⁽¹⁾⁻⁽³⁾. X-rays formed by such a device are of high brightness, of small divergence and adequately monochromated. This device enables us to use high-quality parallel X-rays even in laboratories. Also, this device makes channel-cut 2-bounce beam-conditioner optics more effective, and various measurement techniques for a variety of samples, either powder materials or thin films, are more easily performed with general-purpose X-ray diffractometers⁽³⁾⁻⁽⁵⁾. On the other hand, the most popular optic for powder X-ray diffraction is a conventional Bragg-Brentano para-focusing optic (BB optic), due to ease of setup, high intensity, and high angular resolution. Therefore, general-purpose X-ray diffractometers can be more effectively used if both of these optics, parallel beam (PB) optic and BB optic, can be switched easily.

Rigaku has developed and patented a CBO (Cross Beam Optics) unit that can switch a BB optic and a PB optic using a parabolic multilayer mirror by simply changing the selection slit. Subsequently, the "CBO-E" unit, which has a multilayer mirror forming a convergent beam, was marketed to accommodate diverse measurement needs. In recent years, the "CBO- α " unit, which creates a divergent beam, has been also developed.

In this report, we introduce the features and applications of each member of the CBO unit series to help SmartLab users achieve effective X-ray diffraction measurements and high-quality data acquisitions for precise analyses.

Characteristic of each unit of CBO series CBO unit —parabolic multilayer—

The CBO unit is switchable between the BB optic and the PB optic. As mentioned above, a parallel beam can be formed by a parabolic multilayer mirror. This unit is representative of the CBO series.

First, I will describe the basic concept of a multilayer mirror. For more information, please refer to Reference (3), which has reported in detail the characteristics and functions of multilayer optics for X-ray diffraction analysis and X-ray fluorescence analysis, together with the development history of multilayer optics.

A multilayer mirror is an artificial lattice having a periodic structure in which thin-film layers of a heavy element and those of a light element are alternately stacked⁽¹⁾⁻⁽³⁾. When X-rays of a certain wavelength are incident at an angle to satisfy the Bragg equation for d, which is the repetition period of the stacking structure in the multilayers, X-ray diffraction occurs. Selection of the X-ray wavelength and monochromation can be obtained using the diffraction phenomena. If a multilayer mirror is employed just for shaping a beam, you can alternatively use an optical device called a total reflection mirror, which has a metal coating on a substrate such as glass. Although the total reflection mirror is applicable to various kinds of characteristic X-rays due to its weak dependence on wavelength, the X-rays of wavelengths other than the characteristic X-rays to be used cause background noise in the measurement.

Figure 1 shows a schematic drawing of a multilayer mirror. In the actual parabolic multilayer mirror equipped in the CBO unit, the periodic thickness of the multilayer is continuously changed along the parabolic surface (left-right direction in Fig. 1). This continuous change in thickness governs the interplanar spacing, and controls the direction of the X-rays diffracted from each position. A multilayer mirror of this type is called a



Bragg equation: $2d \sin\theta = n\lambda$ (*d*: interplanar spacing, θ : incident angle, *n*: integer, λ : wavelength)

Fig. 1. Multilayer mirror.

^{*} SBU PDX, X-ray Instrument Division, Rigaku Corporation.

graded multilayered mirror.

Continuous variation of *d* values is produced by precise control of the thickness of the multilayers. This requires extremely high-level synthesis technology. A multilayer with a repetition period of large *d* is relatively easy to manufacture. For this case, the diffraction angle is small and the discriminability of the wavelength decreases, although it shows a high integral intensity. In general, $K\alpha_1$ and $K\alpha_2$ radiation are difficult to separate with a general multilayer mirror, so $K\alpha$ radiation including both characteristic radiations is produced. In addition, some $K\beta$ radiation is also observed.

In order to obtain a parallel beam, it is necessary to control the repetition period of the multilayer according to the position on the parabolic multilayer mirror. The repetition period of the multilayer is controlled to meet a different diffraction condition at each point of the multilayer mirror (Fig. 2). Therefore, to collimate the X-rays diffracted by a multilayer mirror it is necessary to create gradually larger d values as the position on the multilayer mirror moves from a position close to the X-ray source to a position far away from the X-ray source because the diffraction angle close to the source is higher than it is far away from the source.



Parabolic multilayer mirror

Fig. 2. Parabolic multilayer mirror.

By applying a parallel slit analyzer (PSA) or a crystal analyzer on the receiving side, in addition to the use of the parallel beam on the incident side, accurate diffraction angle measurement is possible. This is effective for the measurement of a sample whose surface cannot be made flat. In addition, with the combination of a parallel beam formed by a parabolic multilayer mirror and other optical devices, you can select the incident X-rays depending on your objectives for the measurements. For example, a system with a channel cut Ge (220) 2-bounce beam conditioner and the CBO on the incident side and a U-SAXS (Ultra Small Angle X-ray Scattering) analyzer on the receiving side can be used for extremely high angular resolution U-SAXS measurements (top panel of Fig. 3). This configuration can be used to measure a sample having a particle size of several hundred nm (bottom panel of Fig. 3).

A parallel beam can be applied to various fields. Possible measurement techniques and analyses using a parallel beam are as follows: analysis for degree of preferred orientation, thickness analysis of thin-film from X-ray reflectivity measurements or highresolution rocking curve measurements, reciprocal space mapping measurements, rocking curve measurements,



Fig. 3. Angular resolution of U-SAXS and ultra-small angle X-ray scattering profiles.

particle/pore size distribution analysis from SAXS measurements, in-plane measurements, and so on.

2.2. CBO-E unit—elliptical multilayer—

Since a 1D detector consisting of multiple detecting elements of narrow strip arrays was commercialized, effective measurement in a short time is realized by a 1D detector combined with an optic that focuses the X-rays at the detecting position. The CBO-E is the unit that makes it possible to easily exchange two kinds of systems, the BB optic and the convergent beam (CB) optic with an elliptical multilayer mirror, simply by exchanging the selection slit.

Since the convergent beam from the elliptical multilayer mirror in the CBO-E unit is designed to focus on the detecting surface of the detector, the combination with a 1D detector is effective. This combination enables high-speed, high-intensity and high-resolution measurement in the time delay integration (TDI) measurement.

Figure 4 is a schematic of the elliptical multilayer mirror optic. For the surface of the elliptical multilayer mirror, two focal points of the ellipse are designed to be at the X-ray source and the detecting surface of detector.



Fig. 4. Elliptical multilayer mirror.

The advantages of a convergent beam optic manifest in the characterization of samples that readily exhibits a preferred orientation texture when packed on a sample plate and has a low absorption coefficient, such as a pharmaceutical product. In this case, the sample should be packed in a glass capillary and measured by the transmission method.

Figure 5 shows a section of the X-ray diffraction profile of the topical anti-inflammatory agent indomethacin powder sample. The profile measured with the convergent beam (red line) shows well-separated peaks with high angular resolution, compared with that of the parallel beam (blue line).



Fig. 5. A comparison of the profiles measured with the parallel beam optic and the convergent beam optic by transmission method.

Structure analysis for powder samples using a K α_1 optic is also possible⁽⁶⁾. In this case, a curved crystal of a Johansson-type beam-conditioner is placed between the X-ray source and the elliptical multilayer mirror. The elliptical multilayer mirror is located so as to share a focusing point with the Johansson crystal. Using this configuration, the K α_1 characteristic X-rays monochromated by the Johansson crystal are focused at the detecting surface of the detector by the elliptical multilayer mirror. This facilitates the collection of high-angular resolution and high-intensity data. The details are described in Reference (6).

2.3. CBO-*α* unit—flat multilayer—

In the previous sections, we have described the optics that collimate or focus the divergent beam from the X-ray source using multilayer mirrors. However, the following questions remain: Can a divergent beam be formed using a multilayer mirror? What is the advantage of this kind of optic?

The answer to the first question is that, yes, a

divergent beam can be formed using a multilayer mirror. In this case, the surface of the multilayer mirror is flat. The repetition period should be controlled so as to satisfy the diffraction condition at each position on the mirror surface as explained for other multilayer mirrors (Fig. 6).



Fig. 6. Flat multilayer mirror.

CBO- α can easily exchange the conventional BB optic and the divergent beam (DB) optic with the multilayer mirror simply by changing the selection slit. Although both optics use divergent beams, a significant difference lies in their wavelength distributions.

The divergent beam without the multilayer mirror (BB geometry) is not monochromated. This means that the X-rays have a wavelength distribution that includes $K\beta$ radiation and continuous X-rays (or Bremsstrahlung) as well as the desired K α radiation. On the other hand, the divergent beam produced with a multilayer mirror is almost monochromated and $K\alpha$ radiation diffracted by the multilayer mirror dominates. When using a multilayer mirror, the intensity of the K α radiation becomes weaker than that of the X-ray source since the diffraction efficiency of the multilayer mirror is less than unity. However, the intensity of the measurement comes to be comparable to that with the conventional BB geometry. The secret is in the different ways of how to suppress the K β radiation inevitable for measurements with BB geometry.

To suppress the $K\beta$ components, a $K\beta$ filter (Ni foil with thickness of 15μ m for a Cu source) is commonly used in the conventional BB geometry. This filter weakens the $K\beta$ components to approximately 1/50, while the K\alpha components are also weakened to about 1/2. Since the relative intensity ratio of the $K\beta$ components versus the K\alpha components at the X-ray source is 1:5, the employment of a $K\beta$ filter can suppress the $K\beta$ component to ca. 1% relative to the K\alpha component. This suppression of the $K\beta$ component is brought about by sacrificing roughly half of the K\alpha component.

The intensity of the $K\beta$ component is reduced to less than 0.2% of the K α component in the CBO- α unit without using $K\beta$ filters, whereas the diffraction efficiency for the K α component is generally more than 50%. Therefore, the intensity of the K α radiation with the CBO- α optic comes to be comparable with that of the conventional BB geometry (Table 1).

In addition to the difference in suppression efficiency

Table 1. Comparison of monochromatization methods.

Monochromatic method	$K\beta/K\alpha$ intensity ratio	TDI measurement
K β filter	Approx. 1%	Applicable
СВО-а	Below 0.2%	Applicable
Counter monochromator	Approx. 0.004%	N/A

of K β radiation, a discontinuous step appears in a diffraction profile with the K β filter method, due to the absorption edge of the filter material. Such a profile is not observed in the case of monochromatization using a multilayer mirror (Fig. 7). Such a discontinuous step is not favorable for precise diffraction profile analysis. Considering practical measurement conditions, the flat multilayer mirror of CBO- α is effective to exploit a high-quality monochromated divergent beam with almost the same intensity of K α line as that by the filter



Fig. 7. Absorption edge of $K\beta$ filter.

method.

The optic also suppresses the emission of fluorescent X-rays that cause an increase in background in measured data, due to the limitation of the wavelength inherent in the incident X-rays by the monochromatization of the X-rays on the incident side.

The arrangement of the DB geometry is comparable to that of the BB geometry. The combination with a 1D detector is particularly effective for high-speed and high-intensity measurement in TDI mode. The large improvement in the peak-to-background (P/B) ratio due to the monochromation of the incident X-rays enables the detection of signals too weak to be observed in the conventional BB geometry. Another way to suppress the K β components in the data is the employment of a counter (secondary) monochromator on the receiving side. The degree of monochromatization by a monochromator in front of the detector far outweighs that of the DB method. However, the intensity of the X-rays obtained by the counter monochromator method is approximately two orders smaller than the result of the TDI measurement using the DB optic. The counter monochromator method is impracticable for the TDI measurement of high-speed and high-intensity by a 1D detector (Table 1).

When a Fe-containing sample is to be measured with this optic, increased background can be suppressed by a combination with a Co X-ray source. This method inhibits the X-ray fluorescence that is unavoidable only by the K β filter method, and allows a TDI measurement, which is incompatible with the counter monochromator method. Therefore, the combination of the DB optic and a Co X-ray source is a valuable method to obtain the X-ray diffraction profile for Fe-containing samples with a high P/B ratio, because this system can perform high-speed and high-intensity measurement with the suppression of the background due to fluorescent X-rays.

3. Summary

The original multilayer mirrors were parabolic multilayer mirrors, which form a parallel beam. Now, we also have elliptical multilayer mirrors for a convergent beam and flat multilayer mirrors for a divergent beam.

All the mirrors introduced above are multilayer mirrors for a line focus X-ray source. A point focus X-ray source is applicable to various incident X-rays in combination with two multilayer mirrors that are orthogonally positioned in the vertical and horizontal direction^{(1),(3),(7)}. Utilizating these two multilayer mirrors, the parallel beam type and the convergent beam type are freely selected. For instance, the monochromated X-rays that are parallel in the vertical and horizontal directions can be formed as the incident X-rays⁽⁹⁾. X-rays focused at the detector position in the convergent beam geometry are applied to the structure analysis of single crystals^{(3),(7),(8)}, and X-rays focused at the sample position are useful for the measurement of micro-areas on a sample⁽¹⁰⁾.

The CBO-*f* unit is a device for converting a line beam to a point beam. Using the CBO and the CBO-*f* together, it is possible to form X-rays collimated with a size of sub-millimeter order even with a line focus X-ray source⁽¹⁰⁾. These optics are favorable for the measurement of micro-areas on a sample, and this creates a synergy effect for high-quality data measurement by a combination with a 2D detector^{(11)–(13)}.

The CBO series can provide various types of incident X-rays, in combination with the X-ray sources, the receiving optics and the detector. They are assured to be widely applied to the X-ray measurement of a variety of materials and contribute to precise analysis.

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