

Powder X-ray Diffraction Basic Course

Fourth Installment: Qualitative analysis

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Abstract

An essential feature of the qualitative analysis of the powder X-ray diffraction (PXRD) method is that this provides information on the sample's crystal structure, which often affects the properties and functions of the material. The qualitative analysis by the PXRD method is a phase identification method based on the matching of known patterns (Card) in with measurement patterns. Tips in the phase identification procedure are the quality of the measurement data, the presence of trace phases, and the selection of card. In recent years, the performance of analysis software has been improved, and phase identification can now be done quickly and easily by a computer search. Since the results of computer searches are not always correct, analysts need to evaluate the validity of the analysis results themselves.

1. Introduction

This fourth installment of the Powder X-ray Diffraction (PXRD) Basic Course describes the practical details of the data-analysis procedure in qualitative analysis by the PXRD method. This procedure is just as crucial for obtaining good results as sample preparation and measurement condition selection, which were explained in the third installment of the course⁽¹⁾.

Qualitative analysis by the PXRD method is now widely used as an indispensable tool for evaluation and quality-control purposes in the material industry's research, production, and engineering activities. The main reason is that this method, unlike elemental analysis methods such as X-ray fluorescence (XRF) analysis, provides information on the sample's crystal structure, which often affects the properties and functions of the material. Another reason is that the PXRD method is non-destructive, allowing the user to further analyze the sample by other methods after the PXRD measurement.

It should be noted that qualitative analysis by PXRD still requires the user to check the validity of the results, even though advancements in software technology in recent years have made the analysis much easier than before. The following chapters will describe the basics of qualitative analysis by the PXRD method, along with some tricks and traps users should keep in mind.

2. Basics of Qualitative Analysis

2.1. Crystal structure and diffraction pattern

The following equation expresses Bragg's law, which is the basis of the PXRD method:

$$2d \sin\theta = n\lambda$$

where d is the lattice spacing, θ the Bragg angle, λ is the wavelength of the X-rays, and n is an integer.

A crystalline material has a specific crystal structure,

and its lattice spacings also have particular values. The above formula states that the Bragg angle varies according to the lattice spacing; therefore, each material has a specific diffraction pattern.

Qualitative analysis by PXRD is a phase identification method based on matching known patterns with the measured pattern. If the XRD pattern of a known substance is included in the XRD pattern of the test sample, it is judged to contain the substance in the test sample. The XRD patterns of known substances can be obtained mainly from commercially available databases of PXRD patterns.

Figure 1 shows the phase identification result of α -quartz. The red line and the blue bars indicate the measured data and the known XRD pattern (of α -quartz), respectively. Here, the sample is identified as α -quartz since the positions and the relative intensities of the measured peaks are a good match with the database values.

2.2. Database

The PXRD databases published by the International Centre for Diffraction Data (ICDD) are widely used for phase identification. Other popular databases include the Inorganic Crystal Structure Database (ICSD) and

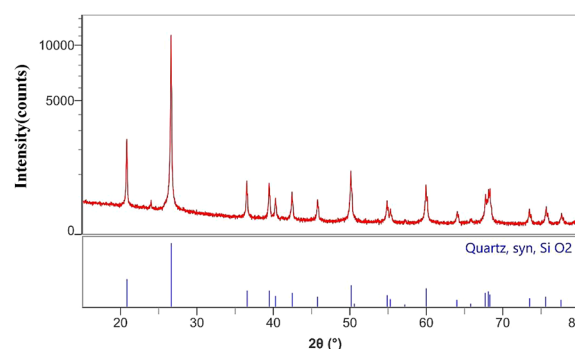


Fig. 1. Phase identification result of α -quartz.

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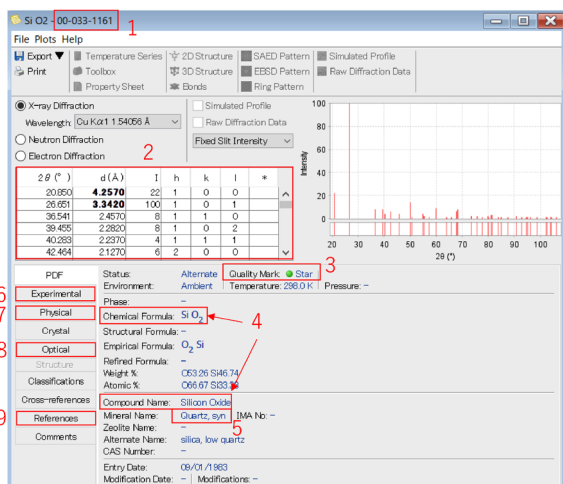


Fig. 2. Card information for α-quartz.

Table 1. Description of information in a card.

| Number | Description |
|--------|--|
| 1 | Card number |
| 2 | List of diffraction peaks with the lattice spacing (d-value), relative intensity, and Miller indices of each line |
| 3 | Quality Mark (Star, Indexed, Calculated, Blank, etc.) |
| 4 | Chemical formula and compound name |
| 5 | Mineral material: Mineral name and formula Organic material: Structural formula |
| 6 | Experimental conditions, etc. |
| 7 | Crystallographic data (crystal system, space group, lattice constants, and the number of molecules within a unit cell, etc.) |
| 8 | Optical data (refractive index, etc.) |
| 9 | References |

the Crystallography Open Database (COD). Each entry stored in these databases is called a “card.” This is because the data was originally distributed as printed cards. Currently, ICDD provides five different Powder Diffraction File (PDF) datasets for different purposes: PDF-2, PDF-4+, PDF-4/Organics, PDF-4/Minerals, and PDF-4/Axiom.

A PDF-2 card includes the diffraction information about a material, such as lattice spacings, relative intensities, and Miller indices of the diffraction peaks. Some cards also contain the substance’s crystallographic data, optical data, measurement conditions, etc. The latest version of PDF-2 as of December 2021, PDF-2 2022, includes 327,624 cards^{(2), (3)}.

Figure 2 shows the information on the α-quartz card and Table 1 describes the information on the card. The Quality Mark (QM), line 3 in Figure 2, indicates the pattern quality. It can be either S (highly reliable), I (indexed data with quality that doesn’t match the S criterion), C (calculated), R (obtained by pattern fitting

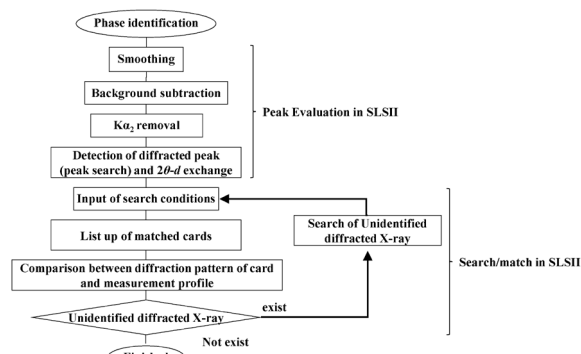


Fig. 3. The general procedure of phase identification by computer search.

such as Rietveld refinement), O (poorly characterized), or B (not evaluated), etc.

2.3. Procedure of phase identification

Manual search and computer search are used for phase identification. In the past, Johnson/Vand⁽⁴⁾ and SANDMAN⁽⁵⁾ were widely-used programs for the computer search. Today, most popular programs are still based on these two, with various improvements for higher precision. Figure 3 shows the general procedure for phase identification by computer search, and Fig. 4 shows the analysis results screen of SmartLab Studio II^{(6), (7)} (SLSII), which is an integrated X-ray analysis software package from Rigaku. The procedure of phase identification using SLSII is described in this section.

First, peak evaluation is performed to calculate lattice spacings and relative intensities for phase identification. In the peak evaluation step, peak search, detection of background profile, and profile fitting are automatically executed as soon as data is loaded, and a peak list and information about background are obtained instantly. Figure 4 (a) shows part of the SLSII window after loading the measurement data of a mixture of α-quartz and α-alumina. Peak profiling is automatically performed and the peak list is created.

The next step is to find matching cards by searching the database. This is called “search/match.” The peak-list data are used as the key for the search, but the user can also define “search conditions” to narrow down the match candidates, which can be excessive in some cases. Search conditions can include tolerance for the lattice constants, specifying the constituent elements, or peak position and intensity weighting in the searching process. Figure 4 (b) shows the dialog box for selecting constituent elements in SLSII.

SLSII can identify multiple phases in a mixture sample by repetitive search/matches. First, the program determines the phase that best matches the measured pattern. The phase is then put on the candidate phase list and its peak intensities are subtracted from the measured peak list. The residual peaks, recorded as a residual peak list and a residual graph, are used in a subsequent search/match. This procedure is automatically repeated by SLSII until the peak intensities of the residual peak



Fig. 4. Procedure of phase identification by SLSII. (a) Peak list, (b) Conditions example for search/match, (c) candidate phase list.

list becomes sufficiently small. Figure 4 (c) shows the window after search/match by SLSII, in which α -quartz and α -alumina are displayed in the candidate phase list.

It is recommended that the user examine the validity of the match results as it is not always safe to rely on the automatic search/match entirely. For example, the match result may include a substance not supposed to be in the sample. A low-QM card in the candidate phase list is another indication of a potential false match. In those cases, the user can remove such substances from the candidate phase list to refine the match result.

The user can also add a candidate to refine the results. This is useful when the user knows the sample composition. Those cases include when the sample was synthesized through a known process or when another analysis result is available. The user can also create new cards for substances that do not exist in the database. These can be created by conducting a PXRD measurement and storing the measurement data as a $d-I$ list in the user database, if the pure substance is available. The $d-I$ list is a list of lattice spacings and relative intensities.

3. Information Obtained by Qualitative Analysis

3.1. State of matter

Crystalline phase identification generally requires the sample to be crystalline. The reason for this is that only crystals, among other states of matter, have pattern characteristics suitable for the search/match processes. As shown in Fig. 5, crystals with a three-dimensional periodic atomic structure show multiple sharp peaks on the XRD profile, while a liquid or amorphous material with low periodicity shows broad peaks called halos.

3.2. Crystalline phase analysis

Phase identification is possible regardless of the sample form, such as powder, plate, bulk, or wire. However, even with crystalline materials, if the crystallinity is low, the peak width will broaden, often making phase identification more difficult.

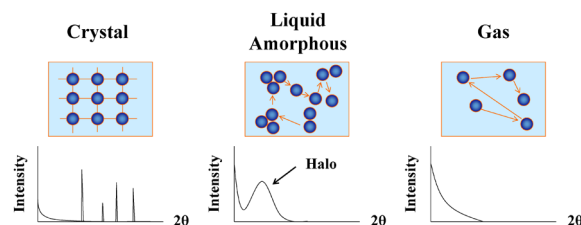


Fig. 5. Change in XRD profile depending on sample state.

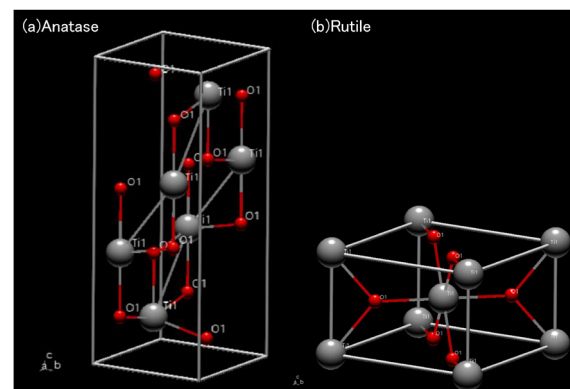


Fig. 6. Crystal structures of (a) anatase and (b) rutile.

The PXRD method can also be used to distinguish different crystalline phases of a polymorphic material. A polymorphic substance is one that has several different crystal structures, even though the chemical composition is the same. As an example, Fig. 6 shows the crystal structures of anatase and rutile, two polymorphic phases of titanium dioxide. Figure 7 shows the results of phase identification of a mixture of anatase and rutile. It is seen that the two polymorphic phases are identified one at a time by the PXRD method. It should be noted that this is not possible by any elemental analysis method.

With the PXRD method, it is also possible to determine whether a test sample exists as a solid solution or as a mixture. The XRD pattern will be that of a single substance if the sample is a solid solution,

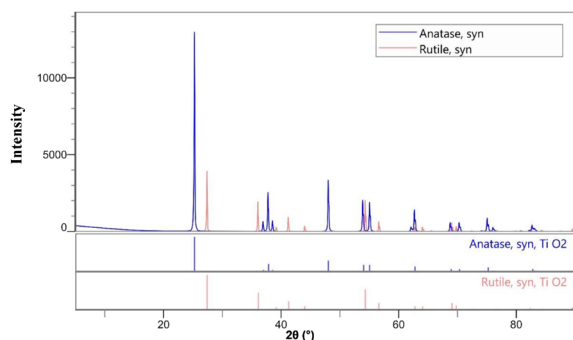


Fig. 7. Phase identification result of the mixture of anatase and rutile.

and it will be the sum of the XRD patterns of the component phases if the sample is a mixture. The XRD pattern of the solid solution differs slightly from the XRD pattern of the pure material due to changes in elemental composition and lattice constants. However, it is difficult to determine the presence of trace amounts of a substance in a solid solution by PXRD alone because changes in the XRD pattern are slight. In such a case, it is necessary to use elemental analysis in combination with the PXRD method.

Another notable application of crystalline phase analysis is the in-situ evaluation of crystalline phase transition. Using an appropriate sample stage designed to control environmental parameters such as temperature, humidity, atmosphere, load, or charge/discharge state (of a battery sample), crystalline phase transitions induced by these parameters can be investigated by the PXRD method without preparing multiple samples.

4. Tips on Phase Identification

4.1. Quality of measurement data

If the quality of the data is poor and correct peak positions and relative intensities are not obtained, that often makes phase identification difficult. When optics alignment, sample alignment, or sample preparation are not properly done, or measurement conditions are not good enough, high-quality data will not be obtained. Peak positions will shift due to the sample's eccentric error from the reference position or misalignment of the zero point of the goniometer. In addition, the presence of coarse particles due to inadequate grinding prevents the acquisition of high-quality data. If the instrument is not well adjusted, appropriate alignments must be performed. If coarse particles are present, grinding the sample again or spinning it during measurement are effective measures to obtain high-quality data.

Measuring a 2D image can help analyze samples with non-ideal Debye rings. While an ideal Debye ring has a uniform intensity distribution over the whole circle ($2\pi > \beta \geq 0$), coarse particles in the sample make the ring spotty and preferred orientation turns the ring into partial arcs, both causing a problem in analyzing the data. Using the information from a 2D image, coarse particles and preferred orientation can be taken

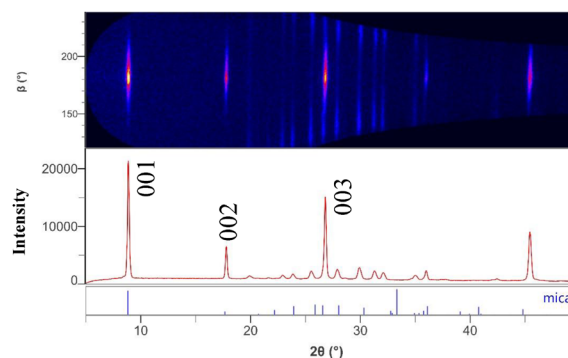


Fig. 8. 2D image and 1D profile of mica.

into account in the phase identification process. Figure 8 shows a 2D image of mica with highly preferred orientation in the $[00l]$ direction and the 1D profile transformed from the 2D image. Note that the Debye rings in the 2D image have been transformed into straight lines. It is seen that the Debye rings have non-uniform intensity distributions over β , with some being extremely strong at $\beta \approx 180^\circ$ and some others being partial arcs in the plot. This nonuniformity indicates the existence of preferred orientation. With SLSII, the whole area of the loaded 2D image is automatically converted to a 1D profile before qualitative analysis. This provides information about the entire 2D image and allows you to observe diffraction peaks from various lattice planes even if the crystal has preferred orientation. The correct intensity ratio may not be obtained, however, even if the data over such a wide range of β is considered. In such a case, correct phase identification results can be obtained by performing a search/match focusing only on the peak positions rather than the intensities.

It should be noted that 0D or 1D detector systems are prone to fail in phase identification if the sample has non-uniform Debye rings. This is because they cannot observe the β variation of the intensity within a circle in that case.

The conditions to obtain high-quality data are described in more detail in the second and third installments of "Powder X-ray Diffraction Basic Course"^{(1),(8)}.

4.2. Identification of trace phases

The detection limit of the PXRD method is lower than that of XRF analysis; it is about 0.01% to 10% depending on the target material^{(9),(10)}. The minimum identifiable phase concentration can be even lower because the PXRD method needs multiple observed peaks of the target phase for identification.

Combining data from XRF and PXRD methods sometimes helps when the latter alone cannot identify a trace phase. This can be easily performed with SLSII and a Rigaku XRF instrument. The software can load Rigaku XRF data to optimize the search/match conditions utilizing the elemental information.

When analyzing small peaks, it is necessary to pay attention to whether the peaks are derived from the trace

phase or not, based on the following points.

(1) S/N ratio

In Section 2.3, “Procedure of phase identification,” it is mentioned that the peak list is automatically obtained by profile fitting after loading the measurement data. Even so, this step requires attention when identifying trace phases because some small peaks may not be listed or background noise may be listed as a peak, depending on the measured XRD profile. In such a case, you can adjust the “ σ cut value” for peak search in SLSII. The σ cut value is a threshold to distinguish noise from peaks. If the signal-to-noise (S/N) ratio is greater than the σ cut value, it is regarded as a peak. By default, the σ cut value is set to 3.

Peaks can also be added or removed manually if the automatic peak search is still unsuccessful.

(2) Peaks derived from undesired characteristic X-rays

It is possible that small peaks are not derived from the $K\alpha$ line. When a strong peak derived from the $K\alpha$ line is observed, another peak derived from the $K\beta$ line may be observed on the lower-angle side of the $K\alpha$ line. If the X-ray tube is used without maintenance for a long time, tungsten from the filament may be deposited on the target metal surface, and diffraction

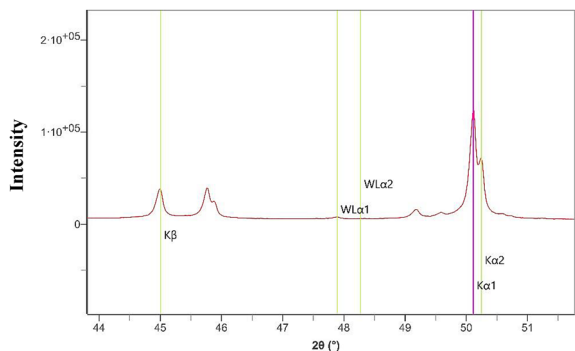


Fig. 9. Check the peak positions derived from characteristic X-rays (Pink bar: $K\alpha_1$, Green bar: the others).

peaks due to the characteristic X-rays of tungsten may be observed. In the case of a substance with good crystallinity, the $K\alpha_1$ and $K\alpha_2$ peaks are separated at high angles. The intensity ratio of the $K\alpha_1$ and $K\alpha_2$ peaks is approximately 2 : 1; therefore, if the $K\alpha_2$ peak appears to be larger than half of the $K\alpha_1$ peak, there is a possibility that different peak(s) overlap with the $K\alpha_2$ peak. As shown in Fig. 9, SLSII can indicate the positions (shown as green bars) that those ghost peaks would appear if the cursor (a pink bar) were on a peak caused by the $K\alpha_1$ line.

(3) Peaks that do not originate from the sample

In some cases, diffraction peaks from the sample holder or the film of the attachment may be observed. Whether these diffraction peaks originate from the sample or not can be determined by making a measurement without filling the holder with sample.

4.3. Differences between the card information and the measured data

In the process of phase identification, the d -value and the relative intensity of each peak to the strongest peak (the normalized intensity) calculated from the measured data of the test sample sometimes differ slightly from those in the corresponding card in the database. This may be due to the card data itself or properties of the sample, in addition to optics, sample alignment and sample preparation issues mentioned above.

(1) Card-related factors

If the wavelength on the card is different from the one with which the test sample is measured, the peak intensity ratios will change. In some cards, the sample composition has not been verified by chemical analysis, meaning the information could be of a different material than indicated. For cards of materials measured by the camera method, the intensities may be smaller at lower angles due to absorption effects. Many cards published before 1950 were measured by the

Table 2. Changing profile by sample property.

| Sample property | Change of profile |
|---|---|
| Preferred orientation | Difference of normalized intensity between measurement and database value |
| Solid solution of contaminant, thermal expansion | Peak shift |
| Small crystallite size (less than 0.1 μm) | Peak broadening |
| Mixed of same type material that lattice constant slightly varies Solid solution that sample composition is not locally uniformly Small strain of unit cell from base structure | Peak split |
| Stacking fault structure | Peak tailing in the high angle of the fault lattice plane |
| Incomplete solid solution | Asymmetric peak |
| Needle crystal, flat crystal | Sharpening of specific peak (the other peak become broad) |
| lattice strain | Peak broadening at high 2θ angle |

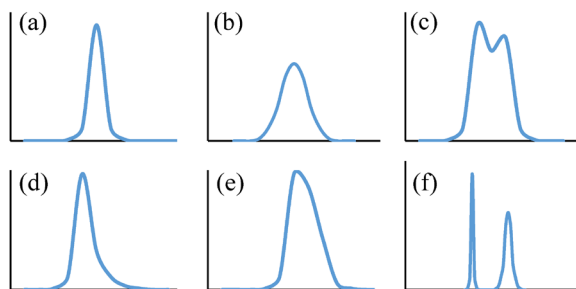


Fig. 10. Change of profile form by property of the sample. (a) Normal, (b) Broadened, (c) Split, (d) Tailed, (e) Asymmetrized, (f) Sharpened.

Candidate phase

| Set | Phase Name | Chemical Formula | QM | FOM/F20 | RIR | DB Card Number |
|----------------------------------|-----------------------|--|----|---------|-------|-----------------|
| <input type="checkbox"/> | Zinc, syn | Zn | S | 0.394 | 3.800 | 00-004-0831 ... |
| <input checked="" type="radio"/> | Zinc, syn | Zn | S | 0.394 | 3.800 | 00-004-0831 ... |
| <input type="radio"/> | Lithium Zinc | Zn _{0.99} Li _{0.01} | I | 0.474 | 8.410 | 01-077-2883 ... |
| <input type="radio"/> | Zinc, syn | Zn | I | 0.476 | 8.490 | 01-073-6858 ... |
| <input type="radio"/> | Zinc | Zn | I | 0.480 | 8.490 | 03-065-5973 ... |
| <input type="radio"/> | Cadmium Zinc | Cd _{0.011} Zn _{0.989} | I | 0.529 | 8.560 | 01-077-7303 ... |
| <input type="radio"/> | Manganese Zinc | Mn _{0.012} Zn _{0.988} | I | 0.535 | 8.470 | 01-077-2964 ... |
| <input type="radio"/> | Cadmium Zinc | Cd _{0.0137} Zn _{0.9863} | I | 0.651 | 8.570 | 01-071-6883 ... |
| <input type="radio"/> | Boron Nitrogen | B N | I | 0.708 | 1.140 | 01-074-5456 ... |
| <input type="radio"/> | Boron Carbide Nitride | B _{0.87} C _{0.4} N _{0.73} | S | 0.732 | 0.940 | 01-076-8771 ... |

Fig. 11. Candidate crystalline phases organized in a group by search/match.

photographic method. In those cards, the accuracy of the X-ray intensity is also poor because the intensities were estimated by eye, double lines of $K\alpha_1$ and $K\alpha_2$ are not separated, reflections with low intensity are missed, and diffracted X-rays with large lattice spacing are sometimes missing. Low-reliability cards are being replaced by new cards.

(2) Sample-related factors

Sample properties that change the profile are summarized in Table 2 and the changes in the profile form are summarized in Fig. 10. The measured profile and the values on the card sometimes may not agree with each other; however, changes in the profile due to properties of the sample cannot be avoided. If the measured data and the card do not agree with each other during the phase identification process, the matters shown in Table 2 should be considered.

4.4. Choosing the appropriate card

In SLSII, cards with the lowest FOM are added to the list of candidate phases in ascending order. FOM is an abbreviation for Figure of Merit, an index that indicates the degree of agreement between the measured data and the card information. In SLSII, the smaller the value, the better the agreement.

Cards with similar XRD patterns but slightly different chemical compositions and lattice constants are grouped together, as shown in Fig. 11. A tip for selecting from such a group is to choose the card with a good FOM and a high QM. It is generally a good practice to choose a card with a QM of S or I.

When a sample with an unknown chemical composition is identified as a solid solution, a common practice is to choose a card with a simpler composition with a similar XRD pattern.

If quantitative analysis is going to be performed after phase identification, the card with the necessary information, such as the RIR value and crystal structure, should be selected.

5. Summary

In the fourth installment of the PXRD basic course, the basics of “qualitative analysis” along with some know-how were explained. Since it is necessary to obtain high-quality measurement data for correct qualitative analysis, please refer to the second installment, “Selection of equipment configuration,” and the third installment, “Sample preparation and scanning conditions,” together with this article.

In recent years, the performance of analysis software has been improved, and phase identification can now be done quickly and easily by a computer search. It is, however, still necessary for the analyst to examine the analysis results by oneself as described in this installment. When there is a trace phase or when performing phase identification from a complex profile, it is recommended to check if the peak search has been done correctly.

In the fifth installment, “quantitative analysis” will be introduced, including analysis principles, know-how, and cautionary points.

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